SULPHUR CHEMISTRY IN MANGROVE SYSTEMS OF TROPICAL COCHIN ESTUARY

Thesis submitted to the
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
in Partial Fulfillment of the
Requirements for the Degree Of

Doctor Of Philosophy
In
Environmental Chemistry
Under The Faculty Of Marine Sciences

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DECEMBER 2002

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CERTIFICATE

This is to certify that the thesis titled "Sulphur Chemistry in Mangrove Systems of Tropical Cochin Estuary" is an authentic record of the research work carried out by Sr. Rosily A. V. under my supervision and guidance in the Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, in partial fulfilment of the requirements for PhD degree of Cochin University of Science and Technology and no part of this has been presented before for any degree in any University.

Kochi 16
December, 2002

Dr. N. Chandramohanakumar
(Supervising guide)

DECLARATION

I hereby declare that this thesis entitled "Sulphur Chemistry in Mangrove Systems of Tropical Cochin Estuary" is an authentic record of the research work carried out by me under the guidance and supervision of Dr. N. Chandramohanakumar, professor and Head, Department of Chemical oceanography, School of Marine sciences, Cochin University of Science and Technology, and no part of this has previously formed the basis of the award of any degree, diploma, associateship, fellowship or any other similar title or recognition.

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ACKNOWLEDGEMENT

With immense joy let me record my deep sense of indebtedness and gratitude to Dr. N. Chandramohanakumar, Professor and Head, Department of Chemical Oceanography, School of marine sciences, Cochin University of Science and Technology, for suggesting this research problem and for his invaluable and inspiring guidance as well as ceaseless encouragement throughout the progress of this work.

My sincere thanks are due to Dr. Jacob Chacko, Dr. Muraleedharan Nair and Dr. C.. H. Sujatha of the Department of Chemical Oceanography for their valuable suggestions and encouragement during my work.

I am grateful to Dr. P. G Kurup, Director, Dr. N. R. Menon, Former director and Dr. N. Damodaran, Dean, of School of Marine Sciences, for all the facilities granted to me in the department to carry out the research work.

I express my deep sense of indebtedness towards Rev.Mother General and team members for their untiring support for the completion of the work.

The work would remain incomplete without expressing my deep sense of gratitude towards Rev.Mother Caroline, our Provincial Superior. The support given by Mother was indelible and I could cherish it throughout my study. I take this opportunity to extend my heartfelt thanks to all the members of the provincial team. The sisters of my congregation deserve much gratitude for their care, support and valuable prayers.

I express my gratitude to Rev. Sr.Isabel, the principal and the Staff of Morning Star college Ankamaly especially to those of the Department of Chemistry for their continuous encouragement and help.

I owe my heartfelt thanks to all my fellow research scholars especially to Sr. Janet Augustine, T. Narayanan, Geetha R, Shally John, Joseph P. V, Geetha Andrews, Lizen, Zeena P Ravi and Sarika for their valuable suggestions and timely help. My sincere thanks to all the research scholars and non-teaching staff of the department of Chemical Oceanography for their timely help.

Every thing that grows says something, every stone

whispers some secret, each creation sings ....

Nature bears God's "signature" and mirrors His glory.

Respect creation-do not waste or destroy.

- St. Francis Assissi– about nature.

Preface

Mangroves represent one of the most natural forest ecosystems suspectable to constant threat by human activities. They have the ability to grow where no other vascular plants can. The mangroves exist under stressful conditions such as violent environments, high concentration of moisture, high and low tides of water, and abundant living micro organisms and insects. They thrive in a very peculiar environment and serve as a bridging ecosystem between fresh water and marine system.

Mangrove wetlands are effective in retaining heavy metals and nutrients from seawater, but it is essentially anaerobic. All soil nutrients vary seasonally, in response to wet and dry periods of climate. Results of the previous studies show that most pollutants are accumulated in the top layer of the soil tray. The wastewater inputs and salinity would have more significant effects on the microbial activities in mangrove soils.

Since anaerobic conditions are prevalent in these ecosystems, the chemistry of Sulphur and its compounds are important. The work is mainly concentrated on Sulphur Chemistry in mangrove sediments. Sulphur is an essential nutrient for vegetation. It is also a major element of seawater and marine sediments. Sulphur is an important redox element, existing in a wide range of oxidation states from –2 to +6 and enter into a variety of biogeochemical processes. The role of sulphate reduction in anaerobic condition and the resultant production of sulphide minerals are very much pronounced. Therefore the Sulphur cycle has received considerable attention. Major forms of sulphur include sulphate and sulphide minerals, dissolved sulphate, and dissolved sulphide and hydrogen sulphide gas. In this attempt, various fractions such as acid volatile sulphur, pyrite sulphur, gregite sulphur, sulphate sulphur, elemental sulphur, organic sulphur and total sulphur in the water and sediments of a few tropical mangroves are accessed.

For the speciation of sulphur, water and sediment samples were collected from three mangrove systems from Cochin area. Station 1 is Mangalavanam a protected forest close to Ernakulam city. This ecosystem is known for the protection it offers to various migratory birds and is named as the green lung of the city. There is one outlet in the form of a canal opening to backwaters. *Avicenia*, *Rhizophora* and *Acanthus* are the three main mangrove species seen here. Station 2 is Nettoor, which can be considered as a vanishing mangrove ecosystem with a long strip of mangrove plants along the canal. This is an ecosystem with much anthropogenic input. The increasing prawn culture and the urbanization affects this area more than the other two. Station 3 is Vypeen, which is semi-enclosed system and lies adjacent to the brackish waters. The Vypeen Island has a number of mangrove species. This is closer to the sea than the other two. Bimonthly collections of both water and sediments were made from all the three different stations from Nov'99-Nov 2000.

The thesis is divided into six Chapters. First Chapter covers a brief introduction about tropical marine ecosystems, significance of mangrove ecosystem and the importance of the sulphur cycle in the aquatic realm. The aim and scope of the present work is also mentioned in this chapter.

Second Chapter is about the study area, sampling procedures and various analytical methods adopted for the work. Besides, variations of hydrographical parameters such as salinity, alkalinity, dissolved oxygen, pH and temperature are given.

Third chapter reveals the sulphur chemistry of water column. The values of the concentrations of dissolved sulphates and sulphides are given in this chapter. Along with this the tidal variations of above describe its influence on the sulphur chemistry of water column.

Fourth Chapter gives Chemistry of Sulphur in mangrove sediments especially in the surface sediments. This has helped in the prediction of the fate of sulphur in the surface sediments.

Fifth Chapter explains Geochemistry of sediments and distribution of various fractions of sulphur throughout the core. In addition to the comparative study between the water, surface sediment and core, the reasons for the variations of sulphur species in above three are given here.

The summary given at the end of the work explains how and partially why the different species of sulphur varies in the different samples. The quantification of the six species of sulphur in these ecosystems has revealed to some extent the nature of the system. Above all the study has contributed much insight into the anoxic conditions, of mangrove ecosystem.

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1.1 The Tropical Marine Ecosystem

Tropical oceans cover a large part of the surface of our planet. The region between 20°S and 20°N is covered in the tropical marine ecosystem, which constitutes about 37 percent of the world ocean viz.131.9×10^6 km^2. Of this, 10.24×10^6km^2 forms the continental shelf (Longhurst et al., 1987). Tropical marine ecosystems, like mangroves, lagoons etc are characterized by high organic productivity and associated with rich fisheries and biological resources. Microbes such as bacteria, fungi and unicellular algae assume greater importance in the tropical marine ecosystems because of their abundance, biomass and activity in a number of chemical and biological processes that provide the driving forces for vital biogeochemical cycles (Chandramohan, 1992). Among tropical marine ecosystems estuaries are one of the highly productive areas and act as a nursery to large number of organisms.

Marine tropical ecosystems, with uniformly high temperature regime, support fast growth, prolonged breeding period and faster turn over rates (Arun parulekar, 1992). About 2 million hectares of estuarine and near shore areas offer immense possibilities for culturing a variety of sea foods. The farming of marine organisms will be economically attractive, as the resource is renewable and of self generating type. Short pulses of higher primary production are a common feature in estuaries. Estuaries and their environments influence the coastal waters to a greater extent. The coastal regions are at least five times more productive than the oceanic realms (Bhattathiri, 1992). The inter tidal mud flat zones of tropical seas and estuaries are occupied by mangrove ecosystems, which are the nursery grounds for a variety of estuarine and marine organisms.

1.2 Mangroves

"Mangroves are coastal tropical formations found along the boarder of the sea and lagoons, reaching up to the edges of the river to the point where the water is saline, growing in swampy soils covered by sea water during high tides" (Aubreville, 1964). Odum et al., (1972) has described the mangrove ecosystem as a 'pass through' type of system because of large flow of organic matter transported through the mangrove coastal zones by physical activities of tides, runoff and rainfall, and the intense biological activities of decomposition, uptake, and bioturbation occurring in the mangroves that are important downstream in marine ecosystem. They are one of the easiest tropical forest types to generate. They have the ability to grow where no other vascular plants can. The mangroves exist under stressful conditions such as violent environments, high concentration of moisture, high and low tides of water, and abundant living microorganisms and insects. They thrive in a very peculiar environment and serve as a bridging ecosystem between fresh water and marine system. These environmental conditions have brought in several modifications in these plants. They are facultative halophytes and hence they can grow in fresh water better than in salt water. To avoid competition, they grow in saline environments and have become halophytes. In order to prevent water loss from the plant they have sometimes thick waxive cuticle or dense hairs to reduce transpiration.

Apart from coping with salt, mangroves also face common problems of water logged, unstable and oxygen deficient soils. Roots perform a number of functions for the plant. They support it and they obtain essential nutrients and oxygen. The main mass of roots is generally within the top of two meters and mangroves do not seem to grow deep taproots, probably because of the poor oxygen supply below the surface. Another special adaptation is the dispersal of certain mangroves' "propagules" which hang from the branches of mature trees. These "propagules" fall off and eventually take root in the soil surrounding the parent tree or are carried to distant shorelines. Viviparity and the long-lived "propagules" allow these mangrove species to disperse over wide areas. Some species of these floating seedlings can survive in a state of suspended animation for up to a year in the water. Once lodged in the mud they quickly produce additional roots and begin to grow.

1.2.1 Mangroves in Kerala Coast

Kerala coast, which comes to about 560 km, extends from Manjeswaram at north to Pozhiyur at south, that is between latitude 9° N and longitude between 75°E and 77°'E. Higher population density in the Kerala coast has resulted in tremendous pressure on the natural ecosystem, particularly on the mangroves. For urbanisation, construction of harbours, ports, prawn farming, coconut plantation and ricefish culture, vast mangal lands were cleared or reclaimed. According to Ramachandran et al (1986) these mangroves of the Kerala State are degraded and grow in isolated patches, confined in the inner reaches of the intertidal margin of estuaries, lagoons, back waters, creeks and criss-cross along the coastal region. Kerala mangroves are distributed in eight coastal districts of which Kannur (755ha) has the largest area followed by Kozhikode (293ha), Ernakulam (260ha), Alappuzha (90ha) and Kottayam (80ha) (Subramanian, 2002).

1.2.2 Mangroves-A Significant Ecosystem

These are highly productive ecosystem with various important economic and environmental functions. The uses of mangroves fall in two categories: Firstly the indirect use of the mangrove ecosystem is in the form of vital ecological functions such as control of coastal erosion and protection of coastal land, stabilization of sediment and natural purification of coastal water from pollution. Secondly, the economic benefits which are many and varied. Apart from prawns, many other species of economic importance are associated with mangroves; these include crabs, shrimps, oysters, lobsters and fish. Mangrove forests accelerate the siltation processes, check soil erosion and protect coastal areas from frequent tidal thrust, cyclonic storm and devastating surges from the bay (Naskar, 1988).

The sediments are effective in retaining heavy metals and nutrients from seawater, but they are essentially anaerobic. All soil nutrients vary seasonally, in response to wet and dry periods of climate. Results of previous studies show that most pollutants are accumulated in the top layer of the soil tray. The wastewater inputs and salinity would have more significant effects on the microbial activities in mangrove soils. Snedaker (1984) has highlighted and emphasized that these world mangrove ecosystems are the most alarming ecosystem, which need urgent protection measure and strict natural conservation strategies. Mangrove plants intake nutrients from the tidal seawater, river courses and the mangrove ecosystems, as such provide natural food to the mangrove dwelling fauna (Odum et al., 1972). The total productivities of mangals are variable, which depend solely on the bio-diversity, growth pattern or habitat of the mangals. These sea-land transitional ecosystems are significantly nutrient rich, much productive, dynamic and probably the major intermediate stage in the evolutionary processes (Mac Nae, 1968).

Previous studies always considered mangrove soils as homogeneous entities, with the observed range of variabilities of major soil parameters being explained by physical factors such as tidal amplitude, inundation period, micro topography and soil granulometry. In the last decade, however, strong evidence has accumulated for significant differences among mangrove soils due to the presence of different mangrove species. For example significant differences in sulphide content (Nickerson and Thibodeau, 1985), acidity (Naidoo, 1980), total organic matter content and trace metals (Lacerda et al., 1993) and redox potential exist between soils colonized by different mangrove species, in particular between *Avicennia* and *Rhizophora* soils. Most of these differences have been attributed to the different capacities of a given mangrove species to alter soil condition adjacent to its root system through specific physiological mechanisms such as releasing oxygen into the reducing soils (Nickerson and Thibodeau, 1986). However different soil conditions can also result from differences in the composition of initial organic inputs from mangrove litter, since mangrove leaves are compositionally complex and their early diagenesis is a selective processes resulting in changes in composition over time. (Benner et al., 1990).

1.3 Anoxic Condition and Importance of Sulphur Cycle

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), salt marsh ecosystem energetics (Howarth, 1984), formation of important resources like petroleum hydrocarbons and coal (Casagrande et al., 1977b), atmospheric sulphur emissions (Adams et al., 1981), metal corrosions (Fjerdingstad, 1967), regulation of global climate (Andreae, 1990) and acid rain (O'Neil, 1985).

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

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 up to 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. This stratification provides the basis of transformations of sulphur compounds through a cyclic series of redox processes.

Biological sulphate reduction is an anoxic process. It can occur in a water column as a result of above-average oxygen consumption or poor circulation. High rates of oxygen removal are related to the content of dissolved and particulate organic matter and to hydrodynamic stability, which prevents the addition of oxygenated water by diffusion or advection (Richards, 1965). Beneath the water column, anoxic conditions are frequently established again as a consequence of the accumulation of organic matter and restrictions imposed on the rate of addition of oxygen. Dissolved sulphate in pore waters of such sediments may be removed by sulphate reducing bacteria within a depth of less than 1 to 2m. The species of bacteria involved in sulphate reduction will then assume a dominant role in degradation of organic matter within the sediment. The metabolic products *ie* CO_2, H_2S, NH_3, PO_4 are chemically reactive and therefore influence subsequent digenetic processes. Metal sulphide precipitation, pH modification and control of methane generation are associated with the bacterial activity.

According to Pettijohn (1949), digenesis primarily refers to reactions that take place within sediment between one mineral and another or between minerals and the interstitial fluid. A number of base and transition metal sulphides have exceedingly low solubility products and might be expected to form during early digenesis. However, these metals are present in only trace amounts (Chester, 1965). Iron sulphides are the only metal sulphides recognized in marine sediments. The important forms of sulphides, which are found in marine sediments are amorphous iron sulphide, Gregite and Pyrite. Pyrite represents the only thermodynamically stable phases and amorphous iron sulphide, mackinawite and gregite are metastable with respect to pyrite (Berner, 1967). In the sulphur rich environment of marine sediments, pyrite is the normal end product of sulphate reduction. The kinetics of transformations involving various iron sulphides may be slow, however allowing the persistence of metastable phases for considerable periods of time. Operationally it is possible to discriminate between pyrite and other sedimentary iron sulfides as pyrite is insoluble in hot HCl while the remaining phases are soluble. The sulphide minerals as a result of sulphate reduction involves reaction with iron oxide.

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

The products formed includes elemental sulphur and acid volatile sulphide phase. Gregite is an intermediate in pyrite formation and Berner (1967) assigned a composition of Fe_3S_4 to gregite. Its formation from FeS (Berner, 1970) is represented by the following 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 gregite 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:

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

The mechanism proposed for slow pyritisation was as follows. In this reaction FeS combines with elemental sulphur to produce gregite. Gregite in turn produces pyrite, either through dissociation or by further reaction with elemental sulphur(Sweeney and Kaplan, 1973).

$$Fe_3S_4 \rightarrow 2FeS + FeS_2$$

$$Fe_3S_4 + 2S^0 \rightarrow 3FeS_2$$

The compounds in Organic sulphur fraction have been classified into two group 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). In the present investigation, the organic sulphur fraction comprises both the ester-sulphate sulphur compounds and carbon bonded sulphur compounds. 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.

Acid volatile sulphides are present in greatest abundance relative to pyrite in rapidly deposited sediments. With increasing depth of burial, the AVS decreases in abundance (Kaplan et al.1963, Berner 1970). Elemental sulphur have found only low concentrations compared to other forms (Kaplan et al.1963). This has been interpreted as indicating continual formation and removal of sulphur by different processes whose relative rates are such that elemental sulphur never builds up to high concentrations (Kaplan et al.1963). The linear relation between the amount of sulphur and carbon in the sediment suggest that a preferred fraction of organic matter deposited is utilized for sulphate reduction. Sulphate reduction occurrs near the sediments surface, but not in the overlying water column. The amount of pyrite formed appears to be dependent on the extent of organic carbon deposition.

1.4 Fate of Sulphur in Mangrove Ecosystem

Mangrove ecosystem is considered as a wetland ecosystem, characterized as, having soils that are frequently or continuously waterlogged and that are often high in organic matter content. The duration and frequency of water logging, however, are quite varied. Intertidal sediments are very sensitive to climate change, they are not wholly passive since they can themselves influence climate change via atmospheric gas cycling (Jickells et al., 1997). These sediments are both sinks and sources of different nutrients and their behaviour change with the tide. There has been intense interest in understanding the sulphur cycle in these ecosystems because high inputs of organic matter into the soils, along with oxic surface and anoxic subsurface zones, potentially allow sulphur to play a critical role in the biogeochemistry of wetlands. Interest in understanding the sulphur cycle in these ecosystems has focused on a variety of issues:

1. Microbial dissimilatory sulphate reduction may account for much of the total organic matter decomposition (i.e. terminal carbon mineralization)
2. Hydrogen sulphide may reach concentrations in soils that are inhibitory or toxic to plants, thereby affecting net primary production.
3. Reduced sulphur may be an important energy source for chemoautotrophic bacteria, leading to new carbon fixation and thus affecting net ecosystem production and carbon balance.
4. Wetlands may be a significant source of sulphur gases to the atmosphere, some of which may be oxidized and redeposited to the earth as acid precipitation.
5. Sulphate reduction may control methanogenesis and therefore methane emission from these systems, of potential importance because methane is a greenhouse gas.

Sulphur exists in this wetland soils in a variety of oxidation states and may be present in gaseous, soluble, and solid forms. The majority of sulphur is present as reduced inorganic sulphur minerals (pyrite, iron monosulphides, and elemental sulphur), organic forms, or sulphate. In general, sulphur gases (Wieder, 1985) and dissolved reduced sulphur compounds (Howarth *et al.*, 1983) contribute little to the total sulphur. Soluble sulphate concentrations are sometimes low but often account for 10 to 20% or more of the total sulphur even at depth in waterlogged soils (Casagrande *et al.*, 1979; Howarth, 1984)

In oxic systems the energy trapped during the formation of organic matter is liberated during decay so the flow of energy follows the flow of carbon. However, when decomposition occurs anoxically, part of the energy present in the organic carbon is not released, but remains conserved in high energy reduced compounds such as hydrogen sulphide (Howarth, 1984).

During dissimilatory sulphate reduction, only 25% of the energy present in the organic matter is available for microbial growth and respiration, while nearly 75% of the energy remains trapped as sulphides. Hence carbon and energy flow are decoupled.

The energy retained in reduced compounds is released when they are oxidized. If this oxidation is carried out chemically, the energy originally present as photosynthetically fixed carbon is lost from the ecosystem. However, a variety of chemoautotrophic bacteria are capable of using the energy released in the oxidation of sulphide and other reduced sulphur compounds to support new carbon fixation. In saline wetlands, where much of the decomposition is carried out by sulphate-reducing bacteria, the amount of energy carried in reduced sulphur compounds is very large (Howarth, 1984). If we assume that 75% of the total decomposition proceeds by sulphate reduction, then more than half of the energy from photosynthesis is trapped, at least temporarily, as reduced sulphur.

A portion of the reduced sulphur produced each year is exported to creeks before being oxidized. The majority of oxidation of reduced sulphur occurs within the soil, or at the soil surface and a large portion of this oxidation may be biologically catalysed.

1.5 Aim & Scope of the Present Study

Mangroves are one of the most important tropical marine ecosystems, the productivity of which is as high as coral reef or seagrass beds. Organic matter production in a mangrove system was reported as 3.4 g $m^{-2}d^{-1}$(Miller, 1972). Pant et al (1980) observed that primary production varied from 0.8 to 2.06 $gCm^{-2}d^{-1}$. Mangrove ecosystem is well known for its support to fisheries, coastal stabilization, repairable coastal protection barrier for maintaining critical habitat for many life forms, international nesting ground and hatching ground of migratory birds and turtles, sustainable natural resources for local industries and rural development. Mangrove areas are famous for honey production and in many countries they are extensively exploited for charcoal production. These areas serve as nurseries of millions of estuarine fishes and edible crabs depending on the mangrove detrital materials. Therefore sustained yield management for estuarine fisheries will get supported along with the development of mangroves.

However a stage has been reached where man faces this highly productive and useful ecosystem with the crisis of extinction and degradation in many parts of the world through maximization of exploitation and indiscriminate land use. The situation demands concerted efforts not only to protect the sensitive areas, but also to bring more and more areas under mangrove vegetation to reverse the trend. There is an urgency for proper management and conservation of mangroves. The study of physio-chemical conditions, especially, the anoxic condition of the mangrove ecosystem is essential for such a management scheme. Mangroves are excellent breeding grounds for fisheries including prawn culture. The natural habitat of prawns should be preserved in view of the economic importance of prawn exports in Kerala. The extent of mangroves present in Kerala has been reduced from 700 km^2 to 17 km^2.

The quality of the environment for the normal life and promotion of natural processes is dependent on the chemical condition, especially, the redox condition, of in the system. Sulphur chemistry is considered to be one of the best index to the redox condition and so the sulphur chemistry of the mangrove ecosystem will reflect the extent of anaerobic conditions existing in the system. Sulphur dynamics contributes to the non proliferation of microorganisms or growth of sulphur dependent chemo autotrophs and thus leading to a nutrient condition essential to the growth of fisheries. The study of sulphur chemistry of mangrove system in Kerala has not yet so far been undertaken and so this study is intended primarly to generate data of sulphur dynamics in this important coastal intertidal zone and to identify the possible geochemical processes and reactivity.

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Chapter 2

MATERIALS AND METHODS

The Cochin estuarine system extends between 9° 40'N and 10° 12'N, 76° 10'E and 76°30'E. It has a length of about 70 kms and width varies between a few hundred meters to about 6 kms. As a shallow semi-enclosed body of water, it falls under the category of a tropical positive estuary (Pritchard, 1967). The Cochin estuary includes a system of inter connected lagoons, bays and swamps penetrating the main land and enclosing many islands in between, whose total area amounts to approximately 500km^2. The hydrography of Cochin estuary very much depends on the short term changes due to the tides and seasonal changes brought about by the monsoon (Quasim, 1979). Mangrove ecosystems are found in isolated patches along the banks of this estuary.

2.1 Station Locations

For the study, sediment and water samples were collected from three mangrove ecosystems in Cochin area. They are Mangalavanam, Nettoor and Vypeen. The area of investigations and the stations locations are depicted in Fig 2.1. A brief description of nature of the concerned stations are:

Mangalavanam

Mangalavanam is represented as Station 1. It can be considered as a closed system with minimum human intervention. There is one outlet in the form of a canal opening to backwaters. *Avicenia, Rhizophora* and *Acanthus* are the three main mangrove species seen here. This mangrove forest is a small bird sanctuary and lies 4 km off south to Cochi. This forest during high tide was represented as 1F-H and at low tide as 1F-L, the canal connecting to this forest at high tide was represented as 1C-H and at low tide as 1C-L in the graph and tables.

Nettoor

Station 2 represents Nettor which can be considered as a vanishing mangrove ecosystem with a long strip of mangrove plants along the canal.

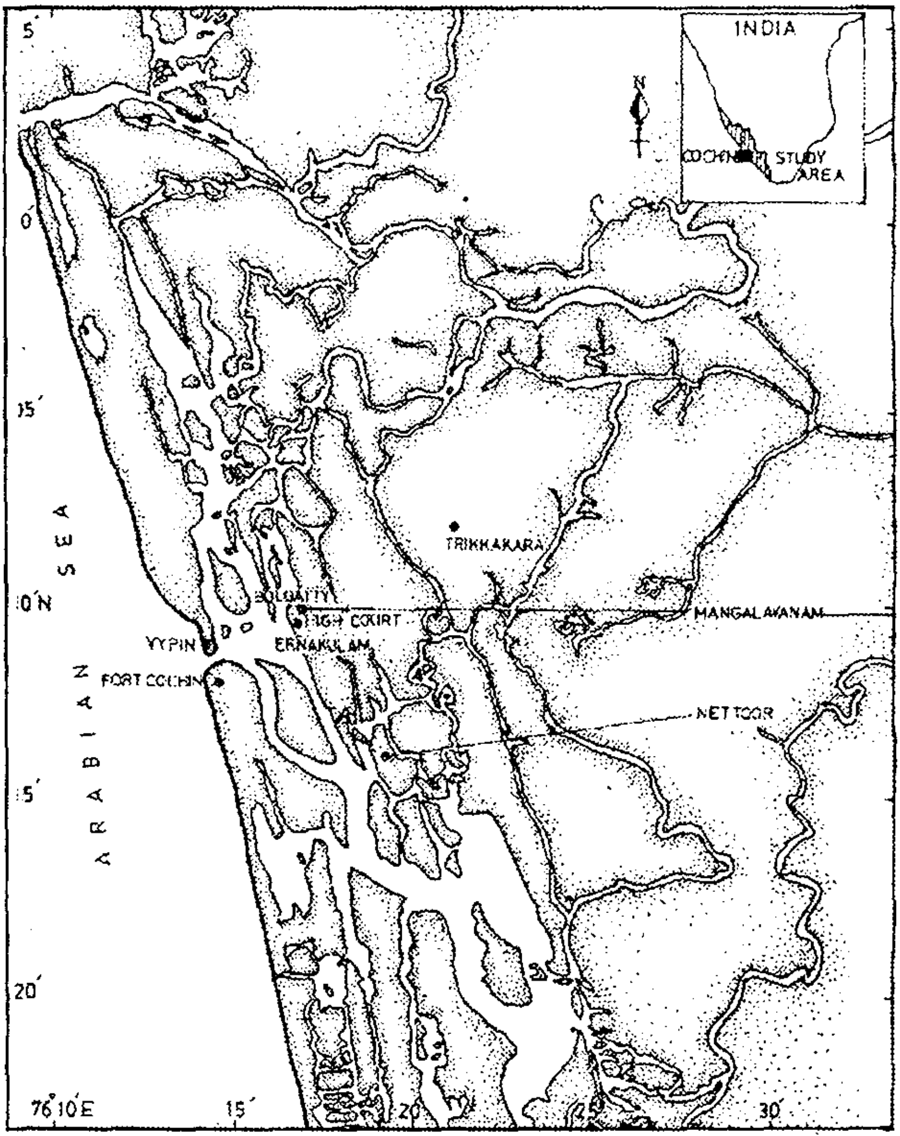

INDIA
N
COCHIN
STUDY AREA
5'
0'
05'
10'N
15'
20'
ARABIAN SEA
TRIKKAKARA
BOLGATTY
HIGH COURT
ERNAKULAM
VYPIN
FORT COCHIN
MANGALAVANAM
NETTOOR
76°10'E
15'
20'
25'
30'

Fig. 2.1

This is an ecosystem with much anthropogenic input. The increasing prawn culture and the urbanisation affects this area more than the other two. This forest and its water masses were designated as 2F& 2C in graphs and tables.

Vypeen

Station 3 is Vypeen, which is semi enclosed system and lies adjacent to the brackish waters. The Vypeen island has a number of mangrove species. This is closer to the sea than the other two. This mangrove area is regularly inundated by a semi diurnal rhythm of Cochin barmouth and the tidal waters bring in lot of fish seed of commercially high value. This forest was marked as 3F and its adjacent water mass as 3C in the graphs and tables.

2.2 Analytical Techniques

2.2.1 Sampling Procedure

Water and sediment samples were collected from the stations at bimonthly intervals from November 1999 to November 2000. Water samples are collected using a clean plastic bucket. Sub-samples were drawn out first for the determination of sulphide, dissolved oxygen and alkalinity in separate bottles. The sulphide was fixed by zinc acetate solution and oxygen by Winkler's reagents. Alkalinity of water samples were also fixed in situ. Samples for other parameters were collected in pre-cleaned polythene bottles.

Surficial sediment samples were collected using a clean plastic spoon. Core sediment samples were collected by penetrating a PVC pipe of 10cm diameter. The core samples were cut into subsamples at 5cm intervals. The sample was then transferred to polythene bags and kept at 4°C until analysis was carried out. All analyses were done in duplicate.

2.2.2 General Hydrographic Parameters

The hydrographical parameters pH, temperature, salinity, alkalinity and dissolved oxygen were estimated by standard methods. pH was measured immediately after collection using a portable pH meter and temperature was determined by the help of a thermometer. The dissolved oxygen fixed in situ was taken to the laboratory, and the analysis was carried out by the Winkler's method (Grasshoff, 1999). Alkalinity of the water samples was estimated by the method of Koroleff (Grasshoff, 1999). The salinity of each sample was determined by using Mohr-Knudsen method (Grasshoff, 1999).

2.2.3 General Sedimentary Characteristics

The sediments were analysed to determine the organic carbon content by the method of Gaudette et al., (1974). Moisture content of the sediment was determined by oven drying the sediment at 105°C for 24 hours. The texture analysis was performed as per the techniques described by Carvar (1971).

2.2.4 Dissolved sulphur fractions

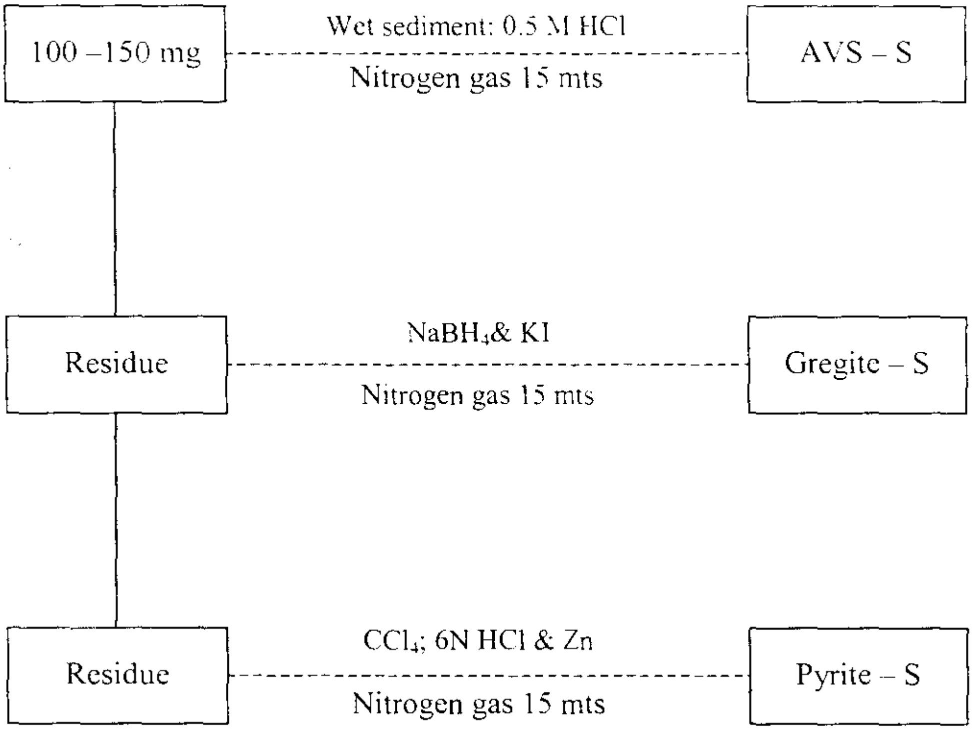
Sulphide was determined spectrophotometrically by the method of Cline (1969), using UV-VIS Hitachi 150-20. The samples fixed with zinc acetate solution were treated with N,N dimethyl p-phenylene diamine dihydrochloride and ferric chloride reagents to develop blue colour. The absorbance was recorded at 630nm.

Sulphate present in the water sample was determined gravimetrically after precipitating with barium chloride solution in acid medium (APHA. 1995). The interference of alkali metal was minimised by adding picric acid. To ensure good crystallisation, precipitation was done from hot solution.

2.2.5 Sedimentary sulphur fractions

Different sulphur fractions in sediment samples were estimated by evolving the corresponding sulphur content as H_2S using suitable reagents.

Nitrogen gas of A.R grade was used as the carrier gas. The liberated H_2S was trapped in 5% ZnAc solution (Jorgensen, 1977) and the concentration was determined spectrophotometrically using Cline's (1969). methylene blue method. Fractionation scheme of AVS gregite sulphur and pyrite sulphur are given in the flow chart below.



H_2S from Acid volatile sulphur was generated using 0.5M HCl and from gregite using Sodium borohydride and KI (Cutter and Oatts, 1987). For the determination of Pyrite sulphur, the dried homogenised sediment was extracted with CCl_4 to remove elemental sulphur and then redried (Cutter and Oatts, 1987). H_2S was liberated with Zn and 6N HCl (Nariagu and Soon, 1985) after expelling any residual H_2S from AVS and gregite with their appropriate reagents. The liberated H_2S was trapped in ZnAc solution and estimated by Cline's method.

Elemental sulphur in the samples was estimated by a method suggested by Fabbri et al., (2001). The samples were treated with toluene to extract elemental sulphur. Toluene solutions were directly oxidised by combustion in a bomb calorimeter, containing sodium carbonate-bicarbonate buffer, which trapped sulphur species generated from elemental sulphur as sulphate ions. These were in turn analysed by turbidimetrically (APHA, 1995)

Sulphate sulphur was determined by the method suggested by Tabatabai and Bremner (1972). Dried sediment sample was extracted with 0.1M LiCl, by shaking for 30mts and centrifuging. The extracted sulphur determined turbidimetrically (APHA, 1995).

For the determination of total sulphur, all sulphur forms were oxidised to sulphate by using H_2O_2 and 20% HNO_3 (Vogel,1985). The oxidised sediment was determined tubidimetrically.

Organic sulphur was taken as the difference between the total sulphur and the total inorganic sulphur forms. The sum of the concentrations of AVS, gregite sulphur, pyrite sulphur, elemental sulphur and sulphate sulphur is referred to as the inorganic sulphur.

2.3 Results of General Hydrographic Parameters

Mangrove swamps develop on the margin of estuarine and coastal regions. This wetland ecosystem is frequently or continuously waterlogged and the duration and frequency of waterlogging are quite varied. These heavily vegetated intertidal wetlands, when submerged are very shallow, with a maximum water depth of 2m in the swamps. Small tidal creeks drain the swamps.

2.3.1 Salinity

The plants are inundated almost daily once or twice and the salinity of water that the plants tolerate ranges from slightly saline to more than sea water (Bhosale et al., 1992). Evaporation during low tide resulted in higher saline conditions but a sudden shower reduced salinity considerably. The salinity in these areas ranges from fresh to brackish, to marine and even to hyper saline in highly evaporative areas.

Table 2.1 Seasonal variation of Salinity (ppt)

STATIONS	PRE-M	MON	POST-M
1F-H	18.5	0.33	10.5
1C-H	18	0.2	12.3
1F-L	19	1.78	11
1C-L	17.5	0.78	9.3
2F	14	0.53	6.3
2C	15	0.99	14
3F	25	3.85	21.6
3C	23	2.35	25

The seasonal distribution of salinity in all stations is given in Fig 2.2 and in Table 2.1. Sharp seasonal differences were noted during premonsoon, monsoon and postmonsoon. During monsoon the salinity of water in and around all the three ecosystems were in the fresh water range. The maximum value was noted in the forest of Station 3 and minimum was observed in the forest of Station 1, at the time of high tide. The values ranged between 0.33ppt - 3.85ppt. The fresh water character was dominant in the forests. The Station 3F is more saline than the canal. The low salinity during this season was due to the heavy rains causing high fresh water discharge into the ecosystems. The salinity was very high during premonsoon. The values were in the range of 14ppt to 25ppt. The maximum value was noted at Station 3F and minimum was observed in Station 2F. Compared to canals all the forests showed high salinity values during this season except in Station 3C. During premonsoon, because of high rate of evaporation and decrease in the tidal water can cause an increase in salinity. During post-monsoon the values were in the range of 6.3ppt to 21.6ppt. The maximum value was observed in station 3F and minimum in station 2F.

The data on salinity clearly establishes the influence of the influx of fresh water and intrusion of seawater. The premonsoon period predominantly characterised by saline water intrusion and monsoon period by river water influx (Lakshmanan et al., 1982).

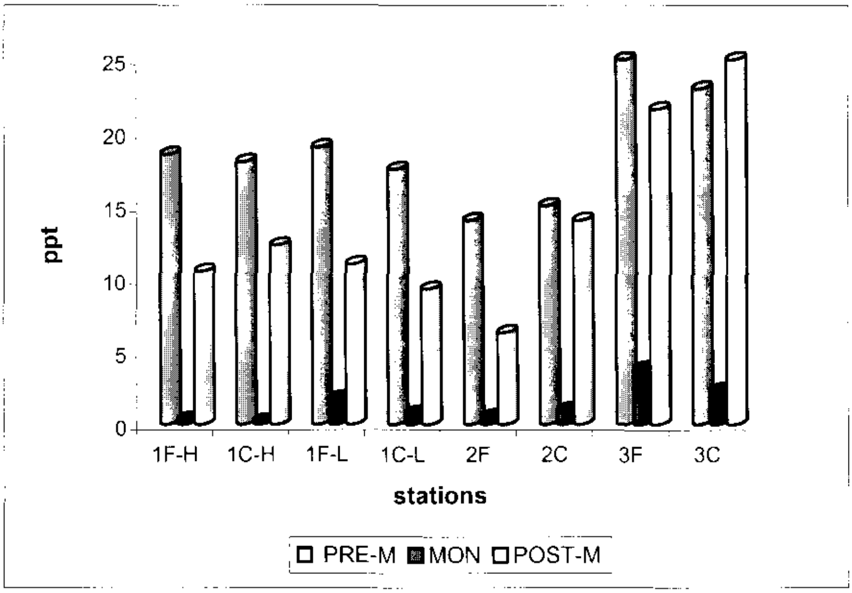


Fig 2.2 Seasonal variation of salinity

2.3.2 Dissolved Oxygen

Occasionally anoxic conditions are encountered in the mangrove swamps due to higher organic load and microbial population (Goswami, 1992). Dissolved oxygen plays significant role in the marine environment. In estuaries phytoplanktons are very important sources of oxygen which is photosynthetic product and thus the dissolved oxygen values may provide a general indication of primary productivity.

Table 2.2 Seasonal variation of dissolved oxygen (ml/l)

STATIONS	PRE-M	MON	POST-M
1F-H	1.25	2.96	3.14
1C-H	3.27	5.10	3.97
1F-L	0	3.91	0
1C-L	1.66	2.06	0.92
2F	3.25	5.96	3.27
2C	3.66	5.02	4.00
3F	1.43	1.64	1.75
3C	1.20	2.62	1.01

The seasonal variations of dissolved oxygen are given in the Fig 2-3.and Table 2.2. During monsoon all the three ecosystems are rich in oxygen. The maximum value was noted at station 2F and the minimum was observed at station 3F. The values ranged between 1.64ml/l-5.96ml/l in the forests. Among the stations 3F&3C, the canal 3C was oxygen rich compared to the forest 3F during monsoon. But among the stations 2F&2C, the forest 2F showed comparatively higher value for oxygen than the adjacent water body. The values were 5.96ml/l and 5.02ml/l respectively. All systems were oxygen deficient during premonsoon. The concentration of oxygen was not detected at station 1F-L during premonsoon and postmonsoon. During premonsoon and postmonsoon the maximum value was noted at station 2C.

High dissolved oxygen recorded during monsoon is due to the greater solubility of oxygen in fresh water and high turbulance. Premonsoonal low values are partially governed by the effect of temperature on solubility.

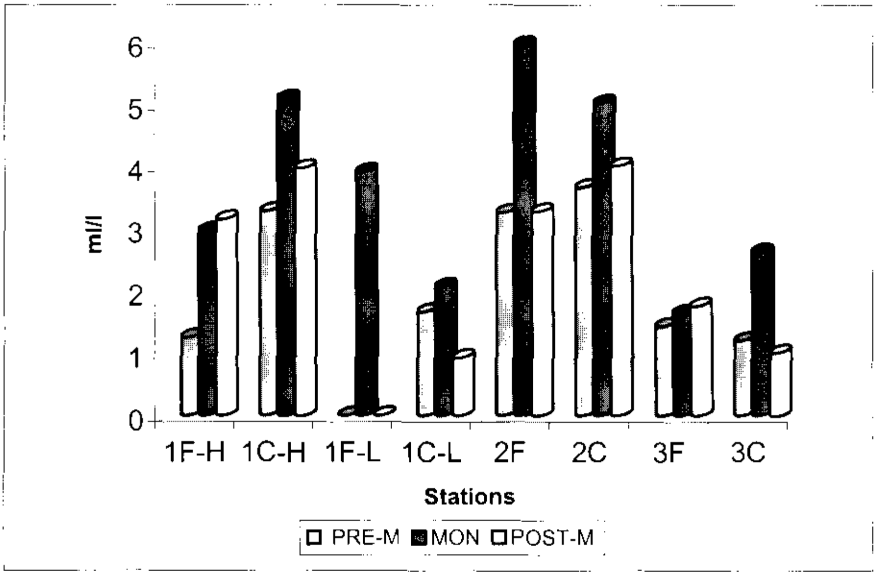


Fig 2.3 Seasonal variation of dissolved oxygen

2.3.3 pH

The pH is an important hydro-chemical factor indicating the level of dissolved CO_2 in the water, which may in turn reflect on the activity of phytoplankton and the level of dissolved oxygen in the water (Skirrow, 1975). Since the mangrove ecosystems support immense varieties of sea life, monitoring of pH variations in the system is highly essential to assess the productivity as well as the pollution in the system.

Table 2.3 Seasonal variation of pH

STATIONS	PRE-M	MON	POST-M
1F-H	8.15	7.90	7.50
1C-H	7.80	7.60	7.20
1F-L	7.75	8.05	7.45
1C-L	7.65	7.65	7.50
2F	7.80	8.30	7.60
2C	7.80	8.30	8.20
3F	7.75	7.10	7.40
3C	7.75	7.75	7.40

Variation of pH during different seasons given in the Fig 2-4.and Table 2.3. From the observations it is clear that, the pH in the three ecosystems were in an alkaline range. The maximum value was noted in stations 2F& 2C, the value was 8.3 and the minimum was observed at station 3F during monsoon. All forests showed lower pH than the adjacent water bodies. The water around the station 1F-H was highly alkaline during premonsoon. During this season the values were in the range of 7.65 to 8.15. During postmonsoon the maximum was noted at the station 3C and minimum at 2C-H. The increased value may be attributed to excessive photosynthetic activity of algae.

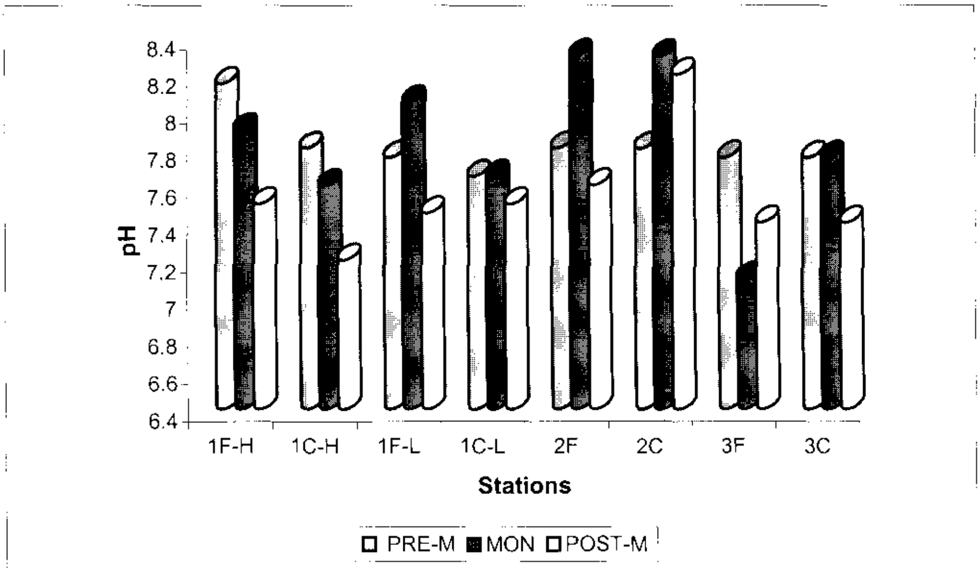


Fig 2.4 Seasonal variation of pH

2.3.4 Alkalinity

Alkalinity of the water is the result of the predominance of basic effectiveness over acid effectiveness. Dissolution of $CaCO_3$, abundance of organic matter, temperature, partial pressure of CO_2 are the influencing factors of the alkalinity of the medium.

Table 2.4 Seasonal variation of Alkalinity (mmol/l)

STATIONS	PRE-M	MON	POST-M
1F-H	1.82	5.66	0.77
1C-H	0.87	3.17	0.89
1F-L	0.48	5.23	1.04
1C-L	1.11	7.06	1.42
2F	1.58	6.48	0.42
2C	2.07	5.33	0.69
3F	1.39	7.14	1.40
3C	1.62	5.95	1.25

The seasonal distribution is given in the Fig2-5 and Table 2.4. The values ranged between 7.14-0.42mmoles/l. The maximum value was obtained at 3F during monsoon and the minimum was noted at 2F during post-monsoon. During monsoon, all forest except 1F-L exhibited lower values than the adjacent water bodies..

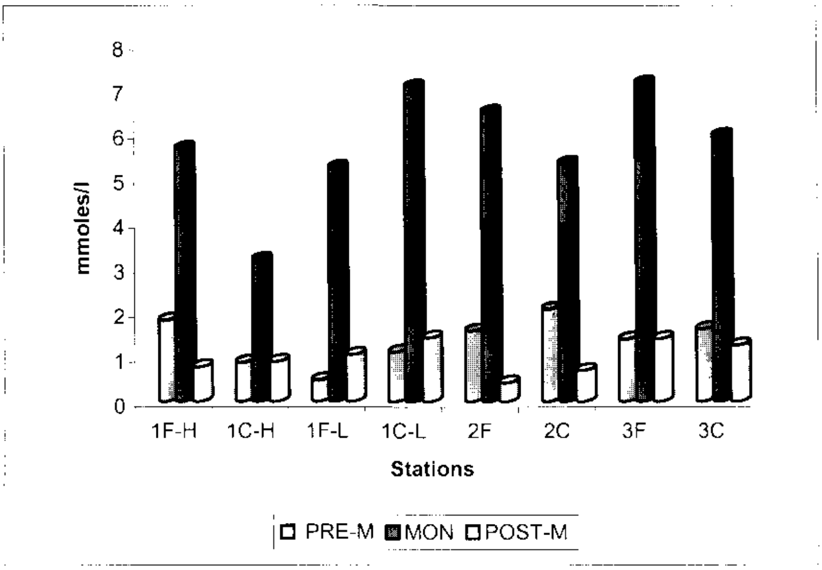


Fig 2-5 Seasonal variation of Alkalinity

During premonsoon the amount of alkalinity was comparatively lower in the forests than in the canals except 1F-H. The values were fluctuated between 0.48-1.82mmoles/l among forests and 0.87-2.07 mmoles/l among canals during premonsoon. During postmonsoon the values were in the range of 0.42 to 1.40 mmoles/l among forest and 0.69 to 1.42 mmoles/l among canals

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Chapter 3

SULPHUR CHEMISTRY IN WATER COLUMN

Biogeochemical transformations of sulphur in mangrove ecosystems are of interest from a variety of perspectives. Sulphur is an important redox element, existing in a wide range of oxidation states from −2 to +6. Sulphur can thus enter into a variety of biogeochemical processes (Luther et al., 1986). Sulphur is involved in sulphate reduction, pyrite formation, metal cycling, energy transport and atmosphere sulphur emissions. Each of these processes depends upon the formation of one or more intermediate states of sulphur, which may be inorganic or organic forms (Luther and Church, 1988).

In the +6 oxidation state, the chemistry of sulphur is dominated by sulphuric acid and sulphate, which are rather involatile chemical species. As, this is the only oxidation state stable in the presence of oxygen, sulphate is the predominant form of sulphur in seawater, fresh water and soils. Therefore, the reduction of sulphate to a more reduced sulphur species is a necessary prerequisite for the formation of volatile sulphur compounds and their emission to the atmosphere. In the global geochemical cycle, there are two types of biochemical pathways, which lead to sulphate reduction: assimilatory and dissimilatory sulphate reduction. The major pathway for the production of H_2S is dissimilatory sulphate reduction (Radford and cutter, 1994), which is used by microbes to obtain thermodynamic energy in an oxygen-depleted environment, where nitrate or sulphate is used as electron acceptors. Dissimilatory sulphate reduction is therefore most commonly observed in marine environments where water circulation, and consequently oxygen availability, is limited, but where sulphate is easily available because of its relatively high concentration in seawater.

Under favourable conditions, the rate of sulphate reduction to H_2S in anoxic environments can be high, of the order of hundreds of mmol m^{-2} day^{-1}. However, as the occurrence of this process is dependent on the existence of a mixing barrier, which prevents oxygen from entering the system, the same barrier will limit the escape of H_2S from the system. In the presence of oxygen, H_2S provides an excellent substrate for microbial oxidation from which certain bacteria can obtain a substantial amount of energy (Kelly, 1982). They are very efficient in removing H_2S and can completely oxidise this compound in a sediment layer. Consequently, the very large amounts of H_2S which are produced in the coastal and marine environment can not usually be transferred to the atmosphere, but are either re-oxidised at the oxic-anoxic interface, or precipitated in the form of iron sulphides and locked up in sediments. In shallow water environments, a fraction of the H_2S escape through temperature, wind driven turnover, through scouring of mud's in tidal channels and through bubbling of gas from anoxic environments. (Andreae, 1990). Significant H_2S emissions from the marine environment are therefore limited to near shore environments such as estuaries and salt marshes.

Hydrogen sulphide can be oxidised through chemical and biologically mediated processes. At some oxic-anoxic interfaces, the downward flux of dissolved oxygen is insufficient to oxidise the upward flux of H_2S (Yao and Millero, 1995). Oxidation of H_2S by Fe(III) hydroxides yields elemental sulphur as the dominant product, which might have an important implication for the formation of the pyrite (Yao and Millero, 1996). The oxidation of hydrogen sulphide by hydrous Fe (III) oxides is a surface-controlled process and first order with respect to both H_2S and $Fe(OH)_3$. In order to explain fate of sulphur in the sediments, we must know the sulphur chemistry of overlying water column, especially in the case of anoxic condition in a water logged system.

3.1 Dissolved Sulphur Fractions

This chapter includes seasonal variation of hydrogen sulphide and sulphate ions in the water column of three mangrove ecosystems and adjacent water body. As an intertidal system, the tidal variations noted at station 1 are also included in this Chapter.

Besides, for comparative purpose the earlier reported values (Beenamma, 1993) of hydrogen sulphide and sulphate concentrations in different stations of Cochin estuarine system and Kerala coast are included here.

3.1.1 Hydrogen Sulphide

Variations in the concentrations of dissolved H_2S in water are given in Table 3.1 and Fig 3.1

Table 3-1 Seasonal variation of Hydrogen sulphide (µmol/l)

STATIONS	PRE-M	MON	POST-M
1F-H	0.77	0.09	0.68
1C-H	0.26	0.08	0.20
1F-L	1.46	0.23	0.77
1C-L	0.62	0.08	0.27
2F	0.52	0.20	0.28
2C	0.25	0.15	0.16
3F	0.31	0.28	0.21
3C	0.27	0.29	0.26

Maximum value for H_2S was observed in station 1F-L during premonsoon and minimum at 1C-H during monsoon. The values varied between 0.08-1.46µmol/l. The water around the forests were rich in H_2S than in the canals. Among the canals the values were ranged between 0.25-0.62µmol/l during premonsoon. During monsoon the values were very low compared to other seasons except at stations 3F and 3C. In this season the values were fluctuated between 0.08-0.29µmol/l. The maximum value was noted at Station 3C and minimum was noted at station 1C-H. During postmonsoon the values were ranged between 0.16-0.77µmol/l. The maximum value was noted at station 1F-L during postmonsoon and minimum was noted at station 2C.

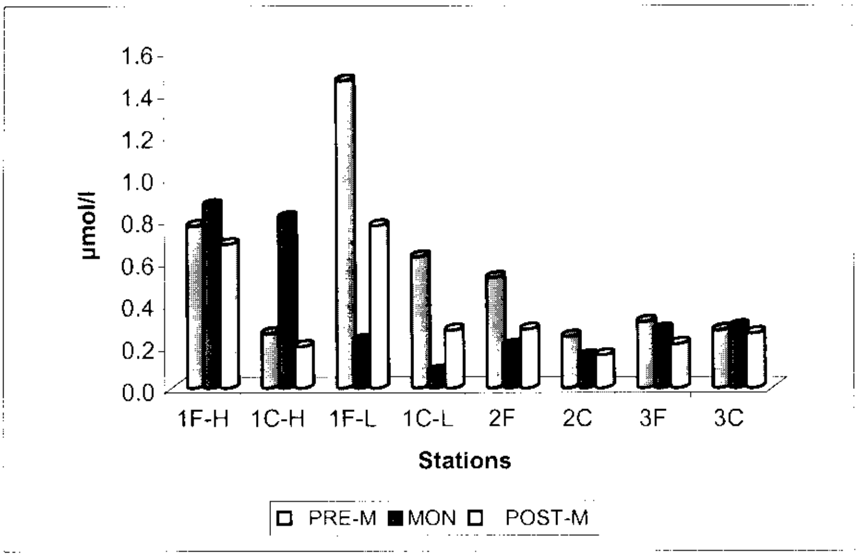

Fig 3-1 Seasonal variation of Hydrogen sulphide

The earlier reported values (Beenamma, 1993) of hydrogen sulphide (µmol/l) in the Cochin estuarine system and Kerala coast are given in the Table 3.2 and Table 3.3 respectively.

Table 3.2

PRE-M	1.098
MON	1.568
POST-M	1.946

Table 3.3

1	0.703
2	0.725
3	1.067

1: Near shore station.
2:Mid station 3:Off shore station

3.1.2 Sulphate

The seasonal variations of sulphate in the water samples were given in the Table 3-4 and Fig 3.2.

Table 3-4 Seasonal variation of Sulphate (mmol/l)

STATIONS	PRE-M	MON	POST-M
1F-H	6.34	1.30	8.53
1C-H	29.97	0.86	36.45
1F-L	24.73	1.23	31.91
1C-L	27.38	0.15	9.34
2F	22.24	0.76	4.37
2C	26.13	0.65	4.14
3F	47.17	3.95	37.51
3C	48.27	2.91	13.86

The concentration of sulphate was maximum at station 3C during premonsoon and minimum at station 1C-L during monsoon. The values were ranged between 0.15mmol/l - 48.27mmol/l. Comparatively higher values noted in the forests during monsoon. During monsoon the values were ranged between 0.15-3.95mmol/l. The adjacent water bodies exhibited higher values than forests during premonsoon. In this season the values were fluctuated between 6.34mmol/l – 48.27mmol/l. During postmonsoon values were higher in the forests except 1F, at the time of high tide. During all seasons 3F &3C possessed higher concentrations of sulphate than other stations. Besides, during monsoon and postmonsoon sulphate concentrations were higher in the forest and during premonsoon the sulphate concentration was high in the canal.

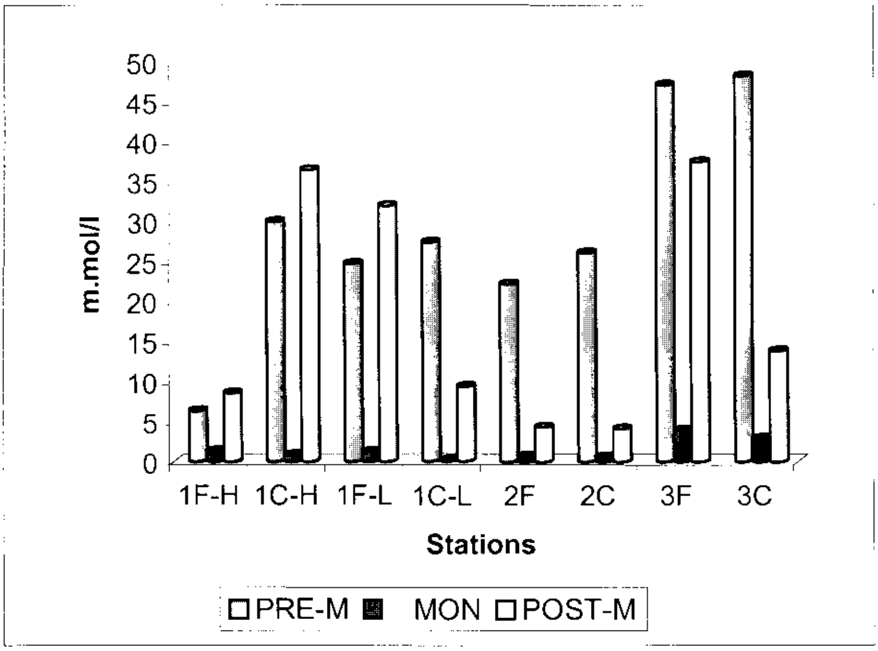

Fig 3-2 Seasonal variation of Sulphate

The previous data, obtained by Beenamma (1993) in Cochin estuarine system and Kerala coast, of concentrations of sulphate (mmol/l) in water column are given in the Table 3.5 and Table 3.6 respectively.

Table 3.5

PRE-M	12.88
MON	2.27
POST-M	5.78

Table 3.6

1	26.898
2	27.178
3	27.317

1:Near shore station

2: Mid station 3:Off shore station.

3.1.3 Tidal Variation

River flow and tidal currents play a major role in creating the environmental conditions of a system. While the net flow is seaward, the direction of flow is reversed once or twice daily according to the tidal regime. In wetlands, the progression of tides from neap to spring to neap produces a characteristic progression of water column chemistry (Vorosmarty and Loder, 1994). The tidal fluxes of sulphur through saline wetlands are usually very large in comparison to the rates of sulphur processing within the ecosystem (Peterson, 1982). Most of the sulphur reduced in the sediment is subsequently re-oxidised or exported to creeks, so only a small percent of the reduced sulphur produced each year is buried.

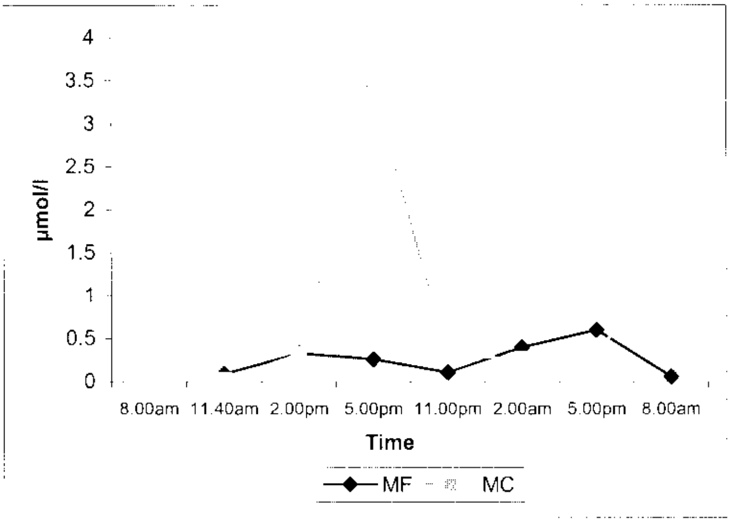

Fig 3-3 Tidal variation of Hydrogen sulphide

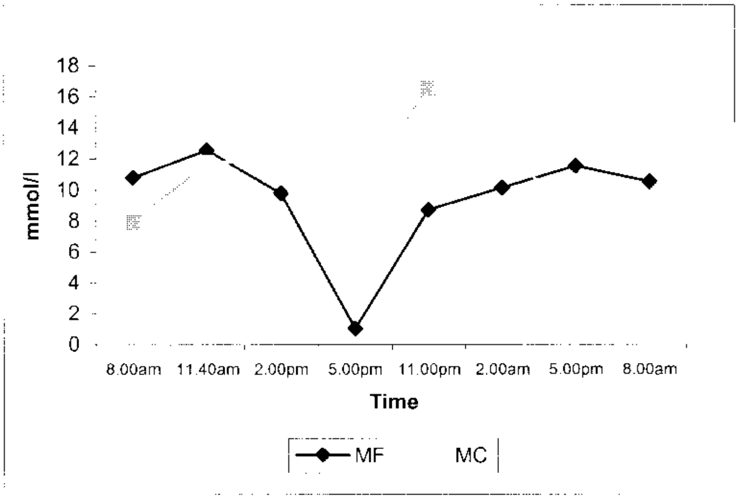

Fig 3-4 Tidal variation of Sulphate

Discussion

The main source of sulphur in this system is the saline water, which intrudes through the canal. The average of salinity of the water body is near 20ppt indicating a substantial input of the sulphate to the system. But the actual values of the sulphate obtained are not found to be a reflection of the salinity. The difference in the concentration between forest and canal and the high tide and low tide, indicate substantial removal of sulphate during the residence of the sulphate in the system. The removal of sulphur, mainly, is either by precipitation as sulphides or sulphate or by conversion to hydrogen sulphide, by the sulphate reduction processes. Generally, it is considered that, the ultimate burial of sulphur in saline water systems, especially in wetlands is usually, much less (King, 1988; Howarth, 1984). The alternate processes where, the sulphate reduction removes the sulphur from the water column, either through the precipitation or by the exchange with atmosphere. It is proposed that, the removal contains some other mechanisms other than that of the above. The high oxidation character of the sulphide compared with the low depth profile of the water column, in fact, suggests rapid conversion of the sulphide to its oxidised forms. Through the energy budgeting studies, it has been proposed that the organic matter through microbial growth and respiration is a promoting factor in the reduction processes and maintenance of the reduced condition.

The studies of Howarth and Teal (1980) and Howarth (1984), indicated that, a major portion of the energy associated with the organic matter is trapped as sulphides. Studies on the nutrient dynamics of the present system have shown that, significantly, high concentration of nitrite at the low tide conditions (Geetha, 2002). Such a condition is indicative of the anaerobic diagenesis, which in turn is a sulphate reduction promoting condition. The significantly high concentration of H_2S observed during pre-monsoon and post-monsson seasons in all the stations coincides with the above observation.

The earlier studies in the adjacent water bodies indicated, significantly high concentration of H_2S during all the seasons. The high sulphide concentration explains as the marginal stability of the ion pairs formed between cations and H_2S. More over the oxidation of H_2S was found to be governing by the pH of the system. Generally, the lower pH promotes the oxidation processes. The present study, the value of pH is not low to promote sulphide oxidation. The observed concentrations of the H_2S, can be considered as the resultant of the above processes.

Table: 3-7 –Sulphate to Chlorinity Ratio of different stations

STATIONS	PRE-M	MON	POST-M
1F-H	0.059	0.685	0.141
1C-H	0.289	0.743	0.514
1F-L	0.226	0.120	0.503
1C-L	0.271	0.032	0.174
2F	0.276	0.250	0.120
2C	0.302	0.114	0.051
3F	0.327	0.178	0.301
3C	0.364	0.215	0.096

The sulphates to chlorinity ratio of different stations are given in the Table 3-7. The sulphate to chlorinity ratio gives a high value against the expectation. No concrete explanation is given here. The major contribution of the sulphate to the system is from the adjacent water body itself and SO_4/Cl values reported earlier in the Cochin estuary and coast of Kerala were within the expected limits (Beenamma, 1993).

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Chapter 4

CHEMISTRY OF SULPHUR IN MANGROVE SEDIMENTS

4.1 Acid Volatile Sulphur

4.2 Gregite Sulphur

4.3 Pyrite Sulphur

4.4 Sulphate Sulphur

4.5 Elemental Sulphur

4.6 Organic Sulphur

4.7 Total Sulphur

4.8 Organic Carbon

4.9 Iron In The Surface Sediments

Marine sediments are the main sink for sea water sulphate which demonstrates that, the sedimentary sulphur cycle is a major component of the global sulphur cycle. The most important mechanisms for removing sulphate from the Oceans to the sediments are

1 The bacterial reduction of sulphate to H_2S, which reacts with iron to form sulphide minerals.

2 The formation of Organic sulphur.

3 The precipitation of $CaSO_4$ minerals in evaporates (Sabine and Jorgensen,1999).

Two types of sulphate reduction can be distinguished. a) assimilatory sulphate reduction, which serves for the biosynthesis of organic sulphur compounds and b) dissimilatory sulphate reduction from which micro organisms conserve energy. Most of the dissimilatory sulphate reduction takes place close to the sediment surface (Iversen and Jorgensen, 1985), depending on the quantity and quality of the organic matter transported into the sediments. Microbial sulphate reduction using organic matter as a food source takes place only under anoxic conditions, as shown in the following equation.

$$R(CHO) + SO_4^{-2} \longrightarrow HS^{-1} + HCO_3^{-1} + R$$

The organic residue is deposited along with the products of reaction of HS^- that combine with available iron to make sulphides. (Berner, 1970; Lein et al., 2002). Goldhaber et al (1974) shown that there is a significant relationship between organic carbon and sulphide sulphur in the sediments. That is, when sulphate is reduced and organic matter is oxidised, the sediment contains a proportional amount of sulphide and residual carbon.

Dissolved hydrogen sulphide that is produced during bacterial dissimilatory sulphate reduction may rapidly react with sedimentary reactive iron compounds to form iron monosulphide (Rickard, 1995), which can further react with dissolved sulphide, elemental sulphur or poly sulphides

(Luther, 1991; Rickard, 1997) to form pyrite. This immobilization of free sulphide within the sediment has major consequences for the cycling of iron and sulphur. Transport processes and turnover rates are significantly reduced by the formation of solid phase iron sulphides. Moreover, the formation of iron sulphides and the subsequent burial in the sediment has been recognised as the dominant pathway for the permanent removal of sulphur and iron (Berner, 1982).

In the absence of sufficient sedimentary reactive iron, H_2S can diffuse into underlying sediments or the water column (Passier et al., 1999), can be chemically or microbially reoxidised to sulphur intermediates or sulphate (Fossing and Jorgensen, 1990) or react with organic matter. Additionally, bioturbating organisms can transport iron sulphide minerals from the reduced to the oxidised part of the sediments, where they are subsequently reoxidised (Aller and Rude, 1988). Thus, benthic organisms might enhance the recycling of sulphur and iron within the sediments by their bioturbating and bio-irrigating activities (Wijsman et al., 2001).

The reaction kinetics of sulphate reduction and associated sulphur cycling depend on the interplay between sulphate concentration and availability of organic matter. The site of sulphate reduction is more often on the surface of the sediment than in the water column (Goldhaber and Kaplan, 1974).The sulphate reduction is very much pronounced in mangrove sediments due to the enrichment of organic carbon. There fore the sulphur chemistry in the surface sediments of mangroves is very much interesting and complex. This chapter reveals various concentrations of different forms of sulphur and explains sulphur chemistry of surface sediments' of concerned mangrove ecosystems. The distribution of different forms of sulphur such as

Acid volatile sulphur, gregite sulphur, pyrite sulphur, elemental sulphur, sulphate sulphur, organic sulphur and concentration of total sulphur are given below.

RESULTS AND DISCUSSION

4.1. Acid Volatile Sulphur

The metastable iron sulphides are often termed "acid volatile" sulphides. The acid volatile sulphides (AVS) are so termed in order to discriminate between the soluble and insoluble iron sulphides. The insoluble and thermodynamically stable phase is pyrite. Acid soluble sulphide consists mainly of metastable iron sulphide phases and includes the mineral gregite along with amorphous iron sulphide and mackinawite (Goldhaber and Kaplan, 1974). Mackinawite is a pure phase in the Fe-S system and is assigned a formula $FeS_{0.94}$ (Ward, 1970). In the present investigation, AVS fraction is determined using the method of Cutter and Velinsky (1988), excluding the gregite mineral. The initial product formed from reaction of ferrous iron with hydrogen sulphide is represented as follows;

$$Fe^{2+} + HS^{-} \rightarrow FeS + H^{+}$$

The method adopted for the determination of AVS is given in the Chapter 2. Variations of AVS sulphur at different stations during different seasons are given in the Table 4.1 and Fig 4.1.

Table 4.1 Seasonal Variation of AVS (ng/g)

	STATION 1	STATION 2	STATION 3
PRE-M	179.56	99.90	70.63
MON	120.00	119.82	50.01
POST-M	189.74	120.02	70.00

The values ranged between 50.01ng/g- 189.74ng/g. The maximum value was observed at Station 1 during postmonsoon and minimum at Station 3 during monsoon. The observed concentrations at Station 1 were high compared to other two Stations. At Station 1,the maximum was observed during postmonsoon and the value was noted as 189.74ng/g and the minimum was 120.00ng/g during monsoon. At Station 2, the maximum observed was 120.02ng/g and the minimum was 99.90ng/g during postmonsoon and premonsoon respectively. At Station 3 the maximum value 70.63ng/g was noted during premonsoon.

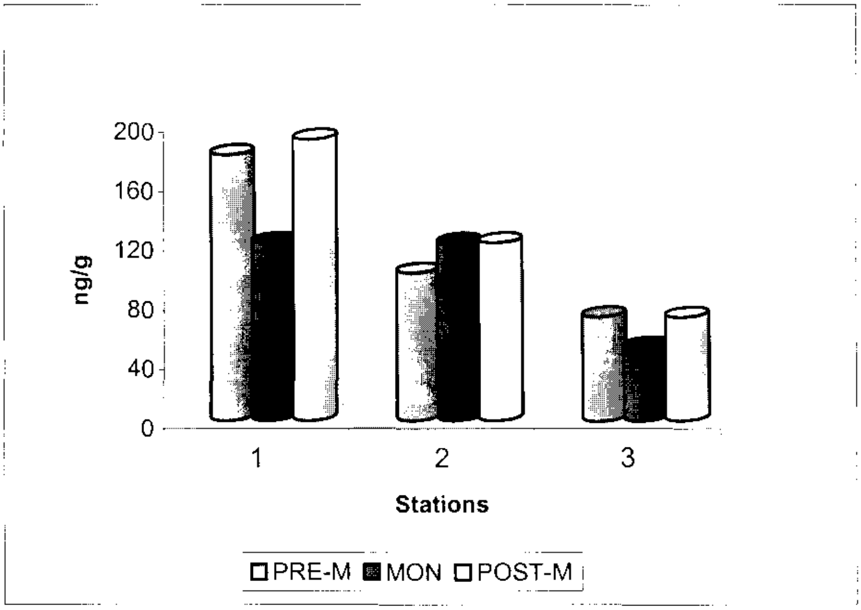


Fig 4.1 Seasonal variation of AVS in the surface sediment

The concentrations obtained in this investigation were considerably lower than that of the previous studies (Table 4.2).

Table 4.2

System	Reported value	Reference
Louisiana Salt Marsh	5.9 - 135μg/g	Krairapanond et al., 1991.
Black sea sediment	1728 – 4896μg/g	Wijsman et al., 2001.
Cochin Estuary	230– 2690 μg/g	Beenamma, 1993
Kerala coast	10 –2710μg/g	Beenamma, 1993.
Present Study	50.01 –189.74ng/g	

The concentration of HCl-soluble sulphide is high from the surface to about 10 cm, below which it decreases to low levels, probably because it is converted to pyrite (Jorgenson and Cohen, 1977). They suggested that the fluctuating FeS concentrations near the surface are not due to fluctuations in the production of sulphide, because free H_2S is present in high concentrations and the accumulated FeS is only a small fraction. This is due to the amount of iron present in the surface at the time of production.

The concentration of AVS fraction in the surface sediments of Black Sea ranges between 153µ mol S/g to 54µ mol S /g (Wijsman et al., 2001). Depth profiles of AVS fraction in Louisiana salt Marsh soils reveals that percentage of AVS fraction to the total sulphur is <1% (Krairapanond et al., 1991). This was in agreement with previous observation of De Laune et al (1983) and Nedwell and Abram (1978). Howarth and Teal (1979) found that the concentrations of iron monosulphides in salt marsh sediments tend to remain relatively low, generally <16µg S/g soil. Further more it has been noted that, the dynamics of AVS is controlled to some extent by temperature (Giblin and Howarth 1984; Cutter and Velinsky 1988; Luther and Church 1988). The seasonal trend shown in the present study is in agree that with the seasonwise distribution of AVS fraction at different stations in Cochin estuarine system (Beenamma, 1993), the actual value but is considerably low.

4.2 Gregite Sulphur

Berner (1967) assigned a composition Fe_3S_4 to gregite and this has a spinel structure (Skinner et al., 1964). The transformation of iron sulphides to Pyrite occurs by the formation of metastable iron sulphides mainly by gregite (Wang and Morse, 1996). The reaction to form gregite from Mackinawite is an oxidation process and takes place in the presence of the oxidising agents like elemental S and iron oxide.

For the estimation of gregite, H_2S was liberated with KI and $NaBH_4$ (Cutter and Oats, 1987) and the value was determined spectrophotometrically. The data observed are presented in Table 4.3 and Fig 4.2.

Table 4.3 Seasonal variation of gregite sulphur (ng/g)

	STATION 1	STATION 2	STATION 3
PRE-M	470.01	660.23	70.00
MONS	280.10	150.03	70.00
POST-MO	430.00	150.03	50.12

The concentrations of gregite sulphur varied from 50.12ng/g to 660.23ng/g. Gregite S was maximum at Station 2 during pre-monsoon and minimum at Station 3 in post-monsoon. At Station 1 the maximum was noted during premonsoon and the minimum during monsoon. The amount varied between 280.10ng/g-470.01ng/g. At Station 2 the maximum value was observed during premonsoon and the concentration was 660.23ng/g. But there was no change in the concentration during monsoon and postmonsoon. Compared to other two stations minimum amount of gregite sulphur was observed in Station 3.

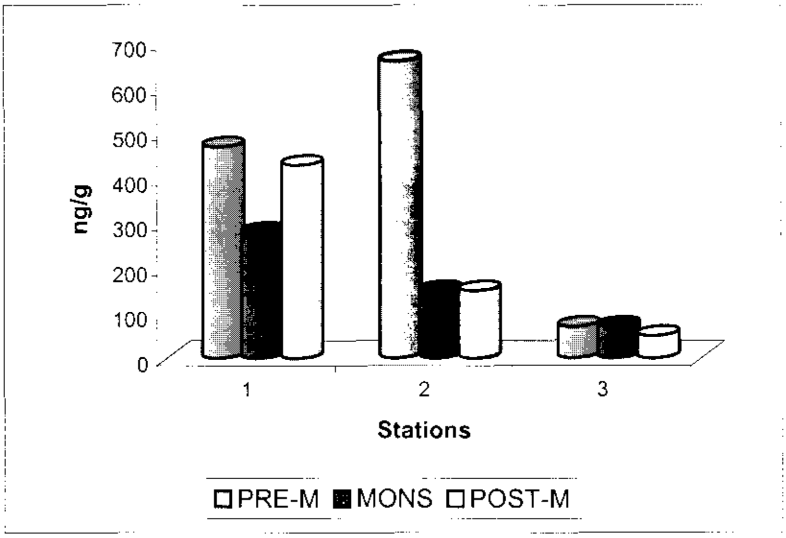


Fig 4.2 Seasonal variation of gregite sulphur in the surface sediments

The maxima obtained at Station 2 during Pre-monsoon can be explained by the higher concentration of S^0 at Station 2 during all other seasons except pre-monsoon. Station 1 contains more amount of gregite sulphur and this may be due to sulphide formation via higher rate of sulphate reduction. There is a significant decrease in gregite sulphur concentration at Station 3, can be due to either decreasing rate of sulphate reduction or enhanced pyrite formation. The concentrations of pyrite, but rules out the possibility of an enhanced pyritisation.

Generally gregite sulphur was considered as a part of the AVS due to its high labile character and only a few reports are available. The earlier works in the sediments of Cochin estuary and Kerala coast gave a concentration of 0.04 – 0.69mg/g and 0.03 – 0.75mg/g of gregite sulphur (Beenamma, 1993). The present values are significantly lower to these values.

There is depletion in gregite sulphur concentration at Station 3 comparing with the trends shown by AVS and pyrite concentrations, this depletion can be accounted as due to a decreased rate of reduction.

4.3 Pyrite Sulphur

Among sulphides, pyrite is the ferrous poly sulphide and it is the thermodynamically most stable phase of the iron sulphides. The method of analysis for the estimation of Pyrite sulphur is given in the Chapter 3. The concentrations noted are given in the Table 4.4 and Fig 4.3.

Table 4.4 Seasonal variation of Pyrite sulphur (ng/g)

	STATION 1	STATION 2	STATION 3
PRE-M	400.00	59.85	0.00
MONS	109.96	0.00	60.01
POST-M	179.90	49.86	10.12

In present study the concentrations of Pyrite sulphur ranged from not detectable level to 400.00ng/g. Maximum value was obtained at Station 1 during Pre-monsoon and the species was not detected at Station 3 during Pre-monsoon and also at Station 2 in monsoon.

At Station 1 the maximum value was observed during premonsoon and minimum value during monsoon. The values were in the range of 109.96 ng/g - 400.00ng/g. At Station 2 surface layer was devoid of Pyrite during monsoon. The maximum amount, 59.85ng/g, was noted during premonsoon. At Station 3, Pyrite was not detected during premonsoon and the maximum amount 60.01ng/g was observed during monsoon.. Pyrite concentrations were very low at Stations 2 and 3 compared to Station 1 in all seasons.

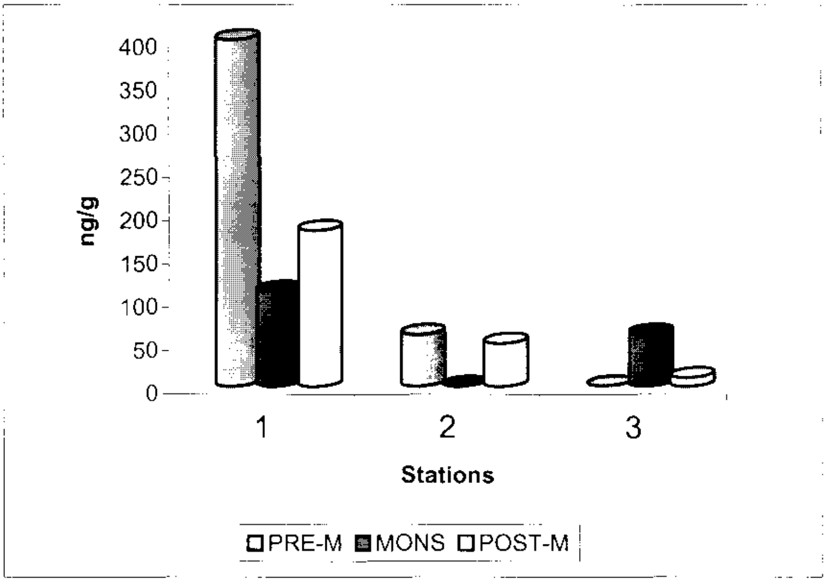


Fig 4.3 Seasonal variation of Pyrite sulphur in surface sediments

Table 4.5

System	Reported value	Reference
Menai Strait, Anglesey, UK	720 - 800 μg/g	Nedwell and Floodgate, 1972.
Louisiana salt marsh	72.8 – 388 μg/g	Krairapanond, 1991.
Cochin estuary	40 – 2060 μg/g	Beenamma, 1993.
Kerala coast	30 – 4820 μg/g	Beenamma, 1993.
Present study	0.00 – 400 ng/g	

A direct comparison of the data with the earlier works (Table 4.5) indicates a significantly low pyrite sulphur concentration in the present study. A probable reason may be that, pyrite also in suscepectable to oxidation and so no accumulation or building up of concentration takes place in the upper layers of the sediment. It is to be noted that in the present study, the analysis was restricted to the top 15cm of the sediment due to practical reasons and the high values reported by the earlier workers refers to a higher depth. The accumulative iron sulphide concentrations in the present study, that is, pyrite plus gregite gives a more comparable value. This also suggests the contribution of the oxidative character of the sediments in governing in the pyrite formation.

More recent studies (Drobner et al., 1990; Rickard, 1997) have demonstrated that Pyrite formation is also possible with H_2S itself acting as an oxidant for metastable iron sulphides according to the following equation.

$$FeS + H_2S \rightarrow FeS_2 + H_2$$

Rickard (1997) suggested this as the dominant pyrite forming path in strictly anoxic systems. The direct reaction path way may proceed within hours, resulting in the formation of small pyrite crystals (Rickard, 1975, Luther et al., 1982). Framboidal pyrite – apart from that formed by the mechanism presented by Drobner et al (1990) and Rickard (1997) - is formed slowly via intermediate iron sulphides (Sweeney and Kaplan, 1973; Raiswell, 1982).

Howarth (1984) and Haering et al (1989) suggested that pyrite accumulation is related to the availability of the iron source. In more reduced sediments (>15cm), where pyrite is formed slowly by the conversion of FeS, the availability of Fe (11) limits the rate of pyritization (Lord and Church, 1983). This is supported by a study of De Laune et al (1983), who reported low dissolved iron concentration of the order of 0.003mg/l in Louisiana salt marsh soils. Only 23% of the total iron in this area studied by Feijlel et al (1988) occurs in the form of pyrite. Comparable amounts of pyrite sulphur, accounting for <2% of total sulphur, were observed in Connecticut coastal sediments (Berner, 1970). These finding provides the evidence that the temporal variability in total S content in this salt marsh is not primarily due to fluctuations in pyrite S content. Haering et al (1989) similarly concluded that pyrite sulphur was not responsible for the variation in total S in Chesapeake Bay tidal marsh soils.

Like marine sediments, the pyritization process in marsh systems appears to be dependent on the other sulphur fractions (Feijtel et al., 1988; Lord and Church, 1983; Cutter and Velinsky, 1988). Beenamma (1993) studied the distribution of pyrite in the sediments of Cochin estuarine system and the concentration ranged from 0.00 mg/g to 4.30 mg/g, which constituted 0 to 36.27 % of total S.

The observations in this study are comparable with, those observed in salt marsh studies (Cutter and Velinsky, 1988), in lake sediments (Nriagu and Soon, 1985) and in Cochin estuarine sediments (Beenamma, 1993). These observations in these studies indicate that the temporal variability in total sulphur in the salt marsh is not primarily due to fluctuation in pyrite S content (Berner, 1970; Haering et al., 1989). But Goldhaber and Kaplan (1974) and Rickard (1975), found that the total S profiles are found very much dependent on the pyrite S. Here pyretic contribution to the total sulphur was found to be a minor fraction. pre-monsoon is the least favourable for an oxidative environment which favoured pyrite formation over pyrite oxidation. The maximum value obtained at Station 1 may be due to increasing rate of sulphate reduction and resultant formation of sulphides in anaerobic conditions. High concentration of Fe (II) also supports this value. The computation of data in the present study supports the observations of Cutter and Velinsky (1988) and indicates that the behaviour of pyrite sulphur in mangroves are more or less comparable with that of the salt marsh and lake sediments.

4.4 Sulphate Sulphur

Sulphate S was determined by the method suggested by Tabatabai and Bremner (1972). Dried sediment sample was extracted with 0.1 M LiCl, by shaking for 30 mts and centrifuging. The extracted sulphate was determined turbidimetrically (APHA, 1995).

The sulphate sulphur estimated includes sulphate trapped in sediments and traces of gypsum present in the sediments. The concentrations of the sulphate in the sediment depend on the dynamics of the overlying water system, which controls the transport of sulphate from the water column to the sediment (Beenama, 1997). The procedure taken for the estimation is given in the Chapter 2.The values obtained were given in Table 4.6 and Fig 4.4.

Table 4.6 Seasonal variation of Sulphate sulphur (μg/g)

	STATION 1	STATION 2	STATION 3
PRE-M	590.00	530.00	610.23
MON	840.01	50.00	330.1
POST-M	579.98	480.21	600.1

The concentration of sulphate varied from 50.00 ng/g to 840.01 ng/g at Station 1 and at Station 2 respectively during monsoon. At Station 1 during premonsoon the value was noted as 590.00ng/g and postmonsoon the value was 579.98ng/g. At Station 2 the values were in the range of 50.00ng/g - 530.00ng/g. Maximum was observed during premonsoon and minimum was noted during monsoon. At Station 3, the maximum value was observed during premonsoon and the minimum was noted during monsoon. The values ranged between 330.10 ng/g – 610.23ng/g.

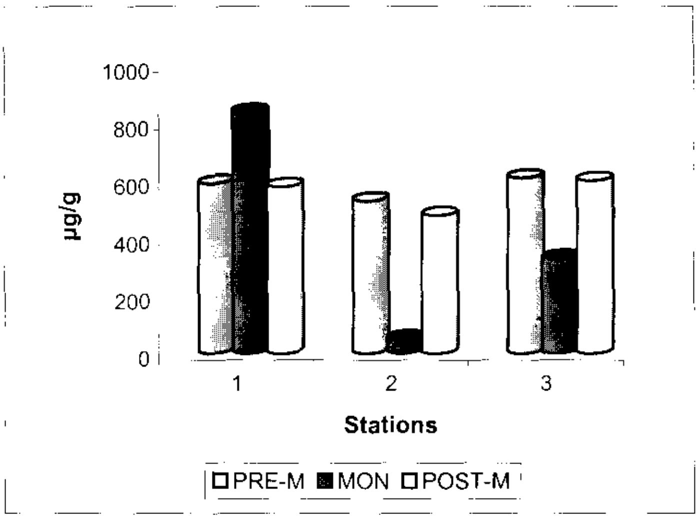


Fig 4.4 Seasonal variation of sulphate sulphur in surface sediments

Sulphate reduction rates were found maximum in the upper 2 to 5 cm of the sediments (Sabine and Jorgensen, 1999). Cycling of oxidised and reduced Fe and Mn phases as well as of organic matter in surface sediments due to bioturbation and mixing have been described by Aller and Rude (1988), Thamdrup et al (1994) and Hase (1997). According to the studies of Hase (1997), Fe-oxides can be recycled up to 50 times in surface marine deposits.

The biogeochemical transformations of sulphur in marine sediments are closely coupled to the cycles of Iron and Manganese (Iversen and Blachburn, 1981). Aller and Rude (1988) showed that Mn(IV), rather than Mn(III) or Fe(III), is the major oxidant of sulphides to SO_4^{2-} under anoxic conditions. This process is especially important in organic rich estuarine and shelf sediments where oxides are in close proximity to the sulphidic zone. Mixing between oxide particles and sulphidic sediment takes place constantly during biogenic reworking, infaunal burrow construction and wave disturbances. Anoxic oxidation will be accelerated by the natural diagenetic enrichments of Mn-oxides in surface sediments or burrow walls, which provide a source of oxidised material during reworking. Thamdrup et al (1993) described an alternative pathway of complete anaerobic oxidation of sulphide to sulphate. The sulphide oxidation occurs by a combination of chemical oxidation of H_2S to S^0 with MnO_2 or FeOOH and subsequent bacterial disproportionation of S^0 to H_2S and SO_4^{2-}. The H_2S regenerated by latter process can undergo renewed oxidation to S^0 and disproportionation.

During summer the soils in the upper layer becomes oxidising, converting sulphide and sulphide minerals, predominantly pyrite to thiols and sulphate (Luther and Church, 1988). The rate of sulphide oxidation is faster than the rate of sulphate reduction at this depth (Lord and Church, 1983). Oxidation of pyrite to sulphate could occur according to either equation (1) or (2) (Giblin and Howarth, 1984)

$$FeS_2 + 7/2\,O_2 + H_2 \rightarrow Fe^{2-} + 2SO_4^{2-} + 2H^+$$

$$FeS_2 + 15/4\,O_2 + 5/2\,H_2O \rightarrow FeOOH + 2SO_4^{2-} + 4H^+$$

Distributions of sulphate sulphur in sediments were found to be consistent with the sulphate concentration in the water column. The lower concentration of sulphate at Station 2 is due to the minimum capacity of sediments to hold SO_4^{2-} ions at the lattice site. Here percentage of grain size is greater than clay and silt. Increasing percentage of clay and silt at Station 3 may be a contributing factor of higher concentration of SO_4.

4.5 Elemental Sulphur

Elemental sulphur in the samples were estimated by a method suggested by Fabbri et al (2001). Elemental sulphur has a major role in the cycling process of sulphur because the transformations among sulphides takes place mostly in presence of elemental sulphur (Berner, 1970). The oxidation of dissolved hydrogen sulphide and ferrous sulphide under natural conditions can lead to the formation of elemental sulphur (Goldhaber and Kaplan, 1974; Cutter and Velinsky, 1988). The elemental sulphur concentrations from the sediment column up to 15cm are reported. The estimated values are as follows.

Table 4.7 Seasonal variation of Elemental sulphur (µg/g)

	STATION 1	STATION 2	STATION 3
PRE-M	303.01	617.2	250.30
MON	219.98	87.23	420.30
POST-M	243.00	679.86	500.00

The values were in the range of 87.23ng/g - 679.86ng/g. Maximum amount of 679.86ng/g was noted at Station 2 during postmonsoon and the minimum during monsoon at Station 2. At Station 1 minimum was noted during monsoon and maximum during premonsoon. But at Station 2 the concentration rose to the maximum during postmonsoon and decreased to a minimum during monsoon. At Station 3 a maximum amount of 500.00ng/g was observed during postmonsoon and a minimum was noted during premonsoon. The values were in the range of 250.30ng/g- 500.00ng/g.

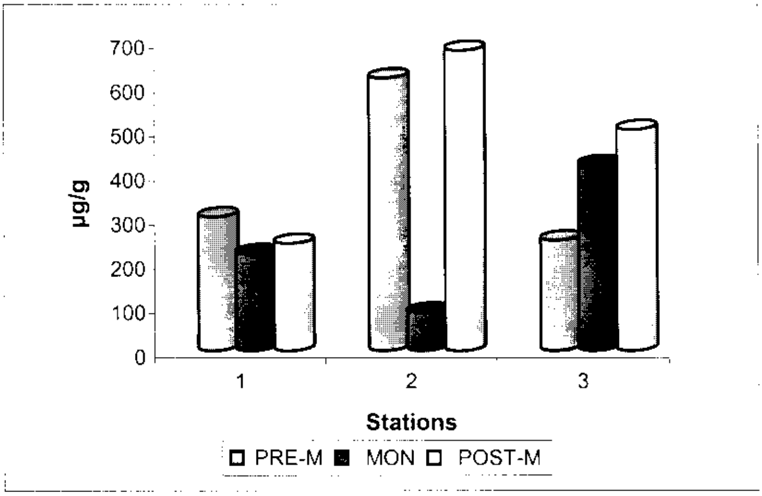


Fig 4.5 Seasonal variation of Elemental sulphur in surface sediments

The elemental sulphur never builds up to a high concentration due to rapid formation and removal (Kaplan et al., 1963). The rate of transformation of AVS to pyrite is limited by elemental sulphur and is the age limiting factor (Berner, 1970).

The concentration of elemental S in Louisiana salt marsh accounted for up to 3 % of total S (Krairapanond et al., 1991) and the mean elemental sulphur concentration was ten times higher than that of AVS and with a significant inverse correlation between elemental sulphur and AVS. The oxidation of dissolved H_2S and FeS under natural conditions can lead to the formation of elemental S (Goldhaber & Kaplan, 1974; Cutter & Velinsky, 1988). A similar observation reported from the marsh of Delaware (Luther and Church, 1988). This sulphur form reaches maximum concentrations within the upper 20 cm depth, which is the oxidised zone of these salt marsh soils (Feijtel et al., 1988). Troelsen and Jorgensen (1982) suggested seasonal fluctuations in S^0 due to the seasonal transition from a more oxidised condition (summer) to more reduced condition (winter).

In this study overall contribution of elemental sulphur to total S was found to be higher, compared to other studies (Table 4.8).

Table 4.8

System	Reported value	Reference
Louisiana salt marsh	107 – 560µg/g	Krairapanond et al., 1
Cochin estuary	70 – 3800 µg/g	Beenamma, 1993
Kerala coast	0.00 – 3810µg/g	Beenamma, 1993
Present study	87.23 - 679.86µg/g	

The higher concentration at Station 2 may be due to the anthroprogenic input into the sediments. Troelsen and Jorgenson (1982) suggested that seasonal fluctuations might be due to the seasonal transition from more oxidised condition to more reduced condition. An active participation of S^0 in the production of organo S compounds have been reported by Casagrande et al (1979). Luther et al (1982) have reported that a dynamic S cycle, in which sulphur is transformed from inorganic to organic and vice versa, seasonally occur in the salt marsh. Such a condition of dynamic sulphur cycling could be expected in the present study also.

4.6 Organic Sulphur

Organic sulphur fraction in this investigation comprises both the ester sulphate S compounds and carbon bonded S compounds. The obtained data are distributed in the Table 4.9 and Fig 4.6.

Table 4.9 Seasonal variation of Organic sulphur (μg/g)

	STATION 1	STATION 2	STATION 3
PRE-M	255.95	21.44	449.33
MONS	309.5	452.5	559.42
POST-M	926.22	149.61	289.77

The concentrations of Organic sulphur varied from 21.44ng/g to 926.22ng/g at Station 1 and Station 2, during post-monsoon and pre-monsoon respectively. The seasonal variation is 21.44ng/g to 449.33ng/g, 309.50ng/g to 559.42ng/g and 149.61ng/g to 926.22ng/g during pre-monsoon, monsoon and post-monsoon respectively.

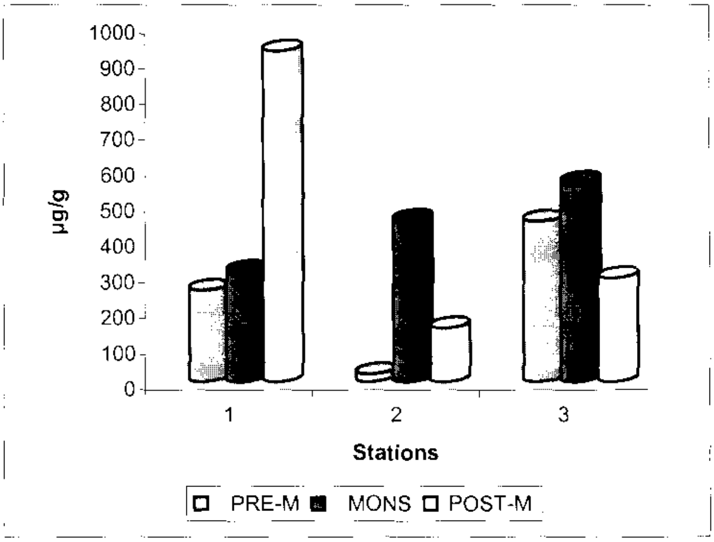


Fig 4.6 Seasonal variation of Organic sulphur in surface sediments

Table 4.10

System	Reported value	Reference
Louisiana salt marsh	64% - 84% of Total S	Krairapanond et al.,1991.
Carolina salt marsh	50 % of Total S	King, 1988.
Cochin estuary	5.8 %--79.13%	Beenamma, 1993.
Kerala coast	55% -75%	Beenamma, 1993.
Present study	1.88%-76.69%	

Percentage of organic sulphur to total S varied from 1.88 % to 76.78 % during three seasons (Table 4.15). Most of the values ranged between 20 % - 53 %. The values are as in all other cases, is low compared to previous studies (Table 4.10). Several studies have reported that most of the sulphur (84 - 97% of total S) in salt marsh and marine sediments is present as inorganic sulphur (Kaplan et al., 1963; Berner, 1964; Howarth and Teal, 1979 and Cutter and Velinsky, 1988).

Wieder et al (1987) claimed that 83 % to 85 % of total sulphur in Big Run Bog peat is present as organic sulphur. Organic sulphur also contributes 90 % to 93 % of total S in British valley sediments (Brown 1985). In marine mangrove peat in the Florida Everglades, about 30 % to 60 % (Casagrande et al 1979) and 76 % (Altschuler et al 1983) of total S are present as organic sulphur. Haering et al (1989) have also reported high organic sulphur levels in Chesapeake Bay tidal marsh soils.

4.7 Total Sulphur

Total sulphur includes both organic and inorganic sulphur. For the determination of total S all sulphur forms are oxidised to sulphate and the oxidised sediment is extracted with dil HCl and the sulphate was determined turbidmetrically. The obtained values are as follows.

Table 4.11 Seasonal variation of Total sulphur (μg/g)

	STATION 1	STATION 2	STATION 3
PRE-M	1150	1170	1310
MONS	1370	590	1310
POST-M	1750	1310	1390

Concentrations of total sulphur ranged from 1750ng/g to 590ng/g at Station 1 and Station 2 during post-monsoon and monsoon respectively. At Station 3 pre-monsoonal and monsoonal values were same. Seasonal variation was 1150ng/g to 1310ng/g; 1370ng/g to 590ng/g and 1750ng/g to 1310ng/g during pre-monsoon, monsoon and post-monsoon respectively. In all stations the maximum value obtained during post-monsoon.

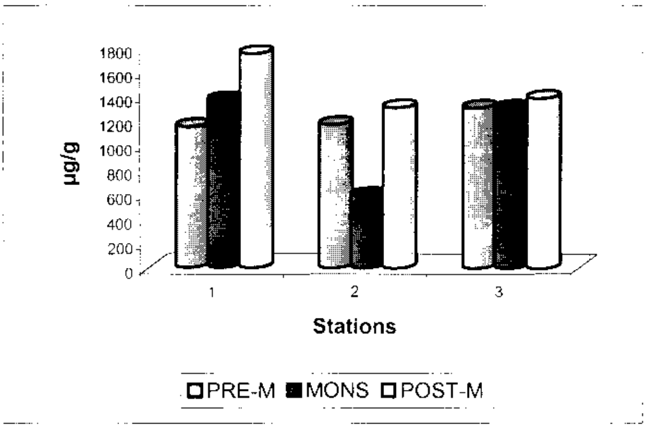


Fig 4.7 Seasonal variation of Total sulphur in surface sediments.(μg/g)

The maximum value at Station 1 is due to the high concentration of organic sulphur during post-monsoon. Besides at Station 1 sulphide formation is higher than other two. Both these support the above result. At Station 1 and Station 2 inorganic sulphur contributes more to total sulphur. In Monsoon the minimum obtained was may be the dilution of water.

Previous studies state that concentration of total sulphur is higher in the deeper profiles than that in the more oxidised surface section and there is a significant correlation with depth and with carbon bonded sulphur (Krairapanond et al., 1991). The variation in total sulphur values, obtained from different investigations shown that variability is due to organic sulphur (Casagrande et al., 1979; Altschuler et al., 1983; Nriagu and soon et al., 1985; Wieder et al., 1987; and Haering et al., 1989). Quantitatively the concentrations of total sulphur in Louisiana marsh soils were comparable to those found in the Great marsh of Delaware and in Chesapeake Bay (Cutter & Velinsky, 1988 and Haering et al., 1989). The data obtained from previous studies are given below.

Table 4.12

System	Reported value	Reference
Louisiana salt marsh	14.1mg/g – 18.1mg/g	Krairapanond et al., 1991.
Cochin estuary	1.39mg/g – 26.31mg/g	Beenamma, 1993.
Kerala coast	2.13mg/g – 26.90mg/g	Beenamma, 1993.
Present study	590ng/g - 1750ng/g	

Sulphur and iron cycling in surface sediments of the north western part of the Black Sea is largely influenced by organic matter supply to the sediment, availability of reactive iron compounds and oxygen concentrations in the bottom waters (Jeroen et al., 2001). River deltas in continental shelf areas play an important role in the global cycles of sulphur and iron and are important sites for the formation and burial of authigenic iron sulphides (Berner, 1982; Jorgensen, 1982). This is due to high rates of organic matter fluxes to the sediments in combination with the input of reactive iron through rivers (Berner, 1982). With increasing load of particles with associated reactive organic matter to the sediment, the relative importance of sulphate reduction usually increases (Canfield, 1989; Thamdrup and Canfield, 1996; Wijsman et al., 2001). Sulphate reduction is therefore the major mineralization pathway in sediments of productive coastal marine systems, accounting for 10-90 % of the total organic matter degradation (Jorgensen, 1977; Henrichs and Reeburgh, 1987; Canfield et al., 1993; Thamdrup and Canfield 1996; Kostka et al., 1999). Dissolved hydrogen sulphide that is produced during bacterial dissimilatory sulphate reduction may quickly react with sedimentary reactive iron compounds to form iron monosulphide (Rickard, 1995), which can further react with dissolved sulphides, elemental sulphur or polysulphides (Berner, 1970; Rickard, 1997).

4.8 Organic Carbon

In marine sediments there is a constant relationship between reduced sulphur and organic carbon (Leventhal, 1983). On a global scale, shelf sediments appear to be major sinks for organic carbon storage (Wollast, 1991) and hence important regulators of atmospheric CO_2. Within the shelf system, wetlands may contain a third of this carbon storage (Twilley et al., 1992). The bulk of this wetland storage is in mangal systems, largely because of the slower decay of the woody material and there for the residence time of carbon in mangal system will be longer. In anoxic condition sulphate reduction is very much pronounced and variations in the sulphate reduction rate depends upon temperature, pressure (which affects the removal of dissolved gases such as H_2S, CO_2), the concentration of sulphate and the concentration of reactive carbon (Ruddy,1997).

Table 4-13 Seasonal variation of Organic carbon (mg/g)

	STATION 1	STATION 2	STATION 3
PRE-M	48.20	29.18	25.2
MON	69.61	38.71	51.1
POST-M	107.20	22.51	50.0

The values obtained are given in the Table 4-13. The maximum value was noted during postmonsoon at Station 1 and minimum was observed at Station 2 during postmonsoon. The values ranged between 107.20mg/g-22.51mg/g. At Station 2, the amount of organic carbon was comparatively lower than other stations except during premonsoon. During all seasons values were maximum at Station 1.

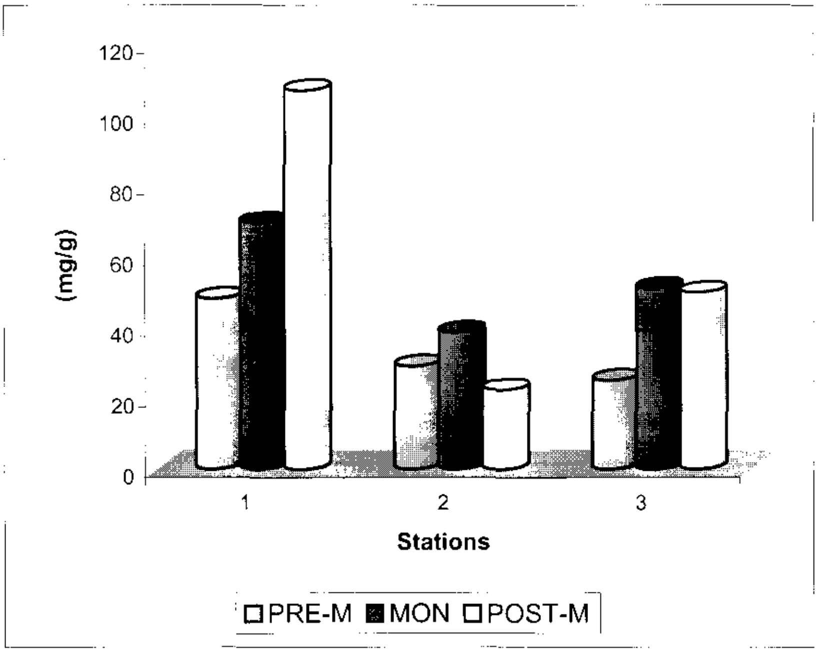


Fig 4-8 Seasonal variation of Organic carbon (mg/g)

4.9 Iron in the Surface Sediments

The availability of iron partly controls pyritisation processes, which in turns is an important control on the cycling of sulphur. Sulphur retention by the sediment system will depend on the presence of layer of reactive iron oxides at the surface to precipitate available sulphides which may in turn control trace metal metabolisation, sediment productivity and community metabolism. Free iron, which is the dominant cation in most of the diagenetic mineral phases, will control the precipitation of environmentally diagnostic mineral assemblages, which suggests that, as an oxidant, Fe (III) accounts for a relatively large proportion of the cycling of electrons. Iron cycling may there for constitute a major part of the budgeting of sulphur in marine sediments (Ruddy, 1997). Seasonal variation of iron in surface is given in the Table 4-14.

Table 4-14 Seasonal variation of iron (mg/g)

	STATION 1	STATION 2	STATION 3
PRE-M	32.68	1.66	33.46
MON	11.68	21.21	29.15
POST-M	12.86	18.68	30.32

Iron concentrations were maximum at Station 3 during all seasons. Values were ranged between 33.46mg/g-1.66mg/g. The minimum value was noted at Station 2 during premonsoon. The maximum was also noted during premonsoon at Station 3. At Station 1, values were ranged between 11.68mg/g-32.68mg/g. the maximum value was noted during premonsoon. At Station 1, the maximum value was observed during monsoon.

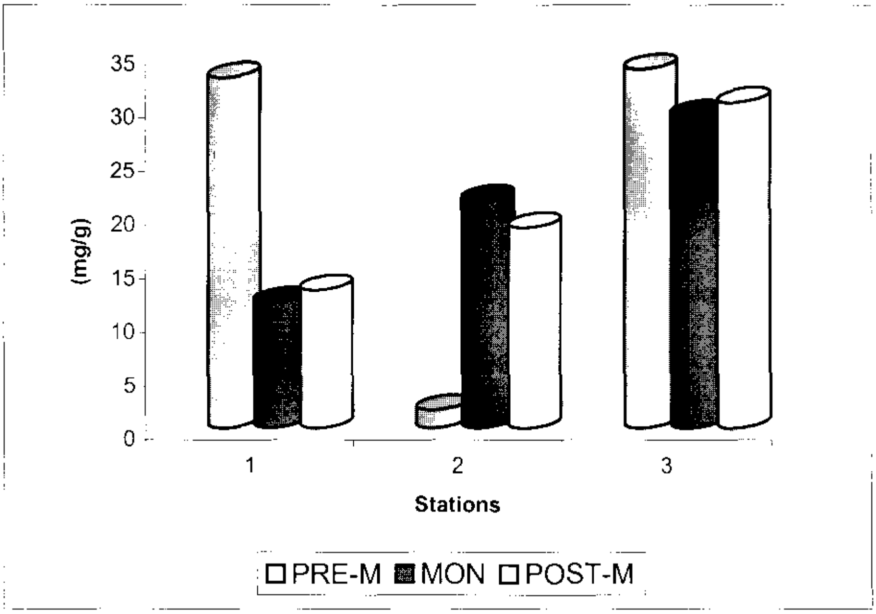


Fig 4-9 Seasonal variation of iron in the surface sediments

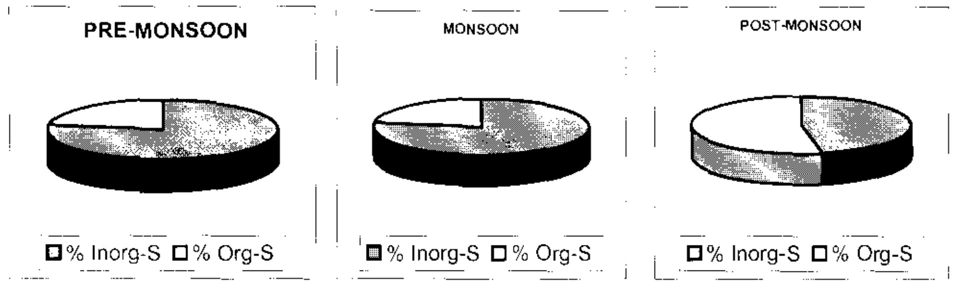
Table 4.15

Percentage of inorganic and organic sulphur in the surface sediment

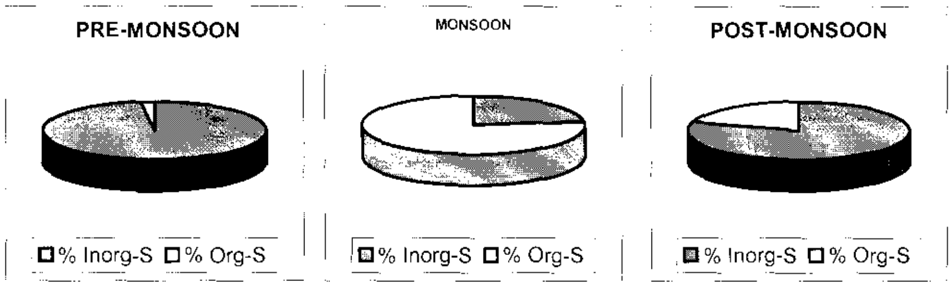
		PRE-M	MON	POST-M
STATION 1	% Inorg-S	77.74	77.41	47.07
	% Org-S	22.25	22.59	52.93
STATION 2	% Inorg-S	98.12	23.31	88
	% Org-S	1.88	76.69	22
STATION 3	% Inorg-S	65.7	57.29	79.15
	% Org-S	34.3	42.71	20.85

Fig 4.10 Seasonal distribution of inorganic and organic sulphur

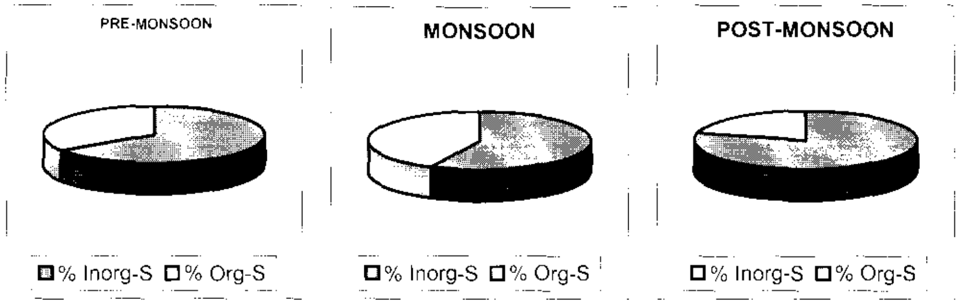
STATION 1



STATION 2



STATION 3



The system under consideration is subjected to continuous drying and flooding during the tidal cycles, which results in significant modifications in the geochemical and sedimentary processes. During the ebb tide the sediment is exposed to atmosphere leading to aerobic chemical processes and will have a net reversal of the anaerobic transformations. This continuous change between oxic and anoxic conditions and processes makes the system totally unstable and unpredictable, with more leaning towards the oxic processes or products. Thus concentrations of reduced species will be considerably low. This character infact has been observed during the budgeting of organic carbon also (Geetha, 2002). The pattern observed in the carbon budgeting does not eliminate the anaerobic process, but indicates, the oxidation of the products generated by the reducing reactions. The present study supports the earlier observation in this respect. The major observation in this study is that, the concentration of the sulphide fractions is significantly low, while the elemental sulphur and sulphate sulphur constitutes the major part of the total sulphur. The general behaviour of the sulphur in aquatic sediment is the reduction of the sulphide, when there is an anoxic or near to anoxic situation is available.

The sulphides, hydrogen sulphide and other labile sulphides, the reduction products of the sulphate are quite unstable and either gets oxidised to sulphate or combines with metallic cations especially iron, to form the sulphide minerals. This reaction includes elemental sulphur as an intermediate and as an entity, which supports the formation of stable pyrite. In this normal channel, of the aquatic sulphur chemistry the oxygen deficient condition does not permit building up of concentrations of the labile intermediates, sulphides and elemental sulphur. In the system under consideration the situation is considerably different. The continuous change over between oxic and anoxic conditions will lead to an unstable redox system and processes. In this study, the observed very low concentration of the exchangeable sulphide fractions including pyrite can be due to either an absence of anaerobic diagenesis or the presence of significantly high oxidation processes of the sulphides.

A detail scrutiny of the value obtained for the fractions of the sulphur and comparison with the sulphide concentration provides sufficient evidence for the operation of both the processes. More or less stable sulphate concentrations during pre-monsoon and postmonsoon period, when the fresh water influx is significantly low, suggests that the major source of sulphate is the tidal discharge of the saline water. The source of the elemental sulphur in recent sediments is reported to be mainly by the oxidation of sulphides by the colourless bacteria *Beggotia* spp (Burhan et al., 2002). They are capable of accumulating the elemental sulphur in the cell membranes and active transport of the sulphur is considered to be done by this processe (Jorgensen, 1977). The presence of a high microbial population and continues flushing of the surface sediments can lead to a high degree of bioturbation. Irregular elemental sulphur distribution and bioturbation activated high elemental sulphur pools have been suggested earlier also (Jorgensen, 1982; Beenamma, 1993). Concentrations of organic sulphides are considered to be reflections of the sulphate reduction processes and generally a higher organic sulphur percentage is indicative of a high sulphate reduction and diminishing trend is associated with a decrease in the sulphate reduction (Rudd et al., 1986). A similar relation has been observed in the coastal sediment also (Beenamma, 1993). The system presented comparatively low organic sulphides, indicating either a low sulphate reduction or the dominance of oxidation of these sulphides.

The possible conclusion one can arrive from the observed data and its interrelation and the comparison with the earlier studies, can be summarised as follows.

1. The significantly high organic load can promote anaerobic diagenetic processes leading to promotion of sulphate reduction. But the tidal

activity considerably modifies the redox condition and results in reversal of the diagenetic parts in favour of an oxidative process

2. The presence of significantly high elemental sulphur and low organic sulphur supports an unstable geochemical condition, which swings between the reduction and oxidation. The very low concentrations of inorganic sulphur species prove these assumptions.

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Chapter 5

GEOCHEMISTRY OF MANGROVE SEDIMENTS

PART-1 DISTRIBUTION OF SULPHUR FRACTIONS IN THE SEDIMENTARY DEPTHS

PART-2 GEOCHEMISTRY OF THE SEDIMENT

PART -1

DISTRIBUTION OF SULPHUR FRACTIONS IN THE SEDIMENTARY DEPTHS

Intertidal sediments occupy a unique position between land and sea giving them an importance, which is only now becoming apparent (Malcolm and Sivyer, 1997). These sediments are a part of the sediment system that has helped to maintain the productivity of the coastal zone via the storage and recycling of nutrients which were imported from offshore waters (Nixon, 1986, 1992). The sediments are subjected to diurnal drying and flooding which leads to major changes in the local transport of material to and from the sediments. A substance whose source is in the water and is consumed in the sediment may become depleted when the water is not present and the sediments are both sinks and sources of different elements and that the behaviour changes with the tide (Malcolm and Sivyer, 1997). These explain the dynamic nature of the intertidal sediments.

In most marine type sediments organic carbon is the only reducing agent to enter a sediment column. The remainder of the sediment load arrives in its oxidised form, and, with the exception of early diagenesis results directly or indirectly from the flow of electrons (Ruddy, 1997). In anoxic condition, when the amenable electron acceptors have been depleted, sulphate is used by sulphate reducing bacteria. The sulphide produced by sulphate reduction is then removed or recycled by different processes depending on the environment of deposition. The variations in the sulphate reduction depend on the temperature, pressure, the concentration of sulphate and the concentration of reactive carbon (Ruddy, 1997). Maximum rates of reduction, and therefore maximum rates of supply of reduced soluble sulphides and alkalinity, occur where the rate of supply of reactive organic carbon is highest and when the temperature is highest.

The removal of reduced products can occur in two ways: firstly, by precipitation of relatively insoluble reduced sulphur, and, secondly, diffusion away from the site of production and subsequent reoxidation. The observed authigenic reduced sulphide minerals include FeS, gregite (Fe_3S_4) and pyrite (FeS_2). Pyrite is the thermodynamically stable form. Lord and Church (1983) found that sulphide precipitation seemed to occur in two separate ways within the sulphate reduction zone. Pyrite concentrations, as single crystals rather than framboids, increased rapidly at the top of the sulphate reduction zone, where as within the zone of pore water accumulation, rates of formation were much slower. The sulphur in pyrite has an average oxidation state of –1 rather than –2, so an oxidising agent is obviously required at some stage in the process, and the oxidising agent might be an oxidised sulphur species such as elemental sulphur (Lord and Church, 1983).

The distribution patterns of the different sulphur species in the sedimentary depths are given below.

5.1 Acid Volatile Sulphur

The values observed in different Stations are distributed in the Table 5.1.

The maximum concentration was observed in Station 1 during postmonsoon and minimum in Station 3 during premonsoon and monsoon. The values were in the range of 280.32ng/g – 40.02ng/g. In Station 1 the maximum was observed at the surface and a gradual decrease towards the depth was noted during monsoon. The maximum and minimum concentrations were 120.00ng/g and 80.00ng/g. The minimum was noted both in 10cm and 15cm layers. In all seasons minimum values were obtained at 15cm layer.

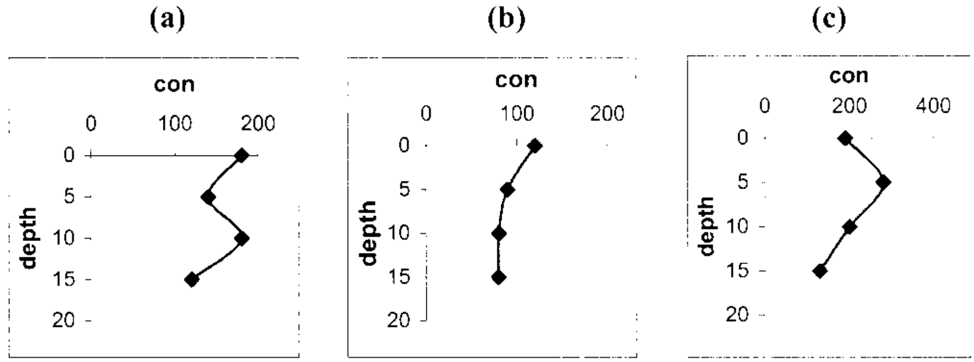
Table 5.1 Distribution of AVS in the surface and core sediments

	DEPTH (cm)	PRE-M (ng/g)	MON (ng/g)	POST-M (ng/g)
STATION 1	0	179.56	120.00	189.74
	5	139.98	90.10	280.32
	10	180.00	80.00	200.10
	15	120.21	80.00	129.89
STATION 2	0	99.90	119.82	120.02
	5	130.00	100.14	159.96
	10	110.41	110.10	80.25
	15	121.21	120.21	139.87
STATION 3	0	70.63	50.01	70.00
	5	40.01	40.02	90.22
	10	70.31	70.30	80.11
	15	50.00	50.00	60.40

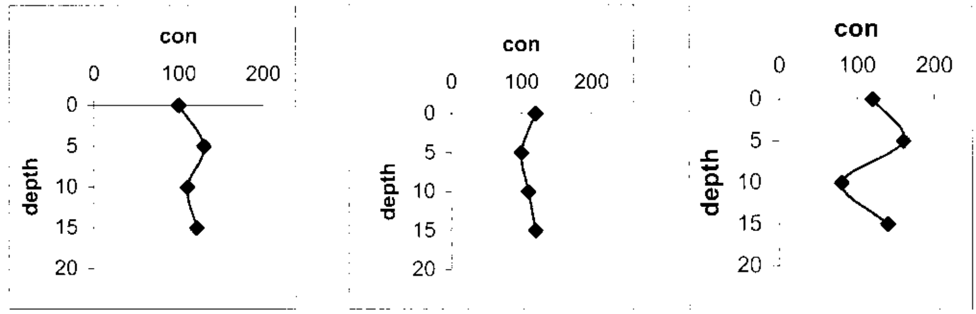
At Station 2 the maximum was found at 5cm layer during postmonsoon and the minimum was noted at 10cm layer during the same season. The observed values were 159.96ng/g and 80.25ng/g respectively. At Station 3 AVS concentrations was less compared to other two Stations. There was no gradual variation towards depth at Station 3. The maximum amount of 90.22ng/g was noted in 5cm layer during postmonsoon and a minimum of 40.01ng/g was observed during the other two seasons. Fig 5.1 shows the graphical representation of the values in Table 5.1

Fig 5.1 Depth profile of AVS in the sediment during three seasons a) premonsson b) monsoon c) postmonsoon

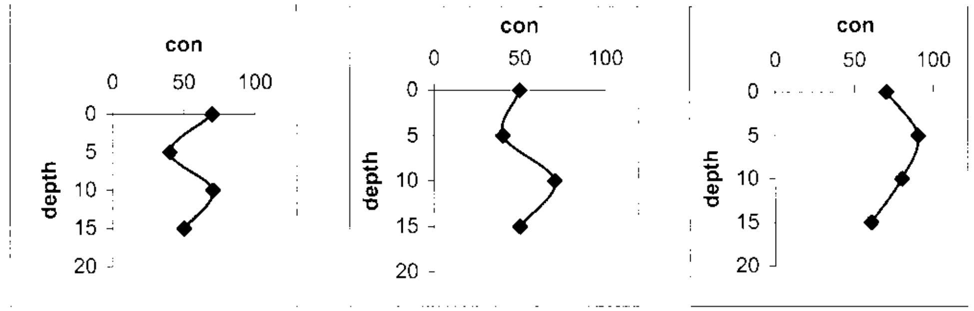
Station 1



Station 2



Station 3



5.2 Gregite Sulphur

Table 5-2 Distribution of gregite in the surface and core sediments

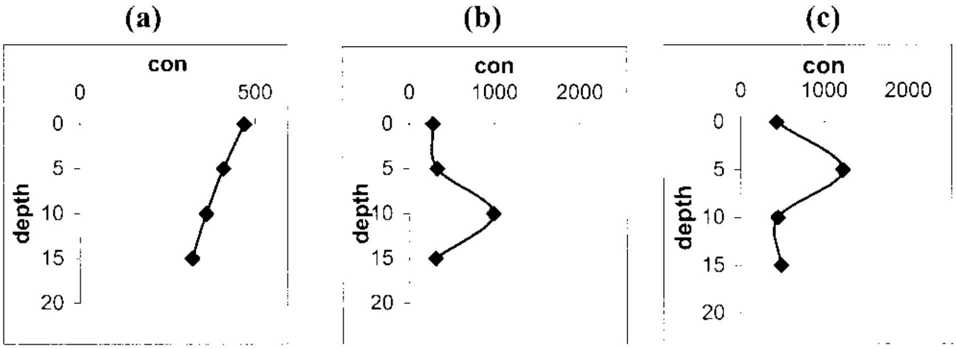
	DEPTH (cm)	PRE-M (ng/g)	MON (ng/g)	POST-M (ng/g)
STATION 1	0	470.01	280.10	430.00
	5	409.99	330.00	1220.00
	10	360.01	990.10	440.01
	15	319.98	309.89	480.24
STATION 2	0	660.23	150.03	150.03
	5	430.00	320.00	80.12
	10	270.00	660.10	160.33
	15	290.12	720.00	130.20
STATION 3	0	70.00	70.00	50.12
	5	40.31	100.23	270.24
	10	30.14	50.00	40.00
	15	39.96	30.15	29.98

During postmonsoon maximum amount of gregite sulphur was noted at Station 1 and minimum at Station 3 during postmonsoon and monsoon. The values were in the range of 29.98ng/g -1220.00ng/g. Station 1 showed a gradual decrease in concentration towards depth during premonsoon, but it was not observed in other seasons. The maximum amount of 990.10ng/g was detected in the 10cm layer during monsoon and 1220ng/g in the 5cm layer during postmonsoon at Station 1.

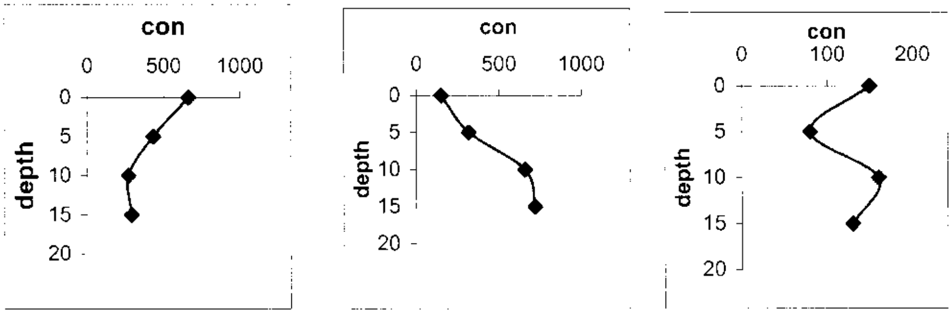
At station 2, the maximum value of 660.23ng/g was noted during premonsoon and 660.10ng/g in the monsoon at the surface and in the10cm layer respectively. The minimum amount of 80.12ng/g was noted in the 5cm layer during postmonsoon. During postmonsoon gregite sulphur concentrations were comparatively very low at Station 2. The amount was gradually increased towards depth at Station 2 during monsoon. The values were varied between 150.03ng/g- 720.00g/g. At Station 3 the maximum was noted during postmonsoon in the 5cm layer and value was 270.24ng/g. The minimum concentration was observed in the 15cm layer during monsoon and postmonsoon and in the 10cm layer during premonsoon. Gregite sulphur concentrations were very less in Station 3 than other two. Fig 5.2 exhibits the seasonal distribution of gregite sulphur and Table 5.2 shows its values.

Fig 5.2 Depth profile of gregite sulphur in the sediment during three seasons a) premonsoon b) monsoon c) postmonsoon

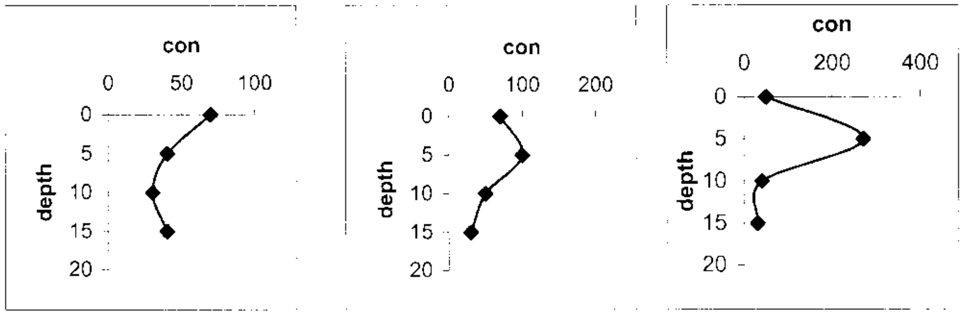
Station 1



Station 2



Station 3



5.3 Pyrite Sulphur

Table 5-3 Distribution of Pyrite Sulphur in the surface and core sediments

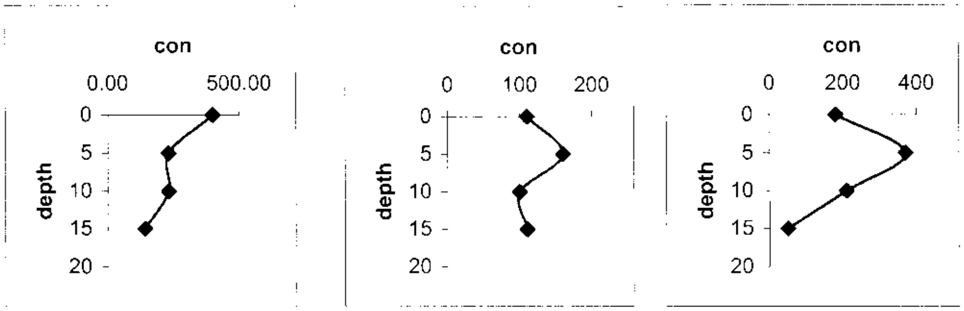
	DEPTH (cm)	PRE-M (ng/g)	MON (ng/g)	POST-M (ng/g)
STATION 1	0	400.00	109.96	179.90
	5	229.96	160.01	370.24
	10	229.96	100.11	210.14
	15	140.21	110.31	50.00
STATION 2	0	59.85	0.00	49.86
	5	0.00	19.95	119.87
	10	0.00	0.00	160.00
	15	60.01	19.95	90.00
STATION 3	0	0.00	60.01	10.12
	5	0.00	100.00	0.00
	10	40.01	60.21	10.21
	15	29.86	80.31	0.00

The values obtained were ranged between 0.00ng/g - 400.00ng/g. The maximum amount was noted at Station 1 in the surface during premonsoon. At Station 1 a minimum of 50.00ng/gwas noted during postmonsoon in the 15cm layer. Pyrite was not detected in various layers of the core during all seasons. At Station 2 Pyrite concentrations were in the range of 160.00ng/g – 0.00ng/g. Values obtained during postmonsoon were comparatively higher than other two seasons. At Station 2 zero 15cm layer was found to be devoid of Pyrite sulphur. 100.00ng/g was the higher concentration obtained at Station 3 during monsoon and it was in the 5cm layer. Here monsoonal values were comparatively higher than other two seasons. Pyrite concentrations were very low during postmonsoon at Station 3 and values were ranged between 10.21ng/g 0.00ng/g. During premonsoon the maximum concentration was obtained was 40.01ng/g in the 10cm layer. Fig

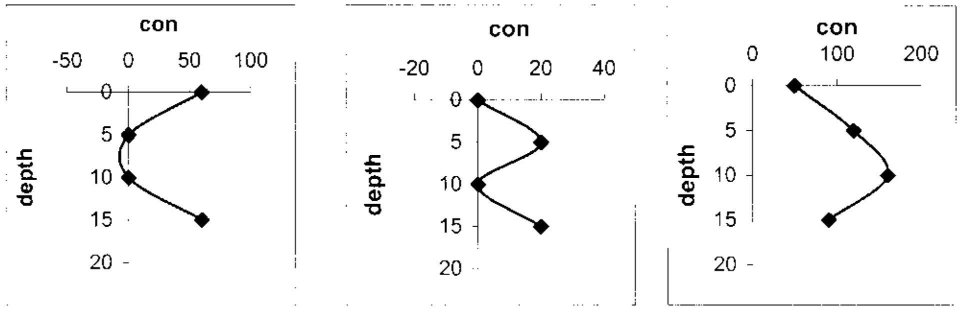
5.3 exhibits the seasonal distribution of pyrite sulphur and Table 5.3 shows its values.

Fig 5.3 Depth profile of pyrite sulphur in the sediment during three seasons a) premonsoon b) monsoon c) postmonsoon

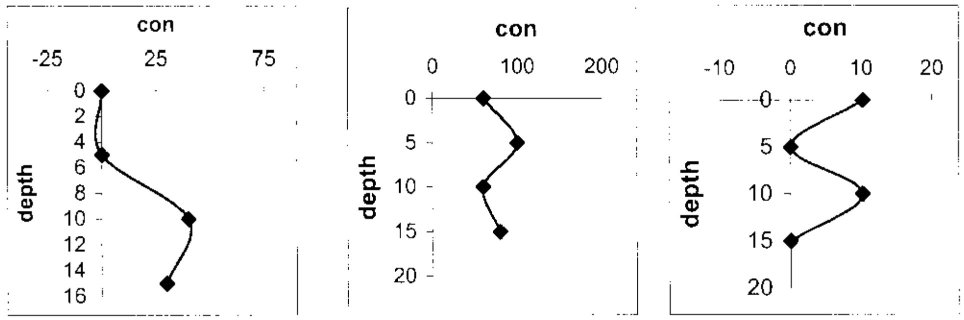
Station 1



Station 2



Station 3



5.4 Sulphate Sulphur

Table 5.4 Distribution of sulphate sulphur in the surface and core sediments

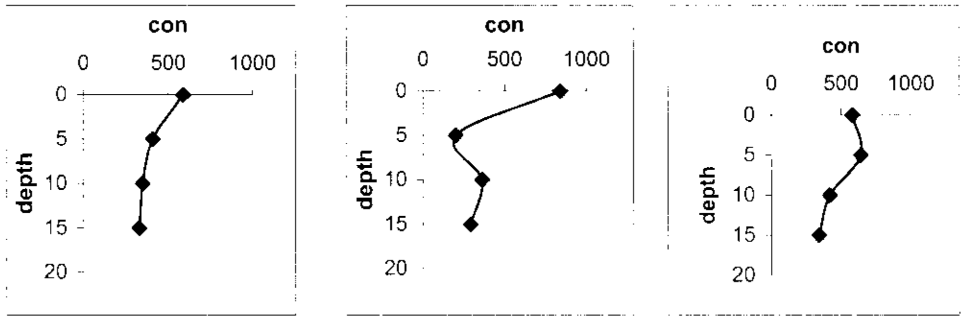
	DEPTH (cm)	PRE-M (µg/g)	MON (µg/g)	POST-M (µg/g)
STATION 1	0	590.00	840.01	579.98
	5	410.01	200.00	640.12
	10	349.75	360.11	420.13
	15	330.22	290.00	339.77
STATION 2	0	530.00	50.00	480.21
	5	130.00	40.12	249.66
	10	139.54	60.33	150.00
	15	119.83	80.22	180.00
STATION 3	0	610.23	330.10	600.10
	5	549.69	340.98	390.12
	10	630.00	210.00	540.22
	15	679.99	369.79	460.14

The values ranged between 40.12µg/g - 840.01µg/g. The maximum concentration was noted in the surface layer of Station 1 and minimum in the 5cm layer of Station 2 during monsoon. In Station 1 the concentration of Sulphate sulphur was maximum in the surface during premonsoon and monsoon, but during postmonsoon maximum was observed in the 5cm layer. At Station 1 there was a gradual decrease in the concentrations towards depth during monsoon, but it was not found during premonsoon and postmonsoon. During monsoon the depth profile from the surface to the 15cm layer exhibited a variation of 590.00µg/g to 330.22µg/g at Station 1. Minimum amount of sulphate sulphur was noted in the 15 cm layer during premonsoon and postmonsoon, but a minimum was observed during monsoon in the 5cm layer. At Station 2, there was no gradual decrease towards depth in any season. The concentrations were very less during monsoon compared to other seasons and values were in the range of 40.10μg/g - 80.22μg/g. In Station 2 at surface concentrations were high during premonsoon and postmonsoon, but during monsoon the maximum was observed in 15cm layer. The values were in the range of 40.12μg/g - 530.00μg/g.

At Station 3 the maximum value was obtained during premonsoon and minimum was noted during monsoon in the 15cm and 10cm layers respectively. Values were in the range of 210.00μg/g -679.99μg/g. During premonsoon from 5cm layer there was a gradual increase of concentration towards depth. There was no significant correlation with depth was observed during other seasons. The maximum concentration was in the 15cm layer during premonsoon and monsoon, but during post monsoon it was noted in the surface. The values observed during premonsoon at Station 3 were higher than Stations 1 and 2. Fig 5.4 shows the graphical representation of the values in the Table 5.4.

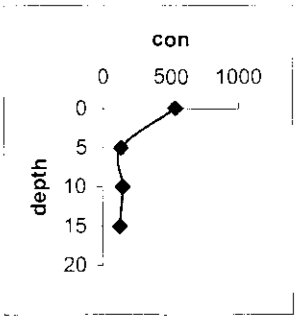
Fig 5.4 Depth profile of sulphate sulphur in the sediment during three seasons a) premonsoon b) monsoon c) postmonsoon

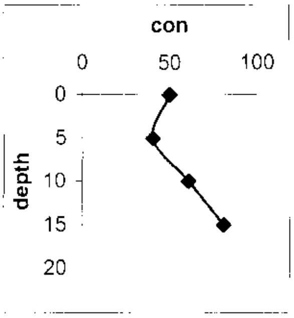
Station 1

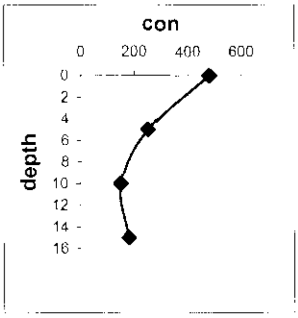


(a) **(b)** **(c)**

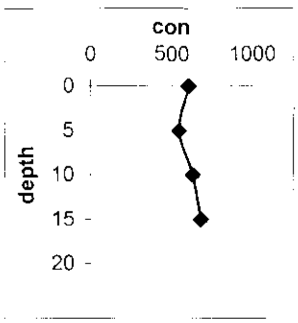
Station 2

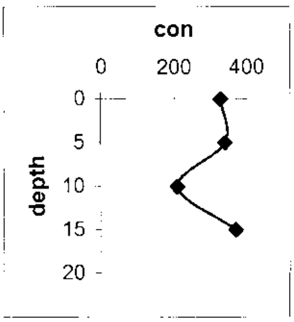


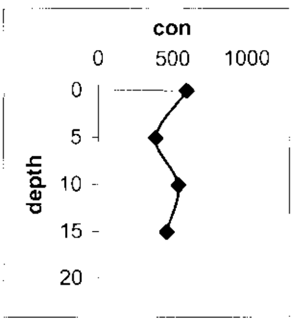




Station 3







5.5 Elemental Sulphur

The values observed in the sediments up to 15cm depth are as follows.

Table 5.5 Concentration of Elemental sulphur (μg/g)

	STATION 1	STATION 2	STATION 3
PRE-M	303.01	617.2	250.3
MON	219.98	87.23	420.3
POST-M	243.00	67.86	500.0

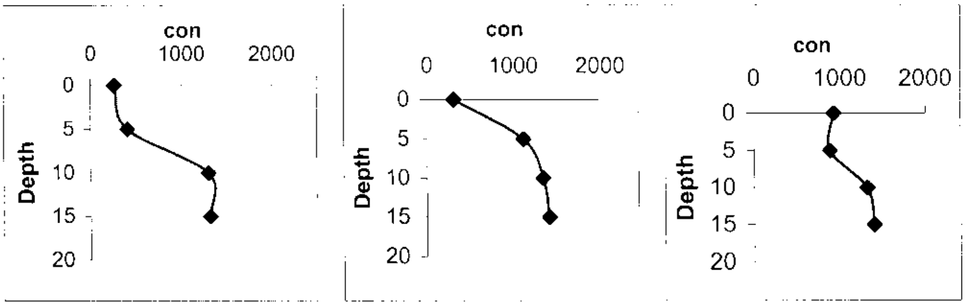
Table 5.6 Distribution of Organic sulphur in the surface and core sediments

	DEPTH (cm)	PRE-M (μg/g)	MON (μg/g)	POST-M (μg/g)
STATION 1	0	255.95	309.50	926.22
	5	406.20	1119.44	885.01
	10	1296.47	1338.74	1316.02
	15	1316.19	1409.52	1396.57
STATION 2	0	21.44	452.5	149.61
	5	102.24	22.21	930.19
	10	552.79	81.67	99.74
	15	252.50	181.69	139.78
STATION 3	0	449.33	559.42	289.77
	5	499.93	568.48	947.71
	10	329.56	119.74	759.65
	15	369.59	409.75	389.77

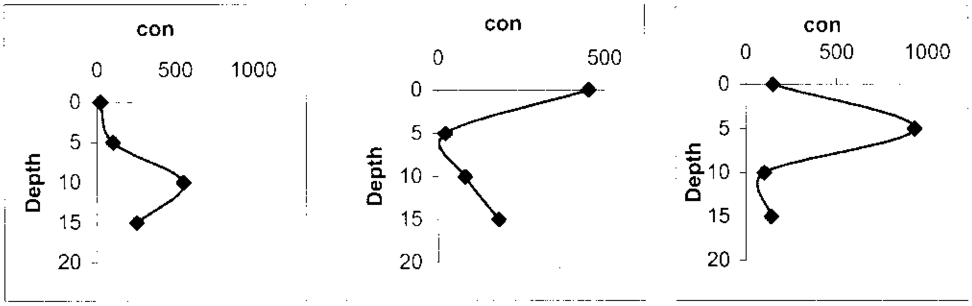
Fig 5.5 Depth profile of Organic Sulphur in the sediment during three seasons a)premonsoon b)monsoon c)postmonsoon

Station 1

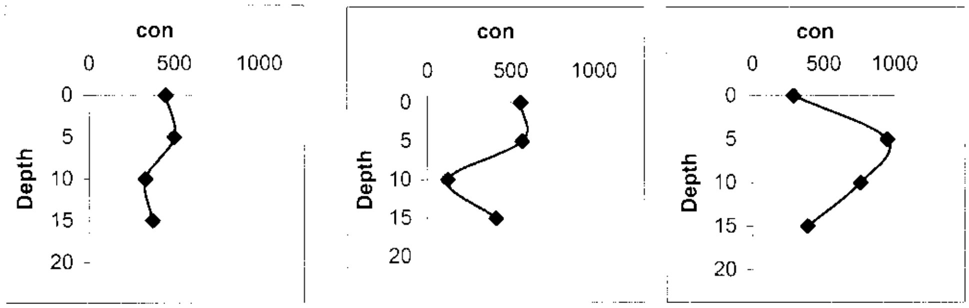
(a) **(b)** **(c)**



Station 2



Station 3



5.6 Total Sulphur

Table 5.7 Distribution of Total sulphur in the surface and core sediments

	DEPTH (cm)	PRE-M (µg/g)	MON (µg/g)	POST-M (µg/g)
STATION 1	0	1150	1370	1750
	5	1120	1540	1770
	10	1950	1920	1980
	15	1950	1920	1980
STATION 2	0	1170	590	1310
	5	850	150	1860
	10	1310	230	930
	15	990	350	1000
STATION 3	0	1310	1310	1390
	5	1300	1330	1840
	10	1210	540	1800
	15	1300	1200	1350

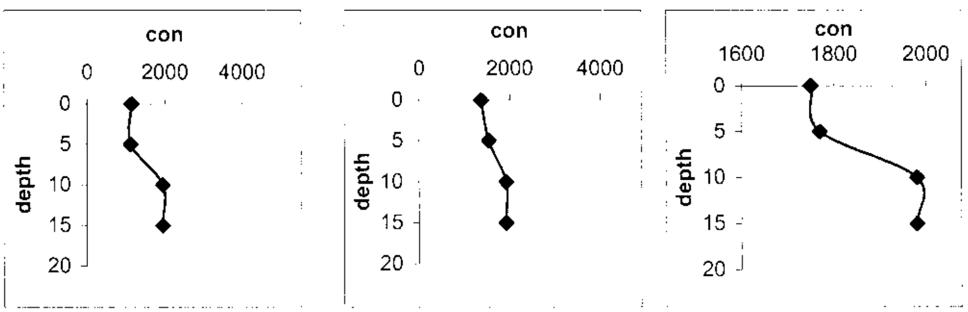
At Station 1, a maximum of 1980µg/g was noted and the minimum 150µg/g during monsoon at Station 2. At Station 1 same concentrations were observed in 10 and 15cm layers in all seasons. There was a gradual increase of concentrations towards depth were noted between surface and 5cm layers during monsoon and postmonsoon, but it was not observed during premonsoon. At Station 1 the values were in the range of 1980µg/g-1120µg/g.

At Station 2 during monsoon concentrations were very less. The maximum value noted was 590µg/g in surface and the minimum 150µg/g in the 5cm layer. In this Station the maximum value obtained was 1860µg/g in layer during postmonsoon. There was a gradual increase in concentration with depth from 5cm layer during monsoon at Station 2.

Total sulphur concentrations were almost same during premonsoon at Station 3. During monsoon the values were in the range of 540µg/g-1330µg/g in the 5cm layer and10cm layer respectively. During postmonsoon the maximum value noted was 1840µg/g in the 5cm layer and a minimum of 1350µg/g in the 15cm layer.

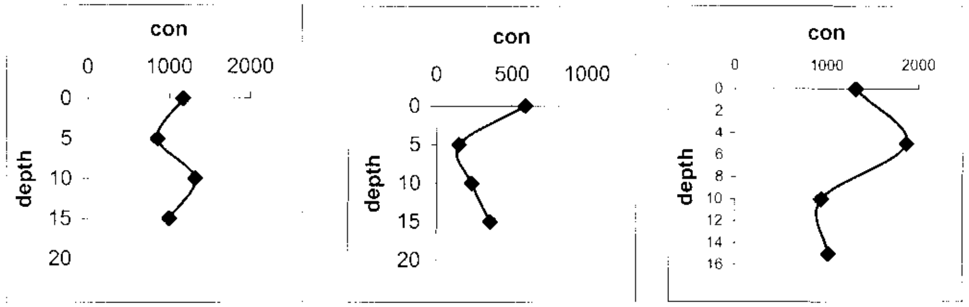
Fig 5.6 Depth Profile of Total Sulphur in the sediment during three seasons a) Premonsoon b) Monsoon c) Postmonsoon

Station 1



(a) **(b)** **(c)**

Station 2



Station 3

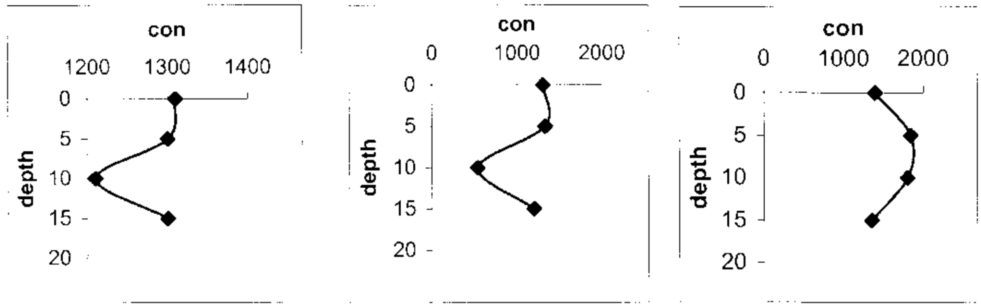


Table 5.8 Percentage of Inorganic and Organic sulphur in the surface and core sediments

		PRE-MONSOON		MONSOON		POST-MONSOON	
		% Inorg-s	%Org-s	% Inorg-s	%Org-s	% Inorg-s	%Org-s
STATION 1	0	77.747	22.25	77.41	22.59	47.07	52.93
	5	63.73	36.27	27.31	72.69	50.00	50.00
	10	33.52	66.48	30.27	69.73	33.54	66.46
	15	32.50	67.50	26.59	73.41	29.47	70.53
STATION 2	0	98.12	1.88	23.31	76.69	88.00	22.00
	5	87.97	12.03	85.19	14.81	49.99	50.01
	10	57.80	42.20	64.50	35.50	89.28	10.72
	15	74.50	25.50	48.09	51.91	86.03	13.97
STATION 3	0	65.70	34.30	57.29	42.71	79.15	20.85
	5	61.54	38.46	57.26	42.74	48.49	51.51
	10	72.76	27.24	77.83	22.17	57.80	42.20
	15	71.57	28.43	65.85	34.15	71.13	28.87

Fig 5.7 Distribution of Inorganic and organic sulphur

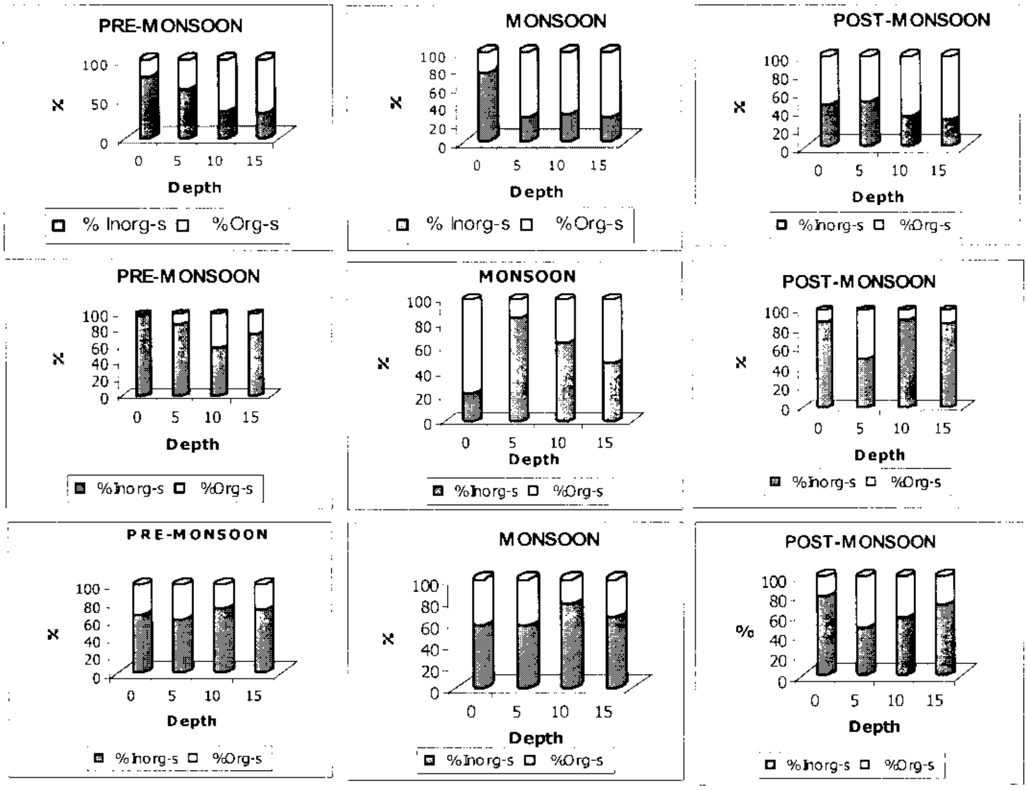


Table 5.9 Distribution of organic carbon
in the surface and core sediments

	DEPTH (cm)	PRE-M (mg/g)	MON (mg/g)	POST-M (mg/g)
STATION 1	0	48.2	69.61	107.2
	5	24.2	65.00	34.5
	10	23.3	60.70	33.6
	15	20.4	36.10	26.4
STATION 2	0	29.18	38.71	22.51
	5	8.05	18.12	13.00
	10	9.50	12.50	13.50
	15	9.90	6.40	5.46
STATION 3	0	25.20	51.10	50.00
	5	26.14	61.75	35.40
	10	26.02	52.25	35.13
	15	28.88	45.37	49.14

5.7 Discussion

The observed values in the case of all the sulphur fractions exhibit significant seasonal variations in all the depths studied. The seasonal variation can generally be explained only on the basis of the contributions from the pore water, which plays a significant role in the transportation of different chemical entities between the layers. In this particular case, the contribution of the pore water dynamics could not be assessed due to difficulties in separation of pore water from the sediment. At the same time, the significance of the contribution is well evident on a detailed analysis of the concentration of the different species, with respect to the depth. In almost all cases in this study the zero cm or 5 cm depths were having the maximum concentration of the different sulphur species. This trend is well within the expectation and the earlier studies (Bertolen et al., 1995, Jorgensen and Cohen, 1977). In the case of other depths, they are having low values than the surface. The general diffusion character restricts the transport of any entity from a lower to higher concentration. The normal diagenetic process in the sediment is in favour of sulphate reduction and a higher concentration of the sulphide at the zero and 5 cm depths. Here also, this remains only as a logic conclusion under the assumption that the surface and the near surface sediments have the maximum probability for reduction because of the higher concentrations of the microbial organisms. The sulphate reduction is considered to be more or less microbial processes, especially, take place in the surface sediments, but the availability of conditions favorable for oxidation of the sulphide or suppression of sulphate reduction can lead to a lower sulphide concentration at zero and 5 cm depths. The conditions available at the sediment depths are supportive to a reducing environment and diagentic processes resulting significant sulphate reduction and formation of sulphide formation. This can lead to the development of a concentration gradient between the layers with respect to sulphide leading to transportation of sulphide through the pore water and diffusion from the depths to the surface. This flow of sulphide from the bottom sediment can result in a low concentration of sulphides in the deep sediments. This, but should lead to a substantial fall in the organic carbon between the surface and the deep sediments.

Station 1 clearly indicates such a fall in organic carbon in all the seasons. The total sulphur concentration in the case of the station 1 is shown to be increasing with depth in all seasons. This represents a contradiction from the general observation. No specific explanation is offered here except that during the premonsoon and postmonsoon, the sediment is subjected to regular drying at the low tide and the water balance and salt balance studies have shown that there is a significant retention of the salt with in the system during these two seasons (Geetha, 2002). The penetration of saline water to the sediment depths so cannot be ruled out. As these depths will not be available for normal suspension and resuspension processes, the sulphate reduced at these depths can get retained there also. The higher concentration observed during the monsoon points out to such a retention.

The seasonal variations observed at sediments depths indicate a direct or indirect involvement of the seasonal geochemical modifications in the deep sediments. Such an involvement can be accounted only by considering the diffusion and pore character of the sediments. The modifications in the decay pattern with such a transport between the surface and deep sediments is also possible. The studies with sulphur isotope have indicated that the reservoir effect of the dissolved sulphate (Jorgensen, 1979) cannot answer the observed pyrite and other sulphide concentrations of the down core samples (Vaynshteyn et al., 1986; Wijisman et al., 2001). In the present systems an earlier study on the reactivity of the sediments indicated a varying reactivity with depth and seasons (Geetha, 2002). As the quantification of the pore water could not be done, the porosity of the sediments is not estimated here. But the texture of the sediments indicates significant amount of sand (**Table 5.10**) and there fore a higher porosity and a higher transport of components to deeper sediments are probable phenomena.

Table 5.10

Sand %

	PRE-M	MON	POST-M
Station 1	16.47	23.03	33.06
Station 2	63.41	91.87	85.13
Station 3	16.19	2.84	39.32

Silt %

	PRE-M	MON	POST-M
Station 1	38.62	32.98	16.56
Station 2	8.53	1.32	6.72
Station 3	44.12	47.56	24.65

Clay%

	PRE-M	MON	POST-M
Station 1	44.77	43.56	49.83
Station 2	27.92	6.31	7.57
Station 3	40.81	49.13	34.81

The comparatively higher sulphate concentration observed at the 10 cm and 15 cm sediment depths can be due to the interplay of all the above factors. The low concentration of the sulphide fractions and the high concentration of elemental sulphur (compared to sulphides) along with the high values of sulphate point either to a very low reduction processes or a significantly high subsequent oxidation of the sulphides to elemental sulphur and sulphate or to a comparatively very low reactivity of the system. The significantly high organic carbon content and the reported reactivity and presence of high microorganisms content and vascular plants rules out third option and with the same reasons the first option also. The presence of higher percentage of inorganic sulphur at the surface layers (0 and 5 cm) and the higher percentage of organic sulphides (**Table 5.8**) also point out the interplay of the oxidation and reduction processes at all the depths, with the surface sediments the balance is in favour of an ultimate oxidation and deep sediments to reduction. Such interplay has been observed earlier also (Howarth and Teal, 1979; Lord and Church, 1983; Giblin and Howarth, 1984). A better understanding of the processes can be obtained from the correlation analysis.

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PART 2

GEOCHEMISTRY OF THE SEDIMENT

The wetland systems are well known for its heterogenic behaviour in geochemical processes. Generally the heavy organic load reaching the system converts the sedimental compartment more or less anoxic leading to anaerobic processes and sulphate is the major element contributing to the redox conditions. Thus an increased rate of sulphate reduction and an increased amount of sulphide minerals are expected to be the conditions available in the wetland systems. These conditions but are strictly dependant on the availability of oxygen. The dynamic character of the overlying water, with continuous flushing over the sediment surface with oxygen saturated water, may tend to convert the surface sediment unstable and deep sediments anoxic (Teal and Kanwisher, 1961; Ingram, 1978; Howest et al., 1981). Many other factors also can contribute towards this transition between oxic and anoxic condition, which include presence of vascular plants (King, 1983; Dacey and Howest, 1984). The mangrove system represents a similar situation.

To identify the detailed character of the sediments, it is essential to identify the various geochemical processes that can take place in the system and the available contribution from the different system compartments. The system under can be at the first instance itself, considered as three entirely different systems with possibility of different geochemical processes. The factors contributing to the geochemical processes of the sediment in the present systems are (1) the overlying water, which is significantly saline except in monsoon. The depth of the overlying water is dependent more or less on the tidal activity. During low tide no overlying water over the sediment is a regular observation. (2) The oxygen availability for the surface sediment is considerably high as the overlying water is the contribution of the adjacent dynamic positive tropical estuary and also due to the direct exposure of the sediment to the atmospheric oxygen during low tide. The presence of vascular plants also can contribute to the higher oxygen availability (3) The significantly heavy load of organic matter, which is brought to the system through the land drain and the detritus as part of the biological activity in the system. (4) Presence of significantly high concentration of microbes, which will promote the diagenesis of materials that reach the sediment.

All the above situations are available uniformly in all these systems, with varying degrees and so the geochemistries of the systems are to be analysed on the same lines. The major factor which makes the system different in the extend of openness of the system to the adjacent water mass in this respect station 1 as mentioned chapter 2, is an almost closed system with minimum exchange potential and station 2 is an open system with continuous charging and recharging form the adjacent water body. Station 3 is classified as semi closed. Though this has profound contribution to the net observed concentrations of all dynamic chemical entities, the over all behaviour of the geochemical processes will be same or similar in character.

The factors discussed above suggest the following geochemical processes in the present system.

1 1. Microbial dissimilatory sulphate reduction associated with the total organic matter decomposition in the sediments as suggested by Gibline (1988).

2 Formation and storage of stable sulphide minerals.

3 Oxidation of sulphides at the surface sediments and overlying waters limiting the formation of sulphide minerals

4 Formation of elemental sulphides and sulphate during the oxidation of sulphide.

The correlation of the data from the sediments of the geochemical reactivity zone up to 15cm depth of AVS, gregite sulphur, pyrite sulphur, sulphate sulphur, elemental sulphur, organic sulphur and total sulphur is attempted here to identify the process character.

5.9 Correlation Analyses

The correlation analysis of the individual species of the sulphur between themselves at the depth of the sediment does not give much significant correlations. The values are given in the **Tables 5.11 - 5.14**

Table 5.11 Correlation coefficient (r) between different sulphur fractions at 0cm depth (n = 7)

Station 1

	AVS	Gregite-S	Pyrite-S	SO_4-S	Total-S	OC	Fe
AVS	1	0.582299	-0.40654	-0.53588	-0.08308	-0.25062	-0.51877
Gregite-S		1	0.391795	-0.25117	-0.17745	-0.55751	-0.39768
Pyrite-S			1	0.187794	-0.10504	-0.33975	0.140791
SO_4-S				1	-0.07666	-0.19097	0.58012
Total-S					1	0.725598	0.05075
OC						1	-0.25937
Fe							1

Station 2

	AVS	Gregite-S	Pyrite-S	SO_4-S	Total-S	OC	Fe
AVS	1	-0.87226	-0.71159	-0.2704	0.05527	0.00760	-0.64112
Gregite-S		1	0.804381	0.43130	0.33790	-0.26169	0.76477
Pyrite-S			1	0.64865	0.53017	-0.15899	0.88620
SO_4-S				1	0.80806	-0.01602	0.83677
Total-S					1	-0.30628	0.67863
OC						1	-0.06824
Fe							1

Station 3

	AVS	Gregite-S	Pyrite-S	SO_4-S	Total-S	OC	Fe
AVS	1	0.615295	-0.56534	0.295114	0.419127	-0.6754	-0.47876
Gregite-S		1	-0.31345	-0.28236	0.353911	-0.61121	-0.59128
Pyrite-S			1	-0.50944	-0.41263	0.892788	0.564412
SO_4-S				1	0.293762	-0.14329	-0.1244
Total-S					1	-0.35892	-0.92647
OC						1	0.617729
Fe							1

Table 5.12 Correlation coefficient (r) between different sulphur fractions at 5cm depth (n = 7)

Station 1

	AVS	Gregite-S	Pyrite-S	SO_4-S	Total-S
AVS	1	0.93507	0.91521	0.76453	0.22378
Gregite-S		1	0.87626	0.62101	0.46942
Pyrite-S			1	0.65412	0.14629
SO_4-S				1	0.19054
Total-S					1

Station 2

	AVS	Gregite-S	Pyrite-S	SO_4-S	Total-S
AVS	1	-0.23483	0.13279	0.10207	0.66329
Gregite-S		1	-0.49071	-0.17476	-0.40867
Pyrite-S			1	0.71739	0.51381
SO_4-S				1	0.51381
Total-S					1

Station 3

	AVS	Gregite-S	Pyrite-S	SO_4-S	Total-S
AVS	1	0.66345	-0.34476	-0.08133	0.76574
Gregite-S		1	-0.36293	0.07206	0.18798
Pyrite-S			1	-0.80663	-0.13539
SO_4-S				1	0.01836
Total-S					1

At station 1 at the 0 cm level AVS and gregite sulphur is observed to have the maximum correlation with sulphate sulphur while, all other parameters does have no correlation with any other parameters. In the case of station 2 all the sulphide fractions are found to have maximum correlation with sulphate sulphur. In this station Fe showed better correlation with all the sulphur fractions. In station 3 no correlation, which requires any specific correlation, is observed except that in shown by AVS with gregite and sulphate sulphur and pyrite with organic carbon, Fe and sulphate sulphur.

Table 5.13 Correlation coefficient (r) between different sulphur fractions at 10cm depth (n = 7)

Station 1

	AVS	Gregite-S	Pyrite-S	SO_4-S	Total-S
AVS	1	-0.21477	0.53243	0.10675	0.48149
Gregite-S		1	-0.11686	-0.12971	-0.36566
Pyrite-S			1	-0.21369	-0.34197
SO_4-S				1	0.10771
Total-S					1

Station 2

	AVS	Gregite-S	Pyrite-S	SO_4-S	Total-S
AVS	1	0.21922	-0.07882	-0.09927	-0.32709
Gregite-S		1	-0.35146	-0.44874	-0.52777
Pyrite-S			1	0.71053	0.25546
SO_4-S				1	-0.34730
Total-S					1

Station 3

	AVS	Gregite-S	Pyrite-S	SO_4-S	Total-S
AVS	1	-0.25387	0.21567	0.06675	-0.20732
Gregite-S		1	0.15717	-0.65351	-0.16159
Pyrite-S			1	-0.67651	-0.13539
SO_4-S				1	0.72570
Total-S					1

The surface sediments thus exhibit a very complex geochemical character. Though sulphate emerges as the major source of the sulphur in the system, the observed concentrations of the sulphur fractions are not fully the reflection of the concentration of the sulphate. Such inconsistent behaviour can only be due to the varying redox conditions during the tidal cycles, available in the system. It has been reported earlier also that under varying redox conditions, reoxidation of sulphide can take place (Gibblin and Howarth, 1984). The isotopic studies with S^{34} have shown that, the sediments that are open to the availability of oxidants, repetitive cycles of sulphate reduction, oxidation and disproportionation are the most favoured possibilities (Canfield and Thamdrup, 1994, Wijisman et al., 2001).

Table 5.14 Correlation coefficient (r) between different sulphur fractions at 15cm depth (n = 7)

Station 1

	AVS	Gregite-S	Pyrite-S	SO_4-S	Total-S
AVS	1	0.59640	0.33656	0.17624	0.17797
Gregite-S		1	0.15854	0.50517	-0.15145
Pyrite-S			1	-0.13616	-0.20165
SO_4-S				1	0.16535
Total-S					1

Station 2

	AVS	Gregite-S	Pyrite-S	SO_4-S	Total-S
AVS	1	0.64788	-0.37946	-0.74898	-0.21973
Gregite-S		1	-0.42492	-0.41355	-0.26081
Pyrite-S			1	0.74039	-0.54616
SO_4-S				1	-0.20934
Total-S					1

Station 3

	AVS	Gregite-S	Pyrite-S	SO_4-S	Total-S
AVS	1	-0.02983	-0.51607	0.46555	-0.10851
Gregite-S		1	0.81058	-0.74308	0.57138
Pyrite-S			1	-0.75451	-0.63388
SO_4-S				1	0.57138
Total-S					1

At the sediment depth 5 cm, station 1 gave significant correlations for AVS with gregite sulphur, pyrite sulphur and sulphate sulphur. Pyrite sulphur and gregite sulphur also showed significant correlation between themselves and sulphate sulphur. No reportable correlation is available at station 2 and station 3. Generally sediment upto 5 cm is considered to be the most reactive zone and the study of the carbon dynamics have shown that such a condition is valid in these system also (Geetha, 2002). The correlations observed at station 1 indicate a normal behaviour of the sedimentary processes at this depth. The concentrations rely mostly on the sulphate reduction and sulphide concentration.

In deeper sediments no significant correlation was observed in any of the stations except that in shown by pyrite with sulphate at station 2 and 3. Being more stable levels one should expect significant correlations between the fractions.

Significant differences in the correlation pattern are observed when all the values corresponding to the individual species at a station were pooled together and inter species correlation is taken (**Table 5.15**).

Table 5.15 Correlation coefficient (r) between different sulphur fractions at 0-15cm depth (n = 21)

Station 1

	AVS	Gregite-S	Pyrite-S	SO_4-S	Total-S	OC
AVS	1	0.57071	0.73709	0.56982	-0.00632	-0.00632
Gregite-S		1	0.49895	0.39470	0.10968	-0.07935
Pyrite-S			1	0.327899	-0.12243	-0.40117
SO_4-S				1	0.03087	-0.10747
Total-S					1	-0.25159
OC						1

Station 2

	AVS	Gregite-S	Pyrite-S	SO_4-S	Total-S	OC
AVS	1	0.25557	-0.11108	-0.16452	0.02289	0.42385
Gregite-S		1	-0.32954	-0.30885	-0.37875	0.14710
Pyrite-S			1	0.67641	0.33463	-0.16619
SO_4-S				1	0.52156	-0.14720
Total-S					1	-0.10421
OC						1

Station 3

	AVS	Gregite-S	Pyrite-S	SO_4-S	Total-S	OC
AVS	1	0.34612	-0.18087	0.06351	0.14608	-0.24160
Gregite-S		1	-0.06802	-0.18076	0.09232	0.11510
Pyrite-S			1	-0.71787	-0.49045	0.67955
SO_4-S				1	0.45235	-0.66773
Total-S					1	-0.34189
OC						1

This is a well expected chemical conditions available in each system is different. But pooling of all the individual fractions with out considering the system variability, comparatively good agreement with between the fractions is observed (**Table 5.16**)

Table 5.16 Correlation coefficient (r) between different sulphur fractions in all stations (n = 63)

	AVS	Gregite-S	Pyrite-S	SO_4-S	Total-S	OC
AVS	1	0.62185	0.57584	0.04140	0.09694	0.22147
Grgite-S		1	0.39712	-0.02692	0.08132	0.26659
Pyrite-S			1	0.17337	0.36027	-0.11008
SO_4-S				1	0.51564	-0.40803
Total-S					1	-0.26564
OC						1

One can infer from these observations that though the systems have contributions from different biological, physical, geological and chemical conditions, the over all reactivity is governed by the processes which maintains the redox patterns. In this respect, the highest contribution will be the tidal activity. Other factors like suspension, resuspension and presence of vascular plants also will be contributing significantly.

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Summary

Mangroves are highly productive ecosystems with various important economic and environmental functions. The uses of mangroves fall into two categories: Firstly the indirect use of the mangrove ecosystems are in the form of vital ecological functions such as control of coastal erosion and protection of coastal land, stabilization of sediment, natural purification of coastal water from pollution. Secondly, the economic benefits which are many and varied. Apart from prawn fisheries, many other biological species of economic importance are associated with mangroves; these include crabs, shrimps, oysters, lobsters and fish. Mangrove forests accelerate the siltation processes, check soil erosion and protect coastal areas from frequent tidal thrust, cyclonic storm and devastating surges from the bay.

Mangrove sediments are effective in retaining heavy metals and nutrients from seawater, but it is essentially anaerobic. All soil nutrients varies seasonally, in response to wet and dry periods of climate. Results of the previous studies show that most pollutants are accumulated in the top layer of the soil tray. The wastewater inputs and salinity would have more significant effects on the microbial activities in mangrove soils. Mangrove plants intake nutrients from the tidal sea water, river courses and the mangrove ecosystems, as such, provide natural food to the mangrove dwelling fauna.

Mangrove ecosystem is considered as a wetland ecosystem, characterized by soils that are frequently or continuously waterlogged and that are often high in organic matter content. The duration and frequency of waterlogging, however, are quite varied. Intertidal sediments are very sensitive to climate change, they are not wholly passive since they can themselves influence climate change via atmospheric gas cycling. These sediments are both sinks and sources of different nutrients and that the behaviour changes with the tide. There has been intense interest in understanding the sulphur cycle in these ecosystems because of the high inputs of organic matter into the soils, and the oxic surface and anoxic subsurface zones, which potentially allow sulphur to play a critical role in the biogeochemistry of wetlands.

Sulphur exists in this wetland soils in a variety of oxidation states and may be present in gaseous, soluble, and solid forms. The majority of sulphur is present as reduced inorganic sulphur minerals (pyrite, iron monosulphides, and elemental sulphur), organic forms, or sulphate. In this study the quantification of different species such as acid volatile sulphur, gregite sulphur, pyrite sulphur, elemental sulphur, sulphate sulphur and organic sulphur were done in a three different mangrove ecosystems like Mangalavanam (station 1), Nettoor (station 2) and Vypeen (station 3) was undertaken.

The possible conclusion one can arrive from the observed data and its interrelation and comparison with the earlier studies, can be summarised as follows.

1. The main source of sulphur in these mangrove systems is the saline water, which intrudes to the systems during the tidal activity. The concentration values observed in the water from the station 1 but generally are not reflections of the salinity mainly because of the significant retention of soul with in the system. The observation is in tune with the water balance studies conducted earlier
2. The concentration of sulphide observed in the overlying water is indicative of the presence of anaerobic diagenesis leading to significant sulphide reduction. The dissolved oxygen content but is not supportive of such an anoxic condition, thereby warranty alternative explanations for the sulphide concentrations. It is to be noted here that the adjacent

water bodies also have shown comparable hydrogen sulphide concentration.

3. The results of the organic carbon indicative of the presence of significantly high organic load which generally can lead to an anoxic condition and anaerobic diagenetic processes. The observed concentrations of the sulphur fractions in the surface sediments but tends one to suggest that the oxidising condition is prevailing over the reducing condition which may be due to the exposure of the sediment to the oxic overlying water. This can also be due to the direct contact with the atmospheric oxygen during the low tide.
4. A preferential formation of elemental sulphur and retention of sulphate in the experimental observation at the different depth of the sediments. This supports the views expressed above : more than the organic carbon load the tidal activity and the presence of higher oxygen content keeps the surface sediments more towards the oxic processes and the different layers of the sediments to the anoxic processes.
5. The over all geochemistry infact presence a very complex character with respect to sulphur. A swing between the oxic and anoxic conditions leads to an unstable redox condition which makes the system more supportive to life.

List of Abbreviations

PRE-MON	Pre monsoon
MON	Monsoon
POST-M	Post monsoon
1F	Mangalavanam Forest
1C	Mangalavanam Canal
2F	Nettoor Forest
2C	Nettoor canal
3F	Vypeen Forest
3C	Vypeen Canal
AVS	Acid Volatile Sulphur
OC	Organic Carbon

Appendix

Table A-1 Monthly variations of different forms of sulphur in the surface sediment at Station 1

Months	AVS (ng/g)	Gregite-S (ng/g)	Pyrite-S (ng/g)	Sulphat-S (µg/g)	Total-S (µg/g)
Nov-99	149.26	510.01	289.38	690.00	1620
Dec-99	230.22	350.00	70.42	469.96	1880
Feb-99	289.12	510.02	110.42	470.00	980
Apr-99	70.00	430.00	689.58	710.00	1320
Jul-99	90.00	250.01	150.02	780.02	1380
Aug-99	150.00	310.01	69.90	900.00	1360
Nov-00	50.00	190.00	90.00	580.00	1400

Table A-2 Monthly variations of dissolved hydrogen sulphide (µmol/l) at Station 1

Months	1F-L	1F-H	1C-L	1C-H
Nov-99	0.95	0.88	0.22	0.88
Dec-99	0.59	0.48	0.33	0.48
Feb-99	2.33	1.22	0.84	1.22
Apr-99	0.59	0.32	0.41	0.32
Jul-99	0.42	0.15	0.14	0.15
Aug-99	0.01	0.03	0.02	0.03
Nov-00	0.89	0.54	1.16	0.54

Table A-3 Monthly variations of dissolved sulphate(mmol/l) at Station 1

Months	1F-L	1F-H	1C-L	1C-H
Nov-99	34.68	0.15	4.41	45.07
Dec-99	29.15	16.92	14.28	27.84
Feb-99	37.91	2.90	46.35	48.03
Apr-99	11.56	9.78	8.41	11.90
Jul-99	2.40	0.98	0.26	0.51
Aug-99	0.06	1.63	0.03	1.20
Nov-00	0.45	0.09	0.65	0.60

Table A-4 Monthly variations of different forms of sulphur in the surface sediment at Station 2

Months	AVS (ng/g)	Gregite-S (ng/g)	Pyrite-S (ng/g)	Sulphat-S (µg/g)	Total-S (µg/g)
Nov-99	120.00	210.04	28.52	470.42	1390
Dec-99	120.04	90.02	70.00	490.00	1230
Feb-99	79.80	1150.00	119.7	540.00	1240
Apr-99	120.00	170.46	0.00	520.00	1100
Jul-99	130.04	180.00	0.00	50.00	1030
Aug-99	109.60	120.06	0.00	50.00	150
Nov-00	110.00	120.00	0.00	30.00	200

Table A-5 Monthly variations of dissolved H_2S(µmol/l) and sulphate (mmol/l) at Station 2

Months	H_2S-2F	H_2S-2C	SO_4--2F	SO_4--2C
Nov-99	0.14	0.12	1.73	1.24
Dec-99	0.42	0.19	7.01	7.04
Feb-99	0.89	0.14	33.53	40.19
Apr-99	0.16	0.35	10.95	12.06
Jul-99	0.22	0.15	0.76	0.65
Aug-99	0.19	0.16	nd	nd
Nov-00	1.37	1.20	0.68	0.01

Table A-6 Monthly variations of different forms of sulphur in the surface sediment at Station 3

Months	AVS (ng/g)	Gregite-S (ng/g)	Pyrite-S (ng/g)	Sulphat-S (µg/g)	Total-S (µg/g)
Nov-99	90.00	70.03	20.24	650.05	1440
Dec-99	50.00	30.21	0.00	550.05	1340
Feb-99	80.01	70.00	0.00	600.46	1460
Apr-99	61.25	70.00	0.00	620.00	1160
Jul-99	60.00	80.00	60.02	190.00	1150
Aug-99	40.02	60.00	60.00	470.20	1470
Nov-00	40.00	10.00	80.00	570.00	1060

Table A-7 Monthly variations of dissolved H_2S(µmol/l) and sulphate (mmol/l) at Station 3

Months	H_2S-3F	H_2S-3C	SO_4--3F	SO_4--3C
Nov-99	0.19	0.22	35.72	2.65
Dec-99	0.23	0.30	39.29	25.07
Feb-99	0.22	0.21	80.61	80.61
Apr-99	0.41	0.34	13.74	15.93
Jul-99	0.32	0.24	3.61	2.91
Aug-99	0.24	0.35	4.28	nd
Nov-00	0.23	0.45	0.86	0.51

Table A-8 Monthly variations of Iron and Organic carbon in the surface sediment (mg/g)

Months	IRON			ORGANIC CARBON		
	Station 1	Station 2	Station 3	Station 1	Station 2	Station 3
Nov-99	15.66	21.23	27.87	78.00	30.08	40.32
Dec-99	10.06	16.12	32.77	120.20	30.14	34.53
Feb-99	2.99	32.311	11.86	36.00	15.09	20.93
Apr-99	20.37	10.107	46.43	60.44	28.2	29.55
Jul-99	49.20	0.228	47.15	56.66	5.93	41.59
Aug-99	16.17	3.08	19.77	82.57	65.55	60.64
Nov-00	10.59	1.861	81.13	123.40	7.33	75.25

Table A-9 Monthly depth profile of Organic carbon in the core (mg/g)

MONTHS	DEPTH (cm)	STATION 1	STATION 2	STATION 3
Nov-99	5	33.5	8.49	16.6
	10	15.2	9.45	10.29
	15	12.3	6.05	22.6
Dec-99	5	28.1	7.09	29.79
	10	52.6	2.53	29.96
	15	11.9	3.3	36.57
Feb-99	5	30.62	15.13	28.31
	10	28.84	13.18	13.21
	15	24.99	14.02	29.55
Apr-99	5	47.95	21.12	23.97
	10	17.66	6.13	38.88
	15	15.84	5.81	28.21
Jul-99	5	17.69	1.071	41.79
	10	39.28	6.06	29.58
	15	16.44	6.38	30.1
Aug-99	5	112.25	16.22	81.62
	10	82.07	18.83	74.92
	15	55.74	nd	90.76
Nov-00	5	41.82	23.44	80.34
	10	33.06	15.44	65.24
	15	28.56	7.05	89.19

Table A-10 Monthly depth profile of Acid volatile sulphur in the core (ng/g)

MONTHS	DEPTH (cm)	STATION 1	STATION 2	STATION 3
Nov-99	5	190.64	119.92	70.46
	10	190.20	120.2	70.41
	15	128.96	50.00	50.82
Dec-99	5	370.00	200.00	109.98
	10	210.00	40.30	69.81
	15	130.82	70.00	69.98
Feb-99	5	170.00	150.00	60.40
	10	190.00	120.00	40.62
	15	130.28	140.63	60.00
Apr-99	5	109.96	110.00	19.62
	10	170.00	100.82	100.00
	15	110.14	101.79	30.00
Jul-99	5	89.96	90.72	40.01
	10	90.00	70.42	79.76
	15	110.00	80.42	60.21
Aug-99	5	90.24	109.56	40.03
	10	70.00	149.78	60.84
	15	50.00	160.00	39.79
Nov-00	5	70.00	180.00	50.00
	10	50.00	210.00	60.00
	15	80.04	160.00	50.04

Table A-11 Monthly depth profile of Gregite sulphur in the core (ng/g)

MONTHS	DEPTH (cm)	STATION 1	STATION 2	STATION 3
Nov-99	5	490.00	70.64	30.48
	10	430.02	170.82	10.00
	15	510.02	199.48	20.46
Dec-99	5	1950.00	89.60	510.00
	10	450.00	149.84	70.00
	15	450.46	60.92	39.50
Feb-99	5	428.00	610.01	50.66
	10	370.50	260.00	30.14
	15	410.00	359.68	29.90
Apr-99	5	390.00	249.99	149.80
	10	349.52	280.00	30.14
	15	229.96	220.56	50.02
Jul-99	5	369.54	210.00	59.50
	10	1630.00	410.00	20.86
	15	329.78	1200.00	19.78
Aug-99	5	290.46	430.00	140.96
	10	350.20	910.20	79.14
	15	290.00	240.00	40.52
Nov-00	5	380.00	110.00	50.00
	10	250.62	220.00	60.00
	15	350.00	670.00	180.00

Table A-12 Monthly depth profile of Pyrite sulphur in the core (ng/g)

MONTHS	DEPTH (cm)	STATION 1	STATION 2	STATION 3
Nov-99	5	230.46	150.41	0.00
	10	190.28	270.21	20.42
	15	150.02	140.00	0.00
Dec-99	5	510.02	89.33	0.00
	10	230.00	49.79	0.00
	15	130.40	40.00	0.00
Feb-99	5	290.46	0.00	0.00
	10	350.00	0.00	0.00
	15	290.52	110.00	0.00
Apr-99	5	169.46	0.00	0.00
	10	109.92	0.00	80.42
	15	169.40	10.02	59.72
Jul-99	5	250.0	0.00	140.56
	10	150.0	0.00	70.00
	15	190.0	0.00	80.00
Aug-99	5	70.02	39.9	59.44
	10	50.21	0.00	50.42
	15	30.62	39.9	80.62
Nov-00	5	110.00	0.00	140.00
	10	190.00	0.00	170.00
	15	250.06	40.00	170.00

Table A-13 Monthly depth profile of Sulphate sulphur in the core (µg/g)

MONTHS	DEPTH (cm)	STATION 1	STATION 2	STATION 3
Nov-99	5	640.35	330.00	410.24
	10	190.26	230.63	650.00
	15	299.54	230.00	440.00
Dec-99	5	639.89	169.32	370.00
	10	500.26	69.37	430.44
	15	380.00	130.00	480.28
Feb-99	5	330.46	180.00	570.00
	10	340.00	190.00	680.00
	15	400.04	140.00	680.00
Apr-99	5	487.54	80.00	529.38
	10	620.00	89.08	580.00
	15	180.00	99.66	679.98
Jul-99	5	240.00	50.24	150.00
	10	360.00	80.00	280.00
	15	310.44	90.45	470.00
Aug-99	5	160.00	30.00	531.96
	10	360.22	40.66	140.00
	15	350.00	69.99	269.58
Nov-00	5	230.02	20.00	200.00
	10	390.00	50.00	70.00
	15	200.00	20.00	30.00

Table A-14 Monthly depth profile of Total sulphur in the core (μg/g)

MONTHS	DEPTH (cm)	STATION 1	STATION 2	STATION 3
Nov-99	5	1580	1070	1760
	10	2010	1030	1840
	15	1770	1030	1910
Dec-99	5	1960	2650	1920
	10	1950	830	1760
	15	2190	970	790
Feb-99	5	870	700	1920
	10	1900	1030	1460
	15	1890	1000	1140
Apr-99	5	1430	1000	680
	10	2000	1590	960
	15	2010	980	1460
Jul-99	5	1610	130	1110
	10	1900	270	360
	15	1930	570	1080
Aug-99	5	1470	170	1550
	10	1940	190	720
	15	1910	130	1320
Nov-00	5	1950	470	1760
	10	1910	300	610
	15	1880	300	160

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