MODELLING OF GEOCHEMICAL PROCESSES IN MANGROVE ECOSYSTEM

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Certificate

This is to certify that the thesis titled "Modelling of Geochemical Processes in Mangrove Ecosystem" is an authentic record of the research work carried out by Smt. Geetha, R., 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 the Ph.D. degree of Cochin University of Science and Technology and no part threof has been presented before for any other degree in any University.

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Preface

The mangrove ecosystem is one of the earth's most endangered ecosystems. These are halophytic ecosystems which have the ability to survive in most harsh environmental conditions. Mangroves in India are under threat from developmental activities and the pressure of human and animal populations. There are many, large threats to its continued survival, and all are interacting to remove it or degrade its functions: clear cutting and land reclamation; pollution; removal and diversion of fresh water resources away from the mangroves and shrimp aquaculture. In Kerala, the estuaries and backwaters supported a rich mangrove flora until a few decades ago, but now restricted to isolated patches and pockets on the banks of the backwater systems. Kerala once adorned with 700km^2 of mangroves along the coast, now has only 17 km^2, Many marine species of fish that are important in both recreational and commercial fishing industries, spend a large proportion of their life cycle in the mangrove swamp. Mangroves are essential to maintain our fishing industries. The disappearance of mangroves will almost ensure an enormous reduction in fish catches. Human destruction of mangroves was quoted as one of the reasons for the unprecedented flood havoc in Orissa. The mangrove forests act as a natural barrier to storm surge and cyclone wind. Their conservation and protection are therefore of vital importance. In this study, the geochemical features of three mangrove ecosystems in Kochi were compared. A model of the mangrove ecosystem is developed on the basis of these observations.

The system selected for the study consists of three stations and their connecting canals. The stations are Mangalavanam, Vypeen & Nettoor. Water, sediment and core samples were collected from these stations for a period of one year. Nutrients, organic compounds organic carbon and hydrographical parameters of the samples were estimated.

The title of the thesis is " Modelling of geochemical processes in Mangrove ecosystem". It is divided into five chapters. The chapters are;

Chapter 1 - Introduction

This chapter includes description of mangroves, their distribution, importance and the need for their protection. The present status of mangroves in the world, India, Kerala is discussed in this. The ecological importance, medicinal values as well as the functions of these plants are also discussed.

Chapter 2 - Materials and methods.

Location of the sampling sites and the various methods used for the study is described in this chapter. The geographical features of the stations and the detailed procedures employed for the estimation of various chemical species are also explained. The results of the hydrographical parameters are also included.

Chapter 3 - Seasonal & Tidal variation of Nutrients and organic compounds.

The observations and results of the distribution of nutrients and organic compounds in water is described in this. The changes in the distribution of various chemical parameters during tide are also explained.

Chapter 4 - The Model

Based on the parameters analysed, a model of the mangrove ecosystem is developed in this. The main theme of the model is carbon flow.

Chapter 5 - Geochemistry of sediments

The geochemical processes in the sediments are discussed in this chapter. The geochemistry of the mangrove ecosystem is explained on the basis of this.

Summary.

A summary of the results and conclusion of the study is given at the end of the thesis.

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List of abbreviations used

Pre-mon	Pre-monsoon season.
Post-mon	Post - monsoon season
Mon	Monsoon season.
POC	Particulate organic carbon
TEA	Terminal electon acceptors
OC	Organic carbon
OM	organic matter
POM	Particulate organic matter
DOM	Dissolved organic matter
DOC	Dissolved organic carbon
DON	Dissolved organic nitrogen

Chapter 1

INTRODUCTION

*The origin of the name ‘mangrove’ is not certain. It could be a combination of the Portuguese ‘mangue’, meaning an individual mangrove tree, with the English ‘grove’, although early versions were ‘mangrove’ and ‘mangrave’. The term ‘mangrove’ may have been derived from a combination of the Malay word manggi-manggi’, for a type of mangrove tree (Avicennia) and the Arabic ‘el gurm’, for the same, as ‘mang-gurm’. As a word, it can be used to refer to a species, plant, forest or community.

Mangroves are the rainforests by the sea. These forests are comprised of taxonomically diverse, salt-tolerant trees and other plant species which thrive in intertidal zones of sheltered tropical shores, "overwash" islands, and estuaries. These trees have specially adapted aerial and salt-filtering roots and salt-excreting leaves that enable them to occupy the saline wetlands where other plant life cannot survive.

These forests literally live in two worlds simultaneously, acting as the interface between land and sea. Mangroves help to protect coastlines from erosion, storm damage, and wave action. The stability mangroves provide is of immense importance. They prevent shoreline erosion by acting as buffers and catch alluvial materials, thus stabilizing land elevation by sediment accretion that balances sediment loss. Vital coral reefs and sea grass beds are also protected from damaging siltation.

1.1 Mangrove Ecosystems

The shallow intertidal reaches that characterize the mangrove wetlands offer refuge and nursery grounds for juvenile fish, crabs, shrimps, and mollusks. They are also prime nesting and migratory sites for hundreds of bird species. In Belize, for instance, there are over 500 species of birds recorded in mangrove areas. Additionally, manatees, crab-eating monkeys, fishing cats, monitor lizards, sea turtles, and mud-skipper fish utilize the mangrove wetlands. There are two types of mangrove communities: fringe mangroves and riverine mangroves. The fringe communities are found right along the coast, while riverine mangroves are found in environments characterised by a larger and more continuous supplies of fresh water (Lugo & Snedaker 1974). The structural development, reproductive capacity, and production of mangroves are inversely related to the availability of fresh water, e.g. tall, robust forests with high leaf litter production are present where fresh water availability is good, whereas stunted forests with smaller stem diameters and lower litter production are present where the availability of fresh water is limited.

Odum (1967) has described the mangrove ecosystem as a "pass through" type of system because of the large flow of organic matter transported through the mangroves to 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 the marine ecosystem. It is noted that mangrove forests differ from terrestrial ones in that the primary source of nutrients lies outside of the forests themselves, and nutrients falling as leaf litter are removed from the forest.

These complex ecosystems are found between the latitudes of 32 degrees north and 38 degrees south, along the tropical coasts of Africa, Australia, Asia, and the Americas. There are varying scientific classifications of what constitutes a mangrove plant. According to two reputable scientific studies, mangroves include approximately 16-24 families and 54-75 species. The greatest diversity of mangrove species exists in Southeast Asia. For example, there are only twelve mangrove species in the New World and only four species of mangroves exist along portions of the coasts of the southern USA. However, over the past several decades, the global area in mangroves has increasingly diminished as a result of a variety of human activities, such as overharvesting, freshwater diversion and conversion to other uses.

Mangroves are estimated to extend over 15 million ha world-wide; there are about 6.9 million ha in the Indo-Pacific region 3.5 million ha in Africa and some 4.1 million ha in the Americas including the Caribbean.

The most extensive and luxurious mangroves extend across the Indo-Pacific regions where they are estimated to cover an area of 22 million ha. They dominate majority of the subtropical and tropical coastline and are best developed in the delta systems of major rivers, e.g. the Ganges-Brahmaputra, Irrawady, Mekong and along very sheltered shores protected by large land masses, notably Madagascar, the Malacca Straits, Kalimantan, the Indonesian Archipelago and Papua New Guinea. The largest intact area of mangroves occurs in Bangladesh, where there is almost 600,000 ha of the Sundarbans ecosystem and a mangrove forest area estimated in 1985 to cover 401,600 ha.

Mangroves also penetrate some temperate zones, but there is a rapid decrease in the diversity of species with increasing latitude. At their latitudinal extremes: 31 N in southern Japan; 31 N on the Pacific coast of Mexico; 32 S in Brazil and 38 S in southern Australia the mangrove vegetation is in each case restricted to a single species.

About 80 species of true mangrove trees/shrubs are recognised, of which around 50- 60 species make a significant contribution to the structure of mangrove forests. Species diversity is much higher in the Southeast Asian region, where approximately two-thirds of all species are found, while approximately 15 species occur in Africa and 10 in the America.

Top Eight Nations with Remaining Mangrove Forests

Nation	Sq km (% World Total)
Indonesia	42,550 (23.5)
Brazil	13,400 (7.3)
Australia	11,500 (6.3)
Nigeria	10,515 (5.8)
Cuba	7,848 (4.3)
India	6,700 (3.7)
Malaysia	6,424 (3.5)
Bangladesh	5,767 (3.2)

1.1.1. Mangrove Distribution in India

India has a coastline of 7,516 km. It has an Exclusive Economic Zone of 2.02 million km^2. Out of its 1 billion population, nearly 20% live in the coastal areas. Along the Indian coastline, the brackish water areas including marshes, backwaters, mangroves, inter- and sub-tidal measure about 14,16,300 ha. These areas act as feeding and nursery grounds for a variety of commercially important fish, prawn and crabs, media for inland transportation, fishing etc. Along the Indian coast mangroves are found along the islands, major deltas, estuaries and backwaters of the East Coast of India. They also exist along the oceanic island groups of the Andaman and Nicobar. The total mangrove area is estimated to be 670,000 ha. While the mangroves along the West Coast of India are dense, they are scattered and comparatively small in area along the West Coast. Gangetic Sunderbans (418,888 ha), Andaman-Nicobar Islands (115,000 ha), Krishna, Kaveri and Godavari deltas and Mahanadi delta are some of the best mangrove formations of India.

There are about 45 mangrove species along the Indian coast. The dominant genera are *Rhizophora, Avicennia, Bruguiera, Sonneratia, Canocarpus, Heretiera, Xylocarpus, Ceriops*, and *Exoecaria.*

Apart from the captive and culture fisheries, mangroves are also important as "coastal stabilizers" and "shelter belt areas". These formations protect the coasts and the landward areas from erosion and cyclonic destructions to some extent. Apart from these the mangrove forests of India have importance from a wildlife, recreation and education point of view. "Project Tiger" of Sunderbans and "Crocodile Sanctuary" in the Mahanadi delta are examples of such activities.

Large areas of the inland mangroves of southern Asia have been converted to agriculture (mainly paddy fields) or salt production. Shrimp farming represents a relatively new form of coastal land use which is a further threat. Traditionally the mangroves of India and Bangladesh have been exploited for timber and fuelwood, bark tannin, animal fodder, native medicines and food (fish, shellfish, honey, wild animals). Population pressure has greatly increased the rate of exploitation, leading to degradation of the remaining forests at an alarming rate. In Bangladesh, where an estimated 300,000 wood and thatch cutters, honey collectors, and fishermen are directly dependent on the Sundarbans, the area of pure sundri (Heretiera forms the main economic timber species) is reported to have shrunk from 31.6 to 21.0% between 1959 and 1983

Heavy exploitation of mangroves in India for firewood and animal fodder has depleted the resource significantly, except in the Indian Sunderbans and the Andaman Islands where selective systems of rotational felling have been practiced. In addition to firewood, strip felling was carried out in the Andamans to extract poles of Bruguiera gymnorrhiza, with successful replanting of Bruguiera seedlings reported.

1.1.2. Adaptations of Mangrove Plants

Mangrove plants live in an environment where there are too many limiting factors and too many odds to cope with. In such a hostile environment it is mandatory for such plants to undergo morphological and anatomical changes. A lot of such adaptive changes have been recognised and documented in mangrove plants. A few of these adaptive changes have been described in the following section.

Mangroves are facultative halophytes, i.e., the presence of salt in the environment is not necessary for the growth of mangroves and they can grow very well in freshwater, on the contrary, the growth of mangroves is better in freshwater. But to avoid competition, the mangroves chose a saline environment and successfully became halophytes. To cope with salinity, the mangroves had to develop mechanisms to regulate the salt concentration in the body. One such mechanism is for the retention of water in the leaves giving rise to leaf succulence in many species, viz., *Sonneratia apetala, S. alba, Lumnitzera recemosa, Salvadora persica* etc. Also, these species show remarkably high concentration of salts stored in their tissue. Another mechanism is extrusion of salt from the root tissue as in *Rhizophora, Ceriops, Bruguiera and Kandelia.* This is achieved by an in-built ultrafiltration mechanism. Only fresh water is allowed to enter the body and the entry of salt is arrested by the semi- permeable membrane of the roots. In case the plants are not equipped with a mechanism for ultrafiltration, yet another mechanism is seen where leaves develop a special tissue called the "salt glands" which help in expulsion of salts from the body as in *Avicennia, Laguncularia, Aegiceras, Acanthus*, etc. Another method of coping with salt is to concentrate it in bark or in older leaves which carry it with them when they drop. (*Lumnitzera, Avicennia, Ceriops* and *Sonneratia* species all use this.).

In addition, a number of features serve to prevent water loss from the plant. These include a thick waxy cuticle (skin on the leaf) or dense hairs to reduce transpiration. Most evaporation loss occurs through stomata so these are often sunken below the leaf surface where they are protected from drying winds.

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 a plant. They support it and they obtain essential nutrients and oxygen. In unstable, sometimes semi-fluid, soil an extensive root system is necessary simply to keep the trees upright. As a result, most mangroves have more living matter below the ground than above it. The main mass of roots, however, is generally within the top two meters and mangroves do not seem to grow deep taproots, probably because of the poor oxygen supply below the surface.

Little oxygen is available in fine, often waterlogged mud. The solution which many mangroves have come up with, is to raise part of their roots above the mud. These roots are covered with special breathing cells called lenticels, which draw in air. They are connected to spongy tissue within the roots. When the roots are submerged in water, the pressure within these tissues falls as the plant uses up the internal oxygen. The resulting negative pressure means that when the root is re-exposed as the tide drops, more air is drawn in through the lenticels.

The fruits and/or seed (ling)s of all mangrove plants can float, which is, of course, an excellent sea dispersal mechanism for plants which live along coastal waters. Certain mangrove species can propagate successfully in a marine environment because of special adaptations. Through "viviparity," embryo germination begins on the tree itself; the tree later drops its developed embryos, called seedlings, which may take root in the soil beneath. Viviparity may have evolved as an adaptive mechanism to prepare the seedlings for long-distance dispersal, and survival and growth within a harsh saline environment. During this viviparous development, the propagules are nourished on the parent tree, thus accumulating the carbohydrates and other compounds required for later autonomous growth. The structural complexity achieved by the seedlings at this early stage of plant development helps acclimate the seedlings to extreme physical conditions which otherwise might preclude normal seed germination.

Another special adaptation is the dispersal of certain mangroves' "propagules" which hang from the branches of mature trees. These fall off and eventually take root in the soil surrounding the parent tree or are carried to distant shorelines. Depending on the species, these propagules may float for extended periods, up to a year, and still remain viable. Viviparity and the long-lived propagules allow these mangrove species to disperse over wide areas. Some species of these floating seedlings (*Rhizophora*) 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.

Some other species (*Avicennia, Aegialitis* and *Aegiceras*) also produce live seedlings but these are still contained within the seed coat when it drops from the plant. The seed of *Avicennia* floats until this coat drops away. Interestingly the speed with which this happens depends on the temperature and salinity of the water. In water of high or low salinity the seed coat is slow to drop off but in brackish water it is shed quickly allowing the seedling to lodge in the favoured habitat of this species. Higher temperatures also favour faster action. *Avicennia* seeds can stay alive in the water for only three to four days.

1.1.3. Main Uses and Functions of Mangroves

Mangroves have long functioned as a storehouse of materials providing food, medicines, shelter and tools. Fish, crabs, shellfish, prawns and edible snakes and worms are found there. Mangrove ecosystems have traditionally been sustainable managed by local populations for the production of food, medicines, tannins, fuel wood, and construction materials. For millions of indigenous coastal residents, mangrove forests offer dependable, basic livelihoods and sustain their traditional cultures.

The fruit of certain species including the nypa palm can be eaten after preparation along with the nectar of some of the flowers. The best honey is considered to be that produced from mangroves, particularly the river mangrove *Aegiceras corniculatum*.

Numerous medicines are derived from mangroves. Ashes or bark infusions of certain species can be applied to skin disorders and sores including leprosy. Headaches, rheumatism, snakebites, boils, ulcers, diarrhoea, haemorrhages and many more conditions are traditionally treated with mangrove plants. The latex from the leaf of the blind-your-eye mangrove *Excoecaria agallocha* can indeed cause blindness but the powerful chemicals in it can be used on sores and to treat marine stings. The leaves are also used for fishing; when crushed and dropped in water, fish are stupefied and float to the surface. This sap is currently being tested for its medical properties and may play a part in western medicine.

Certain tree species, notably the cedar mangrove, cannonball mangrove (relatives of the red cedar) and the grey mangrove, are prized for their hard wood and used for boat building and cabinet timber as well as for tools such as digging sticks, spears and boomerangs. The fronds of the nypa palm are used for thatching and basket weaving. Various barks are used for tanning, pneumatophores (peg roots) make good fishing floats while the wood from yellow mangroves (*Ceriops* species) has a reputation for burning even when wet. Mangrove tannin is used in India and Bangladesh for leather curing and there are some other traditional uses, e.g. for curing fishing nets in Sri Lanka. The gathering of mangrove leaves (Avicennia) for animal fodder remains widespread in the Middle East and Southern Asia, for feeding camels in Iran and India, for example; in fact grazing by domestic animals is a serious cause of mangrove degradation in parts of India.

Mangrove ecosystems are important, "transformative interfaces" between land and sea. The mangrove ecosystem imports inorganic matter from terrestrial systems and exports organic matter as "detritus" (both dissolved and particulate organic matter) to marine ecosystems. Mangroves litter production has been measured at 896 grams dry wt./m^2/year adding 224 g C/m^2/year to the soils and waters. Mangrove leaves are usually colonized by fungi bacteria, nematodes, etc. upon deposition into water. Mangrove leaf litter provides the most important nutrient base for food webs leading to commercially important fisheries. The leaves themselves are poor in nutrients when they fall from the trees but once in the aquatic ecosystem the organic matter is transformed by bacterial decomposition into nutrient-rich, high protein detritus.

About 75 percent of fish caught commercially spend some time in the mangroves or are dependent on food chains, which can be traced back to these coastal forests. Mangroves also protect the coast by absorbing the energy of storm driven waves and wind. The mangrove forests act as natural barrier to storm surge and cyclone wind. The protective mangrove buffer zone helps minimize damage of property and losses of life from hurricanes and storms. In regions where these coastal fringe forests have been cleared, remendous problems of erosion and siltation have arisen, and sometimes errible losses to human life and property have occurred due to destructive torms. Human destruction of mangroves was quoted as one of the reasons for the unprecedented flood havoc in Orissa. Mangroves have also been useful in treating effluent, as the plants absorb excess nitrates and phosphates thereby preventing contamination of nearshore waters. Sediments trapped by roots prevent silting of adjacent marine habitats where cloudy water might cause corals to die. In addition, mangrove plants and sediments have been shown to absorb pollution, including heavy metals.

An increase in level of atmospheric CO_2 through the combustion of fossil fuels, or more precisely its likely effect on the global climate, is cause for concern. This concern has focused the interest of scientists in carbon fixation and storage in individual ecosystems and their overall performance as a sink or source for atmospheric CO_2. Today, mangrove forests cover an area of about less than 1% of the total forest area on the earth. Here at first glance, it seems unlikely that mangrove ecosystems play an important role in the global carbon cycle. However, if we are to actively utilize ecosystems for the enhancement of CO_2 sequestration, our focus should be place on their ability to produce and store organic carbon. It must be kept in mind that mangrove ecosystems are among the most productive ecosystems and their carbon stock per unit area can be enormous (Twilley et al., 1992). Hence, the successful management of mangrove ecosystems has the potential to produce a measurable gain in CO_2 sequestration.

1.1.4. Present status

In Asia large tracts of back mangroves were cleared initially for agriculture, especially rice farming. Other suitable crops include coconut and oil palm and even pineapple. Rice farming can be successful on mangrove soils in the wet season, although yields are only moderate. However in many such areas the soils are alluvial in origin and have acid sulphate or potential acid sulphate characteristics which lead to a rapid reduction in rice production within a few years (due to acidity, iron and aluminium toxicity and lack of available nutrients), after which they are abandoned. These soil problems can be countered by the use of lime and fertilisers, but it may not be economically viable to do so. For example, fertilized potentially acid sulphate soils in the eastern region of the Bangkok plain produced 1,940 kg/ha, whereas yields from non acidic mangrove soils in the western region reached 3,000 to 4,000 kg/ha. Large areas of the inland mangroves of southern Asia have been converted to agriculture (mainly paddy fields) or salt production. Shrimp farming represents a relatively new form of coastal land use, which is a further threat.

Although impossible to quantify, hunting also remains a significant activity in the Sunderbans and in many other areas in Asia where mangroves are still extensive. Unfortunately, this extends beyond hunting to support local food needs, into the poaching of rare and endangered species for sale as skins and stuffed specimens for tourist markets. To a limited degree native medicines and miscellaneous plant extracts (e.g. a fish poison is obtained from the Derris plant) and food items are still collected from mangrove forests only account for less than 6% of the global resource. This destruction has had a devastating effect on coastal fisheries and has led to the marginalisation of subsistence fisherman and the erosion of shorelines. As well as removing the economic values of the forest, the construction of canals and dikes irreversibly alters the hydrological characteristics of the area and thus the ecology of the system.

Traditionally the mangroves of India and Bangladesh have been exploited for timber and fuelwood, bark tannin, animal fodder, native medicines and food (fish, shellfish, honey, wild animals). Population pressure has greatly increased the rate of exploitation, leading to degradation of the remaining forests at an alarming rate.*

1.2 Organic Carbon

1.2.1 In the Aquatic system

Carbon is a fundamental element of life and thus is a key component of all organic compounds. Although the total global reservoir of carbon is massive (more than 10^{19} kg), only a very small fraction of this carbon is actively involved in the fluxes of the carbon cycle, most of the Earth's carbon being locked away in sediments, in carbonate in oceans and in igneous rocks and fossil fuels. The Earth's active pool consists of carbon in living organisms, carbon in the atmosphere and carbon in soil organic matter. It has been estimated that mass of carbon in soil organic matter amounts to about $3X10^5$ kg and this is approximately five times the size of the atmospheric pool. The latter pool is approximately the same size as that in living organisms.

Hedges and Oades (1997) have presented a recent compilation of the reservoirs and fluxes within the global carbon cycle. Most carbon on earth is sequestered on geological time scales in sedimentary rocks, predominately as inorganic carbonates. About 500,0000 Gt of organic carbon is stored in sediments as kerogen at concentrations of <1% by weight. Actively cycling carbon is dominated by dissolved inorganic carbon, largely in the form of bicarbonate, in sea water (360,00Gt). Organic carbon in the contemporary terrigenous environment includes 570Gt organic carbon in plant biomass and 1670Gt OC in soil litter and and humus. In the ocean, the dominant OC reservoir is 700Gt of dissolved organic carbon, 95% of which is in the deep sea. Marine biomass adds 3Gt OC, and 1000Gt is buried in surface sediments. Progressive alteration of sedimentary organic carbon by diagenesis, catagenesis and metagenesis produces the kerogen that ultimately generates petroleum, coal and gas. Fossil fuels may represent 0.05% of sedimentary organic carbon.

Photosynthetic fixation is the dominant process by which inorganic carbon is transformed to organic carbon. Net global photosynthesis is estimated at 110GT/yr, roughly equally distributed between terrigenous and marine systems. In land, most OC becomes in cooperated into soils, while about 0.2GT/yr each is transported as POC and DOC to the ocean. Only about one half the CO_2 emitted to the atmosphere in the last century by fossil fuel burning, tropical deforestation, and cement production has remained in the atmosphere (Sunquist & Broecker, 1984). The fate of the rest of the anthropogenic CO_2 is uncertain, but the ocean is one of the largest, if not the largest, reservoir of this CO_2. The primary source of dissolved and particulate organic materials in the open ocean, as in the coastal zone, is the photosynthesis carried out by phytoplankton. Dissolved organic matter is derived from the phtoplankton in several ways; some organisms secrete a mucopolysaccharide sheath which continually degrades, adding polysaccharides to both the dissolved and particulate pools; those organisms which form blooms will often produce more organic matter than can be utilised immediately by the bacteria and zooplankton present; sloppy feeding by the zooplankton will add to the organic pool some organics will result from metabolic activities of zooplankton and higher organism and many species of phytoplankton, if not all, exude organic material into the solution as a normal part of their growth cycles. The particulate organic matter must eventually derive from the activities of the phytoplankton, either directly or indirectly. Death and decay of all organisms result in the production of some particulate matter small enough or light enough in suspension for some time. Many marine invertebrates produce structures either for feeding or protection, which collect these small particles. Thus the primary source of organic carbon to the oceans is the productivity of the phytoplankton; the contribution from the terrestrial sources is minor, although potentially harmful.

It is self evident that the oceans must be close to a steady state condition for organic carbon. Of the various methods for the removal of organic materials from the oceans, the various photoreactions are very important. While the extent of sea surface presented to sunlight is great, the absorption of more energetic wavelengths of UV light was assumed to limit these reactions to the top few centimeters of the sea surface. Further more, the low concentrations of organic materials made direct reactions seem unlikely. But some man made organic materials, such as pesticides and some petroleum products can be degraded by photoreactions into compounds more injurious to the environment than were the original materials. Hetrotrophy is another way by which the organic matter produced by the phytoplankton is used by all of other organisms in the ocean. Most soft bodied and many hard bodied invertebrates can meet a considerable portion of their carbon requirements from compounds in solution at normal seawater concentrations.

The ultimate sink for organic materials is the sediment. The routes taken on the way to that sink are complex. Walsh (1984) and Walsh et al. (1985) propose that there has been accelerated rate of storage of planktonic organic C residues in continental slope sediments during recent decades. They suggest that this increase has occurred in response to a combination of increased planktonic productivity resulting from large increases in anthropogenic nitrate inputs from rivers and from drastic reductions in the efficiency of recycling of planktonic residues due to over harvesting of higher trophic levels. Each year about 100×10^{15} g of inorganic carbon is converted globally to plant biomass (Trabalka 1985). Less than 1% of this mass is ultimately preserved in marine sediments, which constitute the only quantitatively significant organic carbon repository (Olson et al. 1985). Although photosynthesis occurs essentially world wide, 85% of the preserved organic carbon is concentrated in fine grained clastic sediments that are deposited along continental margins (Baes et al. 1985). Thus the storage of organic matter in coastal sediments controls the passage of organic carbon from the biospere to the geospere and helps modulate the contemporaneous global carbon cycle(Brocker 1982).

1.2.2 In the Mangrove Ecosystem

Coastal wetlands, comprising both salt marshes and mangrove swamps, are considered to be areas of high primary productivity which support economically important detrital- based marine food webs. One fate of the organic carbon produced by marsh plants is incooperation into the soil matrix and subsequent decomposition to CO_2 by soil microbes. Drainage of organic-soil wetlands, primarily for agriculture has reduced the size of the original net sink for C in others, thus shifting the global balance of C movement between wetlands and the atmosphere (Armentano & Menges 1986). C cycling may also be important in wetland stability. Oxidation of organic matter to CO_2 may contribute significantly to the erosion of peat (Stewart & Wheatly 1990), and in coastal marshes, the amount of soil organic matter required for marsh soil formation increases as submergence increases (Nyman et al 1990). Much of the organic matter required for marsh soil formation is needed to compensate for the decomposition of soil organic matter.

In coastal environments the sedimentation rate and the concentration and reactivity of the organic matter is often high. In most marine-type sediments including inter tidal ones organic carbon is the only reducing agent to enter a sediment column. The remainder of the sediment load arrives in its oxidised form. Rate of supply of the various electron acceptors vary depending on :

(a) their rate of burial

(b) particulate nature

(c) molecular diffusion coefficients

(d) re supply by bio mixing from above

(e) regeneration of their oxidizing potential by migration into more oxidizing environments.

Regeneration processes, in particular, are considered to be critical during early diagenesis, since they will usually account for the bulk of potential energy release. Early diagenesis within the mangroves is of particular interest because of the high biological productivity, which is characterstic of such environment, and their position at the interface between marine and terrestrial systems. The initial source of the electrons ie organic matter is sequentially oxidised in microbially mediated reactions. This is because microbial communities outcompete each other for organic carbon. The rate of carbon remineralisation by microbial oxidation has been empirically shown by Middleburg (1989) to follow a first order decay curve. The idealised decomposition reactions in order of their energy yields per mole of carbon from an idealised organic molecule are;

Aerobic respiration;

$$(CH_2O)_x (NH_3)_y (H_3PO_4) - (x+2y)\, O_2 \rightarrow xCO_2 + (x+y)\, H_2O + yHNO_3$$
$$+ zH_3PO_4.$$

Manganese reduction;

$$(CH_2O)_x (NH_3)_y (H_3PO_4)_z + 4xMnOOH + 7xCO_2 + xH_2O \rightarrow 8xHCO_3 + 4x$$
$$Mn^{2+} + yNH_3 + zH_3PO_4$$

Nitrate reduction;

$$(CH_2O)_x (NH_3)_y (H_3PO_4)_z + 4xNO_3^- \rightarrow xCO_2 + 3xH_2O + 4xHCO_3$$
$$+ 2xN_2\ 5yNH_3 + 5zH_3PO_4.$$

Iron reduction:

$$(CH_2O)_x (NH_3)_y (H_3\, PO_4)_z + 4xFe(OH)_3 + 7xCO_2 \rightarrow 8xHCO_3 + 3xH_2O$$
$$+ 4xFe^{2+} + yNH_3 + zH_3\, PO_4.$$

Sulphate reduction:

$$2\, (CH_2O)_x (NH_3)_y (H_3\, PO_4)_z + xSO_4^{2-} \rightarrow 2xHCO_3 + xH_2S + 2yNH_3$$
$$+2xH_3PO_4.$$

Methane production;

$$2\, (CH_2O)_x (NH_3)_y (H_3\, PO_4)_z \rightarrow xCO_2 + xCH_4 + 2yNH_3 +$$
$$2zH_3PO_4.$$

Some important seasonal fluctuations occur such as during summer, carbon mineralisation rates were higher than the oxidation rates and resulted in the build up of reduced end products. For marine type sediments, the important fluxes during the adjustment of incoming energy or diagenesis are likely to be sulphate reduction and the re oxidation of its products by more thermodynamically favourable electron acceptors. For any element capable of undergoing redox reactions, the same pattern of cyclical reduction and oxidation will be evident. The sediment system can therefore be described in terms of a series of redox cells, operating in parallel. These cells accommodate the flux of electrons from the organic matter to their ultimate sinks, in such a way that they minimize the potential difference between the sediment system and its environment.

1.2.3. Nutrients in the Mangrove Ecosystem

Intertidal sediments are a part of the sediment system that has helped to maintain the productivity of the coastal zone through the storage and recycling of nutrients which were imported from offshore waters (Nixon, 1992). Increases in human population, coupled with aquatic sewage systems and the development of intensive agriculture, have resulted in a significant change in the quantities of nutrients supplied from land sources. Now the main source of nutrients is from the land and not from the sea. These sediments are subject to diurnal drying and flooding which leads to major changes in the local transport of material to and from the sediments. As a result nutrients are affected by a variety of processes in this region. Nitrogen is particularly interesting as it exists in different forms, both organic and inorganic, and may be converted from one form to another under different conditions. Nitrogen can be present in a large variety of forms in aquatic systems. The main species of interest are nitrate, nitrite, ammonium together with organic nitrogen, in both dissolved and particulate form. There is a large pool of dinitrogen gas in the atmosphere and dissolved in surface waters but it is considered that nitrogen fixation is not important in coastal systems. Inputs of nitrogen to these intertidal sediments come from the land, in solution via rivers or ground water, and in the form of particulate material following uptake by phytoplankton. Nutrient cycling occurs, in mangrove swamps as in other terrestrial ecosystems, with the uptake of nutrients by plant roots and incorporation during photosynthesis into the mangrove biomass. Biomass is lost by the fall of litter and this decomposes releasing nutrients which can be recycled. In terrestrial ecosystems this nutrient cycle may be essentially closed, but in mangrove swamps it is open with exchange of nutrients, detritus and sediment facilitated by tidal flushing.

Nitrogen fixation converts nitrogen gas to fixed nitrogen and is the main return path of nitrogen from the atmosphere to the biosphere. However, due to the ready availability of ammonium and nitrate in these areas, the nitrogen requirements of plants are not provided by nitrogen fixation. Nitrification and denitrification are the key nitrogen transformation processes but also they provide the most important route for the removal of N_2 from ecosystems. Nitrification is the oxidation of ammonium to nitrate, where the ammonium is produced from organic nitrogen. Coupled Nitrification/ denitrification has been considered to be the dominant source of gaseous nitrogen products in sediments (Lloyd, 1993) but recent work (Rysgaard et al 1994) suggests that under high nitrate concentration denitrification direct from nitrate is the major pathway.

N_2O is a product of both nitrification and denitrification and is of environmental concern as it is an important greenhouse gas. The yield of N_2O during denitrification in marine and estuarine systems is in the order of a few percent of the total denitrificatio in fresh water and terrestrial systems. Thus in effective management policies, and assuming a desire to avoid adding more N_2O to the atmosphere, brackish water and intertidal environmets offer a better nitrogen removal system rather than extensive use of fresh water wetlands (Fleischer et al, 1991).

Compared with nitrogen, the behaviour of Phosphorus in this area is less well known. It is released under anoxic conditions by the degradation of organic material and accumulates in the interstitial water. In intertidal sediments with low organic carbon and phosphorus content the behavior of phosphorus is dominated by the association with iron oxides (Prastika & Jickells, 1995) and is also released to the interstitial water under anoxia. Thus, to a first approximation, inter tidal sediments act as a sink for phosphorus. Disturbance of the sedimentary regime is the only mechanism that will allow leakage of phosphorus from the system.

1.3. Aim and Scope of the Study

The length of the Kerala coast is about 560 km extending from north to south parallel to the Western Ghat. This Kerala coast is having beautiful beaches, estuaries and lagoons, where the population density is very high ie 2362/km^2. This higher population density in the Kerala coast has exerted tremendous pressure on the natural ecosystem, particularly on the mangroves. The mangroves of the Kerala state are degraded and grow in isolated patches, confined in the inner reaches of the intertidal margin of estuaries, lagoons, backwaters, creeks and criss cross along the coastal region. Kerala once adorned with 700km^2 of mangroves along the coast, now has only 17 km^2 On surface survey, thin mangrove patches were reported from Cochin estuary and other areas like Kumarakom, Dharmadom Chetuva, Pappinisseri, Kunjimangalam, Chateri Veli etc. Nearly about 27 species of mangroves were found in Kerala coast.

The available literature on mangrove ecosystem mainly focussed on micro and macro flora and fauna and sediment characteristics. No significant chemical investigation of mangrove ecosystems in Kerala has reported. In order to conserve and sustainably manage the mangrove ecosystem it is necessary to understand the key processes going on in this system. The chemistry of mangrove detritus changes profoundly during decomposition and ageing. The nutrients and other organic compounds from this are exported to the nearby waters as dissolved and particulate organic matter. Most of the commercially important Pisces complete their larval cycles utilising this. Despite the great interest in their conservation, in management of mangrove species, and in their intrinsic value as a carbon source, relatively few studies in the chemical aspects of these ecosystems have been conducted.

Mangroves are subject to diurnal flooding and drying which facilitates the exchange of detritus, nutrients and sediment with the adjacent water body during tidal flushing. Intertidal areas are very difficult to study from a practical point of view and offer conceptual challenges to developing the quantitative budgets required to address questions about transport of carbon between land and sea. The methods employed must take account the key attributes of the environment which include variability and dynamics. The biogeochemical processes, which influence the behavior of carbon, can be routed but what controls them and how they interact is not easy to assess. Due to the same, the budgeting of carbon in this area is not well documented. Within these limitations, this study is attempted in developing a budget for the exchange of carbon between the mangrove and the adjacent water body.

Mangroves are threatened throughout the world by traditional uses exceeding the sustainable yield. In modern times, the non-resident businessmen also started exploiting mangroves for quick economic returns, forgetting the traditional sustainable methods. Many of the planners, politicians, decision makers and the general public still consider mangroves as wastelands that are of no value unless developed through conversion or some other direct method of exploitation for cash products. This is mainly because the productivity of mangroves has not been quantified precisely and that this has not been made known public. Therefore, the ecologic, economic, aesthetic values of these ecosystems need to be stressed and popularized among various target groups. Moreover, much study to be done to understand the structure, function and dynamism of the system. The present wave of mangrove conversion advocates for their immediate protection.

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Chapter 2

MATERIALS AND METHODS

- 2.1 Description of Sampling sites
- 2.2 Analytical techniques
    - 2.2.1 Sampling procedure
    - 2.2.2 Analytical methods
- 2.3 Results of the Hydrographical parameters
    - 2.3.1 pH
    - 2.3.2 Salinity
    - 2.3.3 Dissolved oxygen
    - 2.3.4 Alkalinity

A brief description of the location of the sampling sites and an outline of the methods employed are given in this chapter. Besides, the general hydrography of the study area is also included.

2.1 Description of Sampling Sites

The wetlands of Kerala was a large mangrove swamp centuries ago and anthropogenic activities modified the system into settlements, agricultural fields, filtration ponds and prawn culture fields. The plots employed for this are of 2-10 ha in size and are contoured by low mud dikes planted all along with coconut and other cash crops. The water flow inside the ponds is regulated by sluice gates operated manually. Here, salt resistant paddy is cultivated during monsoon periods. This is known as 'pokkali' cultivation. During inter monsoon period, when seawater enters inside, prawn farming is conducted. Prawn culture is another form of traditional agro silvi aquaculture followed in this country. The conversion of mangroves that has taken place and the ecological loss thereon is difficult to quantify.

The Cochin estuary includes a system of interconnected lagoons, bays and swamps penetrating the main land and enclosing many islands in between, whose total area amounts to approximately 500 km^2. The backwater around Cochin is located between Lat. 9 40'–10 12'N and Long. 76 10'-76 30'E. This estuary is connected with the Arabian Sea by a permanent opening, 450m wide through which tides act within the estuary. The major sources of fresh water in the estuary are the two rivers, the Periyar in the northern part and Muvattupuzha in the southern part. In addition, several small tributaries, irrigation channels and innumerable drains contribute to the system. A large number of heavy industrial establishments are situated on both sides of the river Periyar and on the southern bank of the river Muvattupuzha. These industrial concerns discharge their wastes into the estuary.

Mangrove ecosystems are found in isolated patches along the banks of this estuary. They cover an area of 260 ha. Like many other mangrove ecosystems, these are also subjected to increasing human influences. The important problems concerning the depletion of mangrove forests of Kochi can be classified into two categories. The first is from land reclamation and other developmental activities. The second is from pollution by industrial effluents as well as domestic sewage.

Station Locations

The area of investigation and the station locations are depicted in Fig. 2.1. The stations were fixed so as to compare the complex environmental conditions prevailing in three different mangrove ecosystems. A brief outline of the characteristics of these stations are :

Mangalavanam

This is a patchy mangrove area in the heart of the city of Cochin. This mangrove forest is a small bird sanctuary, located in the heart of the city behind the High Court of Kerala. It lies 4km off south to Kochi. It is the home of many exotic and rare varieties of migratory birds. This is an almost closed system with a single narrow canal linking to the estuary. This forest during high tide was represented as 1H and at low tide as 1L, the canal connecting to this forest at high tide was represented as 2H and at low tide as 2L in the graphs & tables.

Vypeen

Vypeen, the largest single stretch of mangrove in Kerala has an area of approximately 101 ha. 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 valuable species prawns. The mangrove vegetation consists primarily of Avicennia with Rhizopora constituting occasional growth. Perhaps, this is the only site in Kerala where one can see mangroves right along the accreting seacoast. However a lot of developmental pressures, including the proposed gas Thermal plant, is threatening the very existence of these mangroves. This is a typical fringed, semi enclosed system. This forest was marked as 3 and its adjacent water mass as 4 in the graphs & tables.

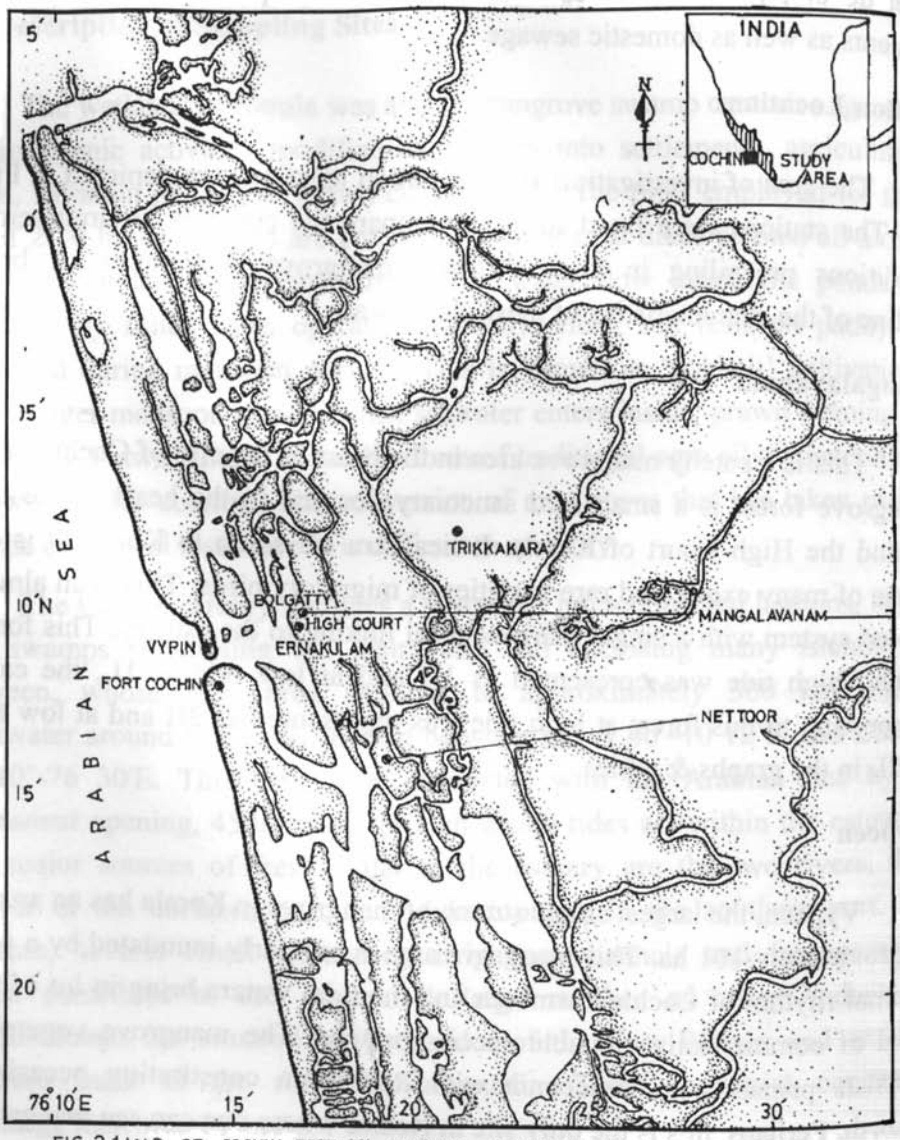

FIG. 2.1 MAP OF COCHIN ESTUARY SHOWING LOCATION OF SAMPLING SITES.

Nettoor

This is a vanishing mangrove ecosystem. It is facing a major threat of land reclamation for construction of roads, buildings etc. During inter monsoon periods, when the seawater enters inside, prawn is cultivated. The chemmeenkettu is another form of agro silvi aquaculture prevailing in this area. This is an open system with maximum human intervention. This forest and its adjacent water masses were designated as 5 & 6 in graphs & tables.

2.2 Analytical Techniques

2.2.1 Sampling Procedure

Water and sediment samples were collected from the stations (Fig.2.1) at bimonthly intervals from November1999 to November 2000. Water samples are collected using a clean plastic bucket. The dissolved oxygen and alkalinity of water samples were fixed in situ. Surficial sediment samples were collected using a clean plastic spoon. Core sediment samples were obtained by penetrating a PVC pipe of 10cm diameter. The core samples were cut into subsamples at 5cm intervals. The samples were taken in polythene bags and stored deep frozen until analyses. All analyses were done in duplicate.

2.2.2. Analytical Methods

a. Hydrographical Parameters

pH was measured in situ and temperature was measured using a sensitive thermometer. Salinity of the water samples was estimated by Mohr- Knudsen method, (Grasshoff, 1999). Modified winkler method was used for the estimation of dissolved Oxyger (Grasshoff, 1999). Alkalinity of the water samples was estimated by the method of Koroleff, (Grasshoff, 1999) and chlorophyll by the method of Strickland and Parsons (1977).

b. Sediment Characteristics

Sediment samples were analyzed for its grain size and total organic carbon. Organic carbon determinations were carried out by the method of Gaudette et al (1974).Grain size of the sediments was determined by the method of Carvar (1971). Moisture content of the sediment was determined by oven drying the sediment at 105°C for 24 hours.

c. Hydro Chemical Parameters

All hydrochemical parameters were estimated spectophotometrically using UV-VIS Hitachi 150-20 after converting each of the species into required colored substances. Nitrite was converted to an azo dye with sulphanilamide and N- (1-naphthyl) ethylene diamine dihydrochloride (Grasshoff, 1999). Nitrate was reduced to nitrite and estimated as nitrite. (Grasshoff, 1999). Formation of phospho- molybdate complex using ascorbic acid as reductant was used for phosphate. (Koroleff, 1983). The protein content was analysed by the method suggested by Herbert et al (1971) and carbohydrates by phenol-sulpuric acid method (Dubois et al 1956). Hydroxylated aromatic compounds (tannin and lignin) was estimated by the method detailed in APHA (1981) and modified by Nair et al (1989).

d. Sediment Parameters.

The protein from the sediment was extracted by 1N NaOH. A weighed amount of the sample was mixed with the extractant and maintained at 80°C for 30 minutes to dissolve the proteins. After cooling, aliquots were transferred to clean test tubes aand 5ml of the coppex reagent were added followed by 0.5 ml of folin - Ciocalteau reagent after10 minutes. Appropriate blank and standards (bovine albumin) were similarly treated and the analysis was carried out (Nayar, 1992).

Total carbohydrates from the sediment samples were leached by the hydrolysis of the sample with 1N H_2SO_4 at 100°C for 1 hour. Cooled and filtered sample aliquots were taken in clean test tubes. Added 1ml of 5% phenol and 5ml of concentrated sulphuric acid. Cooled the test tube and measured the optical density (Nayar, 1992).

Tannin and lignin from the sediment samples were leached with 0.05M NaOH for 90 minutes and filtered. 5ml aliquots of the filtrate was mixed with 1ml of citrate solution followed by the Tannin - lignin reagent and the carbonate tartarate reagent. The optical density was measured at 765 nm (Nayar, 1992)

Total phosphorus was estimated by perchloric acid digestion followed by spectrophotometric analysis (Strickland and Parson 1977) and total nitrogen was estimated using Kjeldhal method and the distilled ammonia was determined by back titration with 0.01 HCl.

Leaves of Avicennia, Rhizophora, Acanthus were dried in an oven below 60°C and analysed for carbon, nitrogen and phosphorus using the above mentioned methods A definite weight of fresh leaves were crushed and extracted with 90% acetone and analyzed for chlorophyll. After the extraction from the sediment and leaves, samples were analysed using the same methods followed for the water samples.

2.3 Results of the Hydrographical Parameters

Water is of obvious importance in an aquatic system. There are a number of processes and factors that affect the rates of materials transport, mixing and circulation in mangrove wetlands. These heavily vegetated inter tidal wetlands, when submerged are very shallow, with a maximum water depth of 2m in the swamps. The swamps are drained by small tidal creeks, called mangrove creeks. This emphasizes the link between mangrove oceanography with the coastal waters. This demonstrates that a mangrove swamp is not an oasis, which is neither land nor sea, but is an important buffer deriving its wealth from both the land and the sea. It enriches the coastal waters and provides an important forestry and fisheries resource. For the effective management of this ecosystem an understanding of the hydrography of its as well as adjacent waters is essential. Monthly variations of all hydrographic parameters are given as appendix.

2.3.1 pH

pH is a measure of the acidity or alkalinity of water. It indicates the level of dissolved carbondioxide in the water. Photosynthetic activity, nature of dissolved materials, discharge of effluents, sewage out fall, solar radiation, temperature etc., influences the pH of a medium. Variation in pH due to chemical and other industrial discharges renders a stream unsuitable for the rearing of fish and other aquatic life (Webb1982). Since 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 2.1 Seasonal variation of pH of water.

Stations	pre-mon	mon	post-mon
1H	8.15	7.9	7.5
2H	7.8	7.6	7.2
1L	7.75	8.05	7.45
2L	7.65	7.65	7.5
3	7.75	7.1	7.4
4	7.7	7.75	7.4
5	7.8	8.3	7.6
6	7.8	8.3	8.2

Distribution of pH during different seasons is given in Fig.2.2. During all the three seasons pH in the three ecosystems was in the alkaline range. Values fluctuated between 7.1- 8.3 during monsoon among all the forests. The maximum was observed in station 5 and minimum in station 3. Except in station 3, all forests exhibited lower pH than the adjacent water bodies. During pre- monsoon waters around the forest 1H was highly alkaline compared to the other two pH of all the forests remained higher than the adjacent water masses during this season. The value ranged between 7.75-8.15. The value remained almost the same in all the three forests during post-monsoon ranging from to 7.4-7.6. But pH of the water masses was higher than the forests during this season.

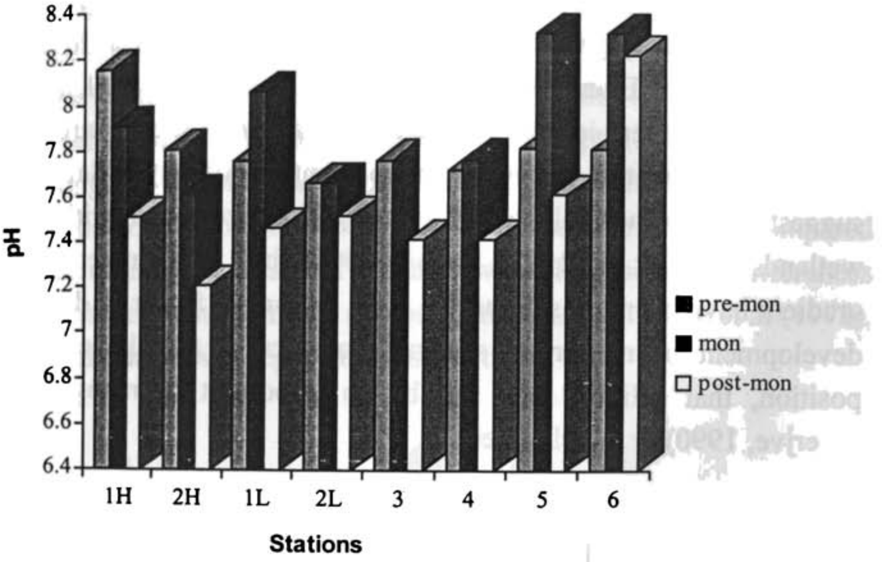

Fig 2.2 Seasonal variation of pH of Water

The three ecosystems studied showed considerable differences in their ranges of pH. The observed increase in pH is may be due to increased photosynthetic activity. In regions in which photosynthetic activity is high, undersaturation with respect to carbon dioxide will occur and the pH will rise. The high photosynthetic production during premonsoon was reported by earlier workers also (Silas and Pillai, 1975; Nair et al., 1975) Higher value of pH in station 1L during monsoon was reported by (Imelda & Chandrika, 2000).

2.3.2 Salinity

Mangroves lie at the interface between land and sea. So the salinity in these areas ranges from fresh to brackish to marine and even to hyper saline in highly evaporative areas. Mangrove species dominate these ecotones because they have evolved several in highly evaporative areas. Mangrove species dominate these ecotones because they have evolved several mechanisms that allow them to be successful under these highly variable salinity regimes. Even though they appear to do quite well in fresh water habitats where there is little competition, mangrove species are adapted to a variable (fresh water –salt water) or constant salt life style. Salinity has been suggested as a possible agent of vegetation zonation within mangrove wetlands (Bunt et al., 1982). As a result of this, in the recent past, salinity gradient have been considered the most important factor in determining the development of mangrove systems however, a few have maintained a position, that salinity may not be so important in mangrove zonation (Kjerjve, 1990) or development.

Table 2.2 Seasonal variation of Salinity (ppt)

Stations	Pre-mon	Mon	Post-mon
1H	18.5	0.33	10.5
2H	18	0.2	12.3
1L	19	1.78	11
2L	17.5	0.78	9.3
3	25	3.85	21.6
4	23	2.35	25
5	14	0.53	6.3
6	15	0.99	14

The seasonal distribution of the salinity in all stations is given in Fig 2.3. The salinity of water in and around all the three ecosystems were in the fresh water range during monsoon. The values in the forests were ranged between 0.33ppt-3.85 ppt. The maximum value was observed in station 3 and the minimum in the station 1H. The fresh water character was dominant in the forests 1H & 3 during this season. But the station 3 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. During pre- monsoon the salinity was very high, the maximum of 25ppt was noted in station 3 and the minimum of 14ppt in station 5. Compared to canals all forests showed high salinity values during this season except in station 6. Excessive evaporation and a decrease in the tidal water caused a hike in the salinity during pre monsoon season. The values fluctuated between 6.3ppt-21.6ppt.during post-monsoon among the forests. The highest was recorded in station 3 and the lowest in station 5. All forests except 1L were less saline when compared with the canals during this season. Thus there were sharp seasonal differences during the monsoon, post monsoon and premonsoon. Untawalae et al (1973), (Imelda & Chandrika, 2000) reported the same trend.

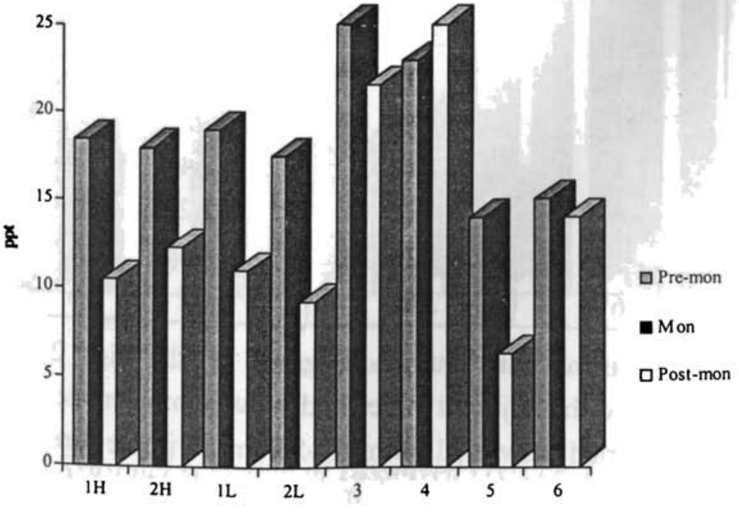

Fig 2.3 Seasonal variation of Salinity (ppt)

2.3.3 Dissolved Oxygen

All aquatic animals depend upon the dissolved oxygen in water. The detritus present in mangrove marshes has a high percentage of fine particulate organic matter, which is decomposed by micro organisms. This microbial decomposition of detritus in estuarine sediments consumes a lot of dissolved oxygen resulting in increased demand on dissolved oxygen in the water. Generally, due to tides and discharge of water, the oxygen is replenished. But any additional burden, like pollution is given in which causes further depletion in the dissolved oxygen, becomes a direct threat to animals dependent on dissolved oxygen. As a result, the variation in the dissolved oxygen of aquatic ecosystems is very determining factor in the study of its productivity.

Table 2.3 Seasonal variation of Dissolved Oxygen (ml l^{-1})

Stations	Pre-mon	Mon	Post mon
1H	1.25	2.96	3.14
2H	3.27	5.1	3.97
1L	0	3.91	0
2L	1.66	2.06	0.92
3	1.43	1.64	1.75
4	1.2	2.62	1.01
5	3.25	5.96	3.27
6	3.66	5.02	4

The seasonal distribution is given in the fig. 2.4. All the three ecosystems and the adjacent water bodies were oxygen rich during monsoon. The values varied between 1.64 ml l^{-1}-5.96ml l^{-1} in the forests. The maximum was noted in station 5 and the minimum in the station 3. Among the stations 3 & 4 the canal 4 was oxygen rich compared to the forest 3 with values 2.62 ml l^{-1} & 1.46 ml l^{-1} respectively during monsoon. But among the stations 5 & 6, the forest 5, showed comparatively higher value for oxygen 5.96ml/l than the adjacent water body 5, 5.02ml/l. All systems were oxygen deficient during pre-monsoon. Oxygen was not detected in station 1L during premonsoon and post monsoon. The concentration of oxygen was higher in all nearby waters except in station 3 during both seasons. The hydrology of wetlands, including frequency and duration of tides as well as the amount of organic matter determines the oxygen availability in wet lands. This trend is in full agreement (George & Tresa, 1993).

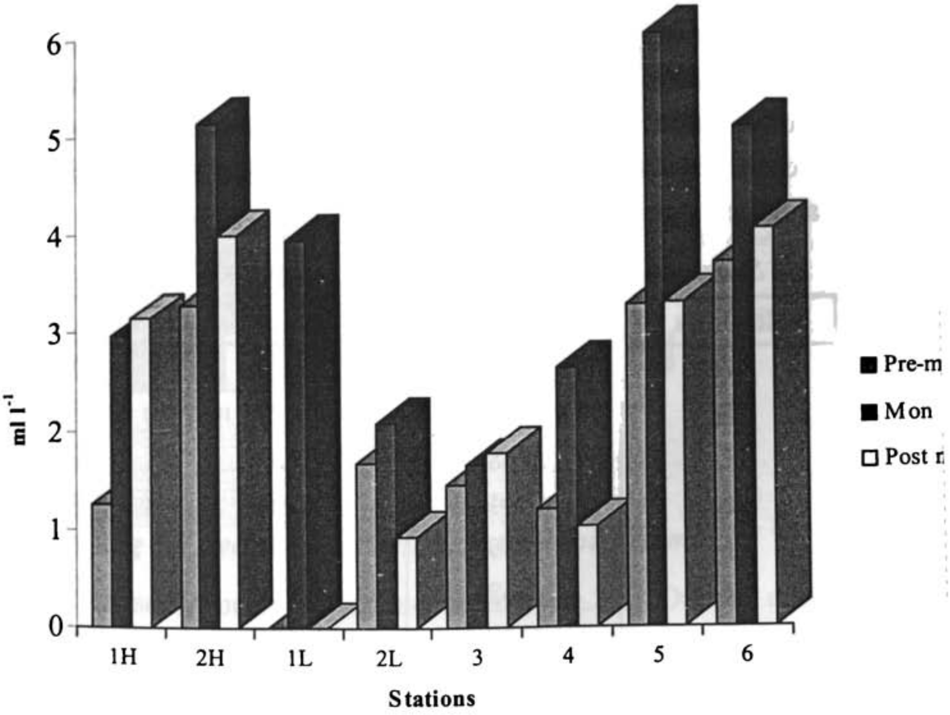

Fig 2.4 Seasonal variation of Dissolved Oxygen (ml l^{-1})

2.3.4 Alkalinity

Due to the burning of fossil fuel and the human impact on land biota the atmospheric concentration of CO_2 is steadily increasing (Keeling et al

1995) As the major greenhouse gas except water vapour, CO_2 interacts strongly with the radioactive balance of the earth and its increasing concentration potentially influences the global climate. However, only about 45% of the total anthropogenic emissions of CO_2 remains air borne (Houghton et al 1990). The hydrosphere has long since been recognised a an important sink for a significant portion of the missing anthropogenic CO_2. Marine phytoplankton have documented role in modulating the oceanic carbon dioxide system and the sea -air exchange of CO_2, fo example in eutrophic temperature (Takashi et al 1993). Fixation of dissolve CO_2 by most photosynthesizing marine phytoplankton, typically leads to concurrent decrease in total CO_2 and inorganic nutrients and subsequen export of organic carbon (Longhrust,1991). The uptake of CO_2 acts t decrease surface ocean pCO_2, thereby increasing the partial pressures of CO in air and seawater, the driving force of CO_2 gas exchange.

Table 2.4 Seasonal variation of Alkalinity (mmoles l^{-1})

Stations	Pre-mon	Mon	Post-mon
1H	1.82	5.66	0.77
2H	0.87	3.17	0.89
1L	0.48	5.23	1.04
2L	1.11	7.06	1.42
3	1.39	7.14	1.40
4	1.62	5.95	1.25
5	1.58	6.48	0.42
6	2.07	5.33	0.69

Mangrove wetlands, in general are considered to be highly producti systems. Alkalinity of the water is the result of the predominance of basi effectiveness over acid effectiveness. Various factors contribute to th alkalinity of a medium. Dissolution of CaCO3, abundance of organic matte temperature, partial pressure of CO2 are a few influencing the alkalinity of medium. Mangrove forests have various mechanisms that contribute to th high production and recycling of organic matter. Leaves are a source of various chemical elements. The study of complex mechanisms involved in the biogeochemical cycles in these ecosystem require a constant monitoring of alkalinity of the medium.

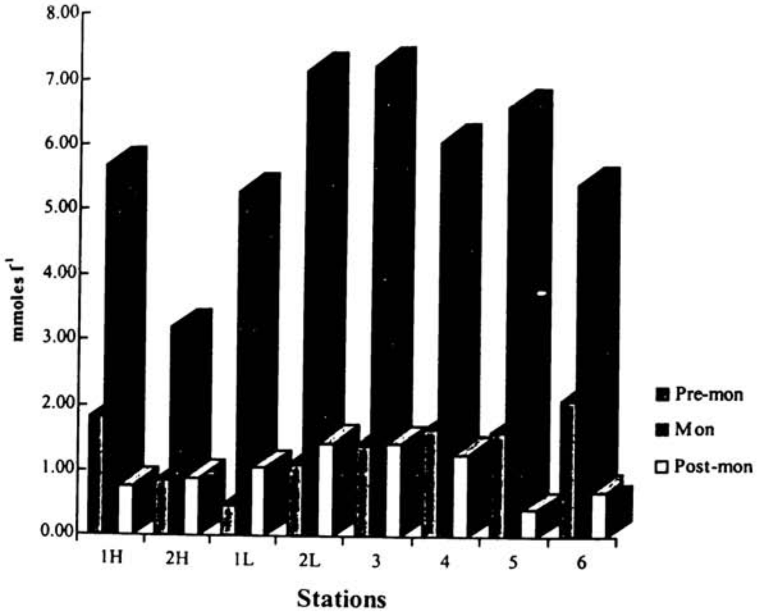

Fig 2.5 Seasonal variation of Alkalinity (mmoles l^{-1})

The seasonal profile is given in the Fig.2.5. During monsoon the alkalinity of water exhibited higher values. The values fluctuated between 7.14 mmoles l^{-1} – 5.23 mmoles l^{-1} among the forests. Maximum was observed in station 3 and minimum in station 1H. During this season all forests except 1L exhibited lower values than the adjacent water bodies. The amount of alkalinity was comparatively lower in the forests than in the canals except 1H during pre-monsoon. The alkalinity increased from 0.48 mmoles l^{-1} at 1H to 1.82 mmoles l^{-1} at 1L in this season. During post monsoon, the same trend was observed except in 4. The values varied between 0.42 mmoles l^{-1} - 1.40 mmoles l^{-1} among the forests.

Bates et al (1996) reported lower values of alkalinity in the open ocean during summer and higher values during winter & spring. Summer mixed layer alkalinity concentrations were typically lower than the winter due primarily to fresher mixed layers and reduced evaporative fluxes during summer months.

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Chapter 3

SEASONAL & TIDAL VARIATION OF ORGANIC COMPOUNDS & NUTRIENTS

Coastal waters throughout the world are being affected by anthropogenic inputs of nutrient elements, of organic matter that undergoes bacterial degradation consuming dissolved oxygen and releasing nutrients, and of potentially toxic trace metals. These inputs are related directly to increases in human population density, agriculture and industrial development in coastal regions. Considering the global carbon cycle and the major role played by the ocean, it seems that the coastal zone must be considered as a specially important area (Wollast 1991). Though representing only a small surface of marine realm (about 8%), it is the most productive area of the ocean (more than 25% of total marine production, Nienhuis, 1981). The cycling and ultimate sequesteration of organic matter in estuaries and coastal zone is controlled by different processes, among which microbiological ones play a key role with regard to production, degradation and mineralization of organic matter (Hoch & Kirchman, 1993). The importance of dissolved and particulate organic detrital matter to the metabolism of aquatic ecosystems has not been fully explored (Boon et al 1982). Dissolved organic matter comprises most of the reduced carbon in aquatic ecosystems and provides energy and carbon sources for the metabolism of heterotrophic bacteria. It is known that humic substances dominate the dissolved organic matter of the stream water and it has been suggested that humic substances play an important role in ecosystem metabolism. Saline marsh contained 2.2 and 4.2 times more organic matter and mineral matter than inactive fresh marsh (Nyman et al, 1990). The high productivity of the coastal zone is mainly related to the influence of the river inputs, enriching the coastal waters in nutrients and organic matter, and to the close coupling between the water and sediment assuring a rapid reutilization of regenerated elements. The type of flora, in the water shed, the distribution and abundance of wetland and littoral plants, and the pathways of release of detrital organic material into the water body have different effects on overall rates of eutrophication and development of aquatic ecosystems (Weizel 1983). Of the four gross compartments into which marine matter may be categorized (inorganic/organic, particulate/ dissolved), the dissolved organic fraction remains the least well understood. Early studies argued the case for major flows of carbon, nitrogen and phosphate through the dissolved organic pool. Four main groups of organic compounds formed by the decomposition of organic matter are;

(a) Nitrogen -free organic matter, (b) Nitrogenous substances, (c) Fat-like substances, (d) complex substances resulting from the groups (a) & (c)

3.1 Particulate Organic Carbon

The particulate matter carried by the river can be divided into four parts; detrital inorganic matter, non- algal organic matter, phyto planktonic organic material and autochtonous calcite particles. Organic carbon generally falls under two categories. It is either in a particulate (> 0.45 μM) or in a dissolved state (< 0.45 μM). The size of the organic carbon depends on a number of factors and the quantities of each usually depend on the stage of decomposition. The particulate and dissolved organic carbon together constitute a minor fraction of total organic carbon of sea water, yet they are very important components in the transformation of carbon. Since the majority of mangrove production goes into the formation of new leaves and since mangroves lose their leaves on a regular or event-driven (high winds, etc.) basis, leaf litter is considered to be one of the biggest losses in mangroves. Once these leaves fall, they begin to be degraded by a number of bacterial, fungal, and meiofaunal organisms. Particulate organic carbon occurs in degradable and refractory forms, the latter is mainly constituted by carbon present in humic material. Further POC can be of living or non living (detrital) nature where the latter fraction may contain the refractory substances that result either from recycled marine matter or from terrestrial sources.

Table 3.1 Seasonal variation of Particulate Organic Carbon (mg l^{-1})

Stations	Pre-Mon	Mon	Post-mon
1H	23.09	24.15	9.23
2H	3.34	1.47	3.98
1L	27.89	37.20	19.35
2L	2.78	5.52	3.68
3	5.75	10.35	3.47
4	4.35	5.54	3.38
5	7.10	1.96	3.50
6	0.00	4.49	2.50

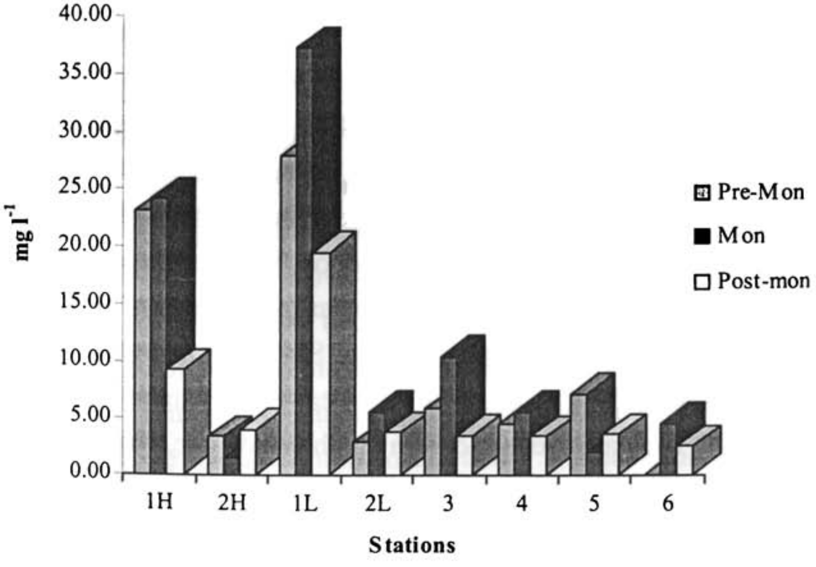

Fig 3.1 Seasonal variation of particulate organic carbon(mgl^{-1})

Monthly data are given in the appendix and seasonal variation is depicted in the Fig 3.1. POC values of the forests varied from 5.75 mg l^{-1} to 27.89mg l^{-1} between the forests 5 and 1L.during pre- monsoon. The concentration of POC was higher in all forests than in the canals during this season. But during monsoon the concentration of the forests fluctuated between 1.96mg l^{-1} - 37.

mg l $^{-1}$ among the forests 3 and 1L. POC was less in the forest 3 than in the canal 4. When stations 5 & 6 were compared, the forest 5 showed a high value than the canal 6. Among the forests the maximum amount of POC was observed in the forest 1L during post-monsoon. In this season, all forests 1H, 1L, 3 & 5 exhibited high values for POC than the canals. The values in the forest were 9.23, 19.35, 3.5 & 3.47 mg l $^{-1}$ respectively.

Table 3. 1a Earlier reported values of POC (mg l^{-1})

No	System	Range	Reference
1.	Bay of Bengal	0.84×10^{-3} - 5.19×10^{-3}	Sarojini et al, 2001
2.	Ross Sea	0.48	Gardner et al, 2000
3.	Arabian Sea	0.025- 0.1	Sardessai et al, 1999
4.	Amazon Basin	1 – 3	Jeffrey et al, 1990

Analysis of data of POC shows that the observed concentration is very high when compared to the reported values (Table 3.1a). POC transport is to a large extent depend on the physical processes governing sediment dynamics. The erosion and deposition cycles can mobilize POC can be deduced from the concurrent patterns of the flux anomalies for POC and bulk suspended sediments (Meade et al, 1985). During the temporary residence of sediment deposited on the flood plain, carbon new to the river could be added through local primary production with the enriched particles cycled back into the river through flooding and erosion The POC is potentially labile, non woody vascular plant debris. High salinity, the shallow and turbid nature of water around the ecosystems led to the accumulation of particulate organic carbon during pre-monsoon. Less dense plant debris settles more slowly than sand, therefore concentrates in suspension when the river velocity decreases. But in monsoon, the increased terrestrial runoff as well as plant remains in the plain contribute to the hike in POC. A summer increase of POC in coastal areas was reported by Williams (1995). Higher primary productivity due to increased convection sustains higher POC in coastal areas during monsoon. Sardessai et al (1999) reported that the relatively higher POC values observed in Arabian Sea during pre-monsoon could have been due to abundant bacterial population.

3.2 Chlorophyll

Viewed from orbiting satellites earth is a green and blue planet. Almost all of the pigmentation outside polar and desert areas is due to plants. Regional events such as droughts, the onset of the rainy season or autumn bring about marked changes in the coloration of vegetation. At this global level much of the greater contribution comes from one group of pigments- the chlorophyll. It has been estimated that each year, the total chlorophyll production globally exceeds 10^9 tonnes 75% from terrestrial plants and the remainder from aquatic organisms, largely marine phytoplankton. In order to grow the plants must be able to convert energy from the sun into a useful form. Humans produce pigments in their skin that protect them from harmful effects of solar radiation; in contrast, exposure of plants to light stimulates them to produce pigments that absorb and utilize energy. In higher plants, the final product of photosynthesis are sucrose, and starch or fructose but in algae wide variety of sugar alcohols and glucose polymers have been found as products of photosynthesis.

There are three classes of photosynthetic pigments in photosynthetic organisms; the chlorophylls, the phycobilins and the carotenoids. The chlorophyll molecule consists of a porphyrin ring with a dense cloud of Πelectrons. They are actually cyclic tetrapyrroles. In the cyclic form, these tetrapyrroles are usually porphyrins. The chlorophylls have a characterstic pattern. The absorption of a photon of light promotes the molecule to an excited state. The long chain lipophilic terpenoid side group unique to chlorophyll a and b may provide hydrophobic bonding components for association within the thylalkaloid membrane or with proteins.

Table 3.2 Seasonal variation of Chlorophyll ($\mu g\ l^{-1}$)

Stations	Pre-Mon	Mon	Post-mon
1H	9.15	74.51	8.51
2H	5.63	96.61	9.28
1L	11.6	82.81	6.75
2L	4.17	44.7	6.71
3	5.35	61.88	4.5
4	4.48	72.86	8.05
5	3.14	38.63	4.44
6	4.41	57.06	6.62

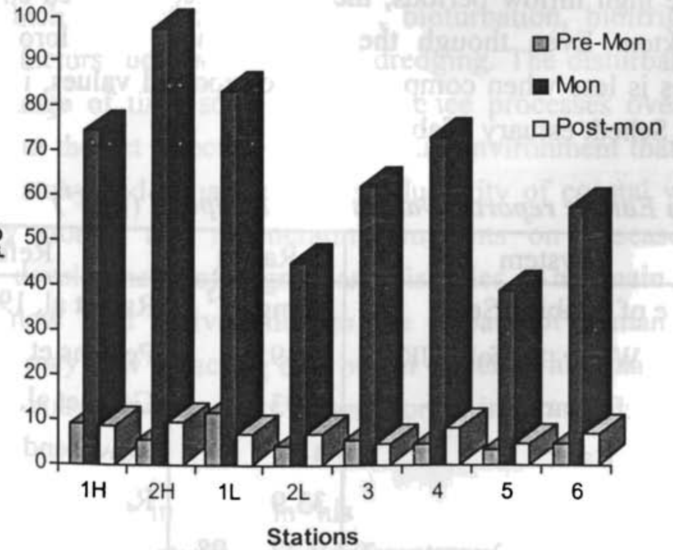

Fig 3.2 Seasonal variation of Chlorophyll ($\mu g\ l^{-1}$)

Monthly variations of chlorophyll a in the three mangrove systems and their connecting canal are given in the appendix. Seasonal variations are given in Fig 3.2. The concentration of chlorophyll of the forests varied from a maximum of 11.6 $\mu g\ l^{-1}$ in station 1L to a minimum of 3.14 $\mu g\ l^{-1}$ in station 5 during pre-monsoon. All forests were rich in chlorophyll than the canals except 3. But in monsoon, canals exhibited higher values for chlorophyll than the forests except 1L. Chlorophyll was high in the canals 4 & 6 compared to the forests 3 & 4. In post -monsoon, the amount varied from 4.44 μgl^{-1} to 8.51 μgl^{-1} between the forests 5 & 1H. During this season also, canals were chlorophyll rich than the forests except 1L.

According to Bianchi et al (1997) high POC: chlorophyll a ratios (<1463) during pre monsoon indicated that most of the chlorophyll was degraded. These high ratios could not be from autochthonous water column production (phytoplankton). The predominantly low chlorophyll a concentrations observed were primarily by inputs of degraded vascular plant detritus with minor contribution from periphyton and phytoplankton.. During the high inflow periods, the high values observed could be due to phytoplankton. Even though the concentration of chlorophyll in these ecosystems is less when compared to the reported values, it is well within that in the Schedt estuary (Table 3.2a).

Table 3.2a Earlier reported values of Chlorophyll ($\mu g\ l^{1}$)

No	System	Range	Reference
1.	Algae of Arabian Sea.	42mg m^{-2}	Rao et al, 1999
2.	Alton. Water. Saffolk UK.	34-95	Perkins et al, 2000
3.	Scheldt Estuary	1-93	Gons et al, 2000
4.	Georges Bank	4-5	Townsend et al 2000
5.	Cochin Harbour Area	33.95	Rasheed et al 2000
6.	Coastal areas of Orissa	0.27- 5.98	Panigrahy et al 1999.
7.	Eastern Arabian sea	32.53	Pillai et al 2000
8.	Bay of Bengal	8-24	Subramaniam et al 1999

3.3 Nutrients

Most of the nitrogen in earth is present as molecular dinitrogen in the atmosphere. The oceanic nitrogen reservoir is also dominated by N_2 followed by nitrate which comprises about 6% of sea water nitrogen. The world ocean appears to be experiencing a net loss of Nitrogen. The magnitude of the input to the sea from rivers, biological fixation and precipitation accounts for about 70 % of the losses by denitrification plus burial. The nitrogen cycle involves electron shifts between the most oxidised form NO_3^- and the most reduced NH_4^+. Uptake by Nutrients are affected by a variety of processes in inter tidal sediments (Klump& Martens 1989). There are many bio physical disturbances that impact on inter tidal sediments. These are tides, waves, storms, runoff events and sediment movements which result from the above, bioturbation, bioirrigation and anthropogenic factors such as fishing and dredging. The disturbances occur over a wide range of time scales and influence processes over different space scales. But the net effect is to produce an environment that, although structured, is patchy and dynamic. The productivity of coastal waters was maintained by storing and regenerating nutrients on a seasonal basis allowing the development of significant fisheries. The main inputs of nutrients are now land derived due to the impact of human activities. Intertidal areas may now be acting as a buffer which, while maintaining the productivity of coastal waters, acts to ameliorate inputs of nutrients to the coastal waters.

The main nutrients involved in this study were NO_2^-, NO_3^- and PO_4^{3-}. Their distributions and variations during different seasons is discussed below.

3.3.1 Nitrate

This is the most oxidised form of N_2. In order for mangrove forests to be both net exporters of particulate nitrogen to coastal ecosystems and nitrogen sinks within the estuaries, there must be significant transformations within mangroves (Twilley et al., 1986). Over the past decade, studies of tidally borne fluxes of particulate and dissolved materials to and from a tropical mangrove system in northern Australia have indicated that nitrogen is largely recycled within the system (Boto & Wellington, 1988). Nitrogen was present in low concentrations in particulate materials (mainly intact mangrove plant detritus) which were exported from the system through tidal action. Hence, despite the considerable total quantities of particulate matter, losses of nitrogen were relatively small, in the order of 3.7 g $Nm^{-2}y^{-1}$, which is equivalent to 13% of average annual forest net primary production nitrogen requirements (Boto & Bunt, 1982). Concentrations of dissolved organic and inorganic forms of nitrogen in the mangrove and near-shore waters were also consistently low in this tidally dominated system,which receives virtually no fresh water or terrestrial influence. Information on rates of nitrogen fixation in mangrove forests is limited, especially estimates of the importance of this process on a whole- forest scale.

Table 3.3 Seasonal variation of Nitrate (µg-at l^{1})

Stations	Pre-mon	Mon	Post-mon
1H	34.72	36.28	32.74
2H	11.5	29.31	51.91
1L	8.66	26.23	38.2
2L	19.91	21.41	38.2
3	3.44	11.86	8.38
4	5.03	14.34	13.17
5	14.46	38.68	10.77
6	14.09	23.76	4.88

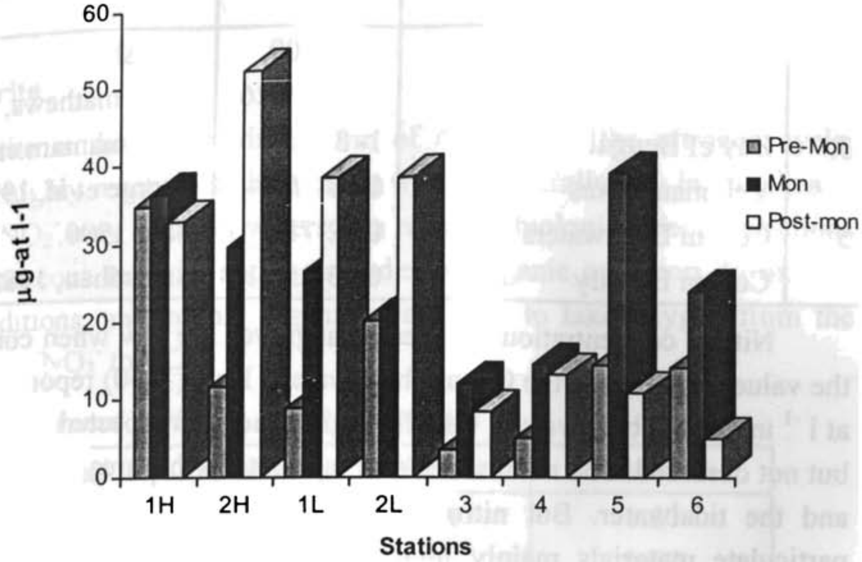

Fig 3.3 Seasonal variation of Nitrate (µg-at l^{-1})

Distribution of nitrate during different months are given in the appendix and the seasonal variations are depicted in Fig 3.3. Analysis of the seasonal distribution of the dissolved nitrate concentrations showed a hike in the monsoon season in all stations. Since this is the high inflow period, the source can be land run off. But the concentration was high in the forests than in the canals except in station 4. The values varied from 11.86 ug-at/l to 38.68ug-at/l among the forests. High concentration of nitrate was noted in stations 2H, 1L & 2L during postmonsoon and the values were 51.91, 38.2 & 38.2ug-at/l respectively. Comparatively lower values were observed during pre-monsoon. During this season also higher values were noted in forests except in station 4. Maximum was noted in station 1H during high tide and the minimum in Station 3. The value ranged between 34.72ug-at l^{-1} - 3.44 ug-at l^{-1}

Table 3.3a Earlier reported values of Nitrate-N (µg- at l^{1})

No.	System	Range	Reference
1.	Kusheswarasthan Wetland	160 -500	Manish et al, 2001.
2.	Kuttanad Wetlands	1.69- 19.26	Lizen mathews, 2000
3.	Bay of Bengal	1- 30	Subramaniam et al, 1999
4.	Veli mangroves	0.88-25.34	George et al, 1997
5.	Cochin Backwaters	0.82-71.6	Nair, 1990.
6.	Cochin Estuary	0.63-25.41	Anirudhan, 1988

Nitrate concentrations in these mangroves are low when compared to the values reported in the Cochin backwaters. Nair (1990) reported 1-70 ug-at l^{-1} in Cochin backwaters. Usually high values are expected in mangroves, but not observed. The main sources of nutrients in this area are the leaf litter and the tidalwater. But nitrogen was present in low concentrations in particulate materials mainly intact mangrove plant detritus which were exported from the system through tidal action. Concentrations of dissolved organic and inorganic forms of nitrogen in the mangrove and near -shore waters were also consistently low in a tidally dominated mangrove ecosystem in the Hichinbrook island, Australia which receives virtually no fresh water or terrestrial influence (Boto & Willington !988). Although the previous studies of this forest have strongly indicated that nitrogen supply is growth limiting, years of observation of the system have given no indication of any long term, continuous degradation of the nitrogen nutritional status. According to Simpson et al (1997) under low flow conditions the river discharge entering the estuary is exported by evapotranspiration through the mangrove system and that net flow discharge from the estuary is small. This is reflected in the premonsoon values. Flux studies in mangrove sediments of Termino Lagoon, Mexico indicated that dissolved inorganic N in tidal waters is trapped in the first centimeters of the sediment surface (Riveria-Monroy et al. 1995a). High inorganic N demand in decomposing leaf litter may regulate an efficient recycling of nitrogen that could serve as a mechanism for nutrient conservation (Twilley et al, 1986b; Twilley 1988; Alongi et al.1992).

3.3.2 Nitrite

Nitrite is the intermediate form of nitrogen in the nitrogen cycle. Nitrite is highly reactive, so its amount will be generally low in the aquatic systems. NO_2^- may occur in waters as a result of biological decompositions of proteinaceous material and is an index of organic pollution. In oxygen poor conditions, autotrophic organisms are able to take oxygen from the reduction of NO_3^- to NO_2^-.

Table 3.4 Seasonal variation of Nitrite (µg-at l^{-1})

Stations	Pre-Mon	Mon	Post-mon
1H	1.57	15.81	1.60
2H	1.06	1.73	0.67
1L	2.81	22.1	0.96
2L	1.72	1.31	0.66
3	2.34	0.92	0.75
4	2.67	1.16	1.57
5	0.94	1.43	1.34
6	6.27	1.19	0.84

Fig 3.4 shows the seasonal variation of this species and the table comprising monthly data is given in the appendix. Seasonal variation showed a maximum peak in the monsoon in all stations. Maximum concentration of nitrite was observed in all forests during all seasons except in station 4 where high amount was observed in the canal. During low tide, the concentration was high in both forest and the canal. The value varied between 0.97 ug-at l^{-1}in station 3 and 22.1 µg-at l^{-1} in station 1L. This variation observed may be due to river runoff. Abnormal high values were observed in station 1L & 2L. Not much variations are noted during premonsoon and post monsoon. The values varied between 0.75µg-at l^{-1}-

1.60μg-at l^{-1} among the forests during postmonsoon and between 0.94ug-at l^{-1}- 2.81ug-at l^{-1}during pre-monsoon.

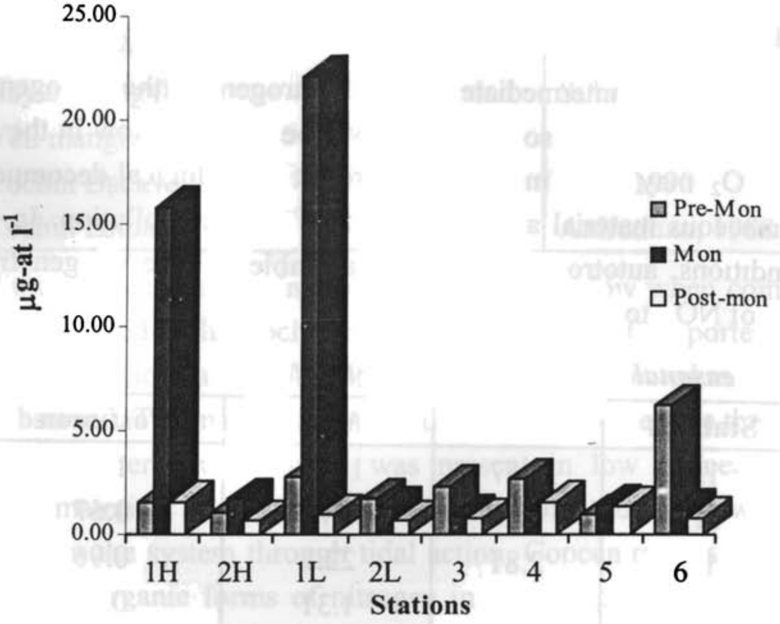

Fig 3.4 Seasonal variation of Nitrite (μg-at l^{-1})

Table 3. 4a Earlier reported values of NO_2 (μg-atl^{-1})

No	System	Range	Reference
1.	Bay of Bengal	0.01-0.5	Sarojini et al, 2001
2.	Kuttanad Wetlands	0.17-0.79	Lizen mathews, 2000
3.	Kayamkulam	0.00 - 0.07	Padma, 1996.
4.	Cochin Backwaters	0.30 -8.30	Nair et al, 1990.
5.	Cochin Estuary	0.63 - 6.68	Anirudhan, 1988.

Earlier reported values are given in the Table 3.4a. Comparatively high values were observed in stations 1l & 2L.Thomas et al (1984) hypothesized that high nitrate and nitrite values at low tide are caused by nitrification within the tidal water or tidal creek sediments. The shallow character, conditions favourable for anaerobic diagensis contributed to the increase in the concentration at 1L & 2L.

3.3.3 Phosphate

Phosphorus is an essential nutrient for the marine ecosystem. On geological time scales the bioavailability of dissolved phosphorus is thought to control biological productivity (Tyrrell 1999). Only a small fraction of particulate phosphorus produced in the euphotic zone is ultimately burried in the sediment, while the remainder is remobilized and reutilized by the marine ecosystem (Brocker and Peng 1982).

Table 3.5 Seasonal variation of Phosphate (μg-at l^{-1})

Stations	Pre-Mon	Mon	Post-mon
1H	11.83	6.18	5.44
2H	10.88	17.06	2.36
1L	12.73	18.75	27.52
2L	1.67	22.63	8.61
3	1.51	14.94	1.91
4	0.56	8.58	1.42
5	2.65	4.66	2.07
6	3.78	4.1	0.68

Fig 3.5 exhibits the seasonal variation of phosphate and the monthly variation is given in the appendix.Comparatively higher amount of phosphate is observed during monsoon in the canals than in the forests except in stations, 5 and 3 which may be due to the river run off. The values observed were greater than the earlier reported values (Table 3.5a). Untawalae et al (1973) reported 0.5-1.5 μg-at l^{-1} of phosphate in mangroves in Mandovi & Zuari estuaries. But George & Teresa (1993) noted a high concentration of 21.6μg-at l^{-1}μg-at l^{-1} in Veli mangroves which could be due to the mixing of sewage with the canal. During post -monsoon among the forests, maximum concentration was noted in the station1L during low tide, 27.52 μg-at l^{-1}. In premonsoon the values varied between 1.51μg-at l^{-1} 11.83 between the

forests 1H& 3. Higher amounts were observed in the forests than in the canal during these two seasons. The higher PO_4^{3-} concentration in premonsoon and post monsoon in 1L during low tide may be due to the decomposition of organic phosphate due to the partial drying of the swamp and consequent exposure of the land.

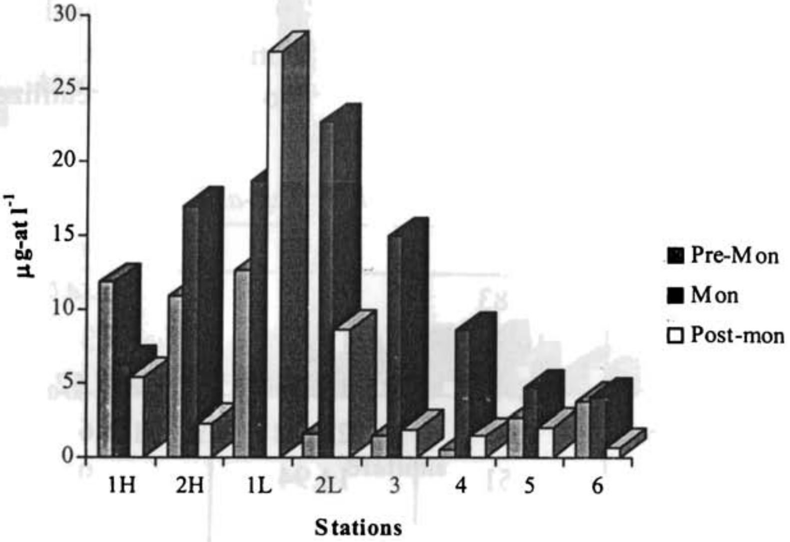

Fig 3.5 Seasonal variation of Phosphate (µg-at l⁻¹)

Table 3.5 a. Earlier reported values of PO_4- P (µg- at l^{-1})

No	System	Range	Reference
1.	Kusheswarasthan Wetland	0.16 -0.5	Manish et al, 2001.
2.	Kuttanad Wetland	2.4 - 7.15	Lizen mathews 2000.
3.	Bay of Bengal	0.02- 1.1	Subramaniam et al 1999
4.	Kumarakom Mangroves	0- 0.40	George Thomas et al.
5.	Cochin Backwaters	0.40 -9.30	Nair, 1990.
6.	Cochin Estuary	0.27- 11.61	Anirudhan, 1988

3.4 Protein

Most aminoacids in living organisms are present as constituents of proteins (Billen, 1984) and proteins account for more than about 50% of the organic matter (Romankevich, 1984) and 85% of the organic nitrogen (Billen, 1984) of marine organisms. Amino acids in cellular constituents of organisms that have been transferred to the pool of DOM might be expected in the form of protein. In nature, the breakdown of proteins is easily brought about by bacterial and fungal action. Dissolved combined amoniacids represent the largest well defined molecular forms of dissolved organic matter (Keil and Kirchman, 1991). Proteins can be broken down by microorganisms through one or more processes. They carry not only carbon, hydrogen and oxygen but also nitrogen and in lesser amounts, such elements as sulfur, iron and phosphorus. They are compounds of high molecular weights and many are of uncertain constitution. As found in fresh plant tissue, they are present in the colloidal state, which further complicates their study. Only a very small number of reports are available on the amount and distribution of dissolved proteins. They are easily hydrolyzable compounds and so they are easily utilised. The plant proteins which constitute nearly 15% of its biomass and related compounds upon decomposition yield other very important products in addition to the carbon dioxide and water. They break down into amides and amino acids of various kinds, the rate of breakdown depending on conditions. Once these compounds are formed, they may be hydrolyzed readily to carbon dioxide, ammonium compounds and other products. The ammonium compounds may be changed to nitrates, the form in which higher plants take up much of their nitrogen.

The seasonal profile in Fig 3. 6 shows high concentrations in all stations during monsoon. Except in the canal 2H, all forests showed higher values than their connecting canals. The same trend was observed during post- monsoon. In the pre-monsoon higher amount of protein was detected in canals except in station 6. Monsoonal hike in the forests indicated that the soluble proteins were leached from the decaying leaf litter. The decomposition of phytoplankton and the vegetation which contains high amount of proteinaceous materials contribute to the protein concentration. A decrease in the concentration during pre- monsoon may be due to the preferential utilisation of protein by the benthic organisms and biological activity or to the N- compounds are incorporated into humic matter through various humification pathways (Bhosle et al, 1988).

Table 3.6 Seasonal variation of Protein (mg l^{-1})

Stations	Pre-mon	Mon	Post-mon
1H	3.89	11.13	5.11
2H	6.74	12.25	6.21
1L	2.36	11.13	3.72
2L	2.96	9.07	3.41
3	7.89	12.88	10.35
4	5.78	10.89	9.23
5	0.99	12.75	3.06
6	1.25	12.04	2.81

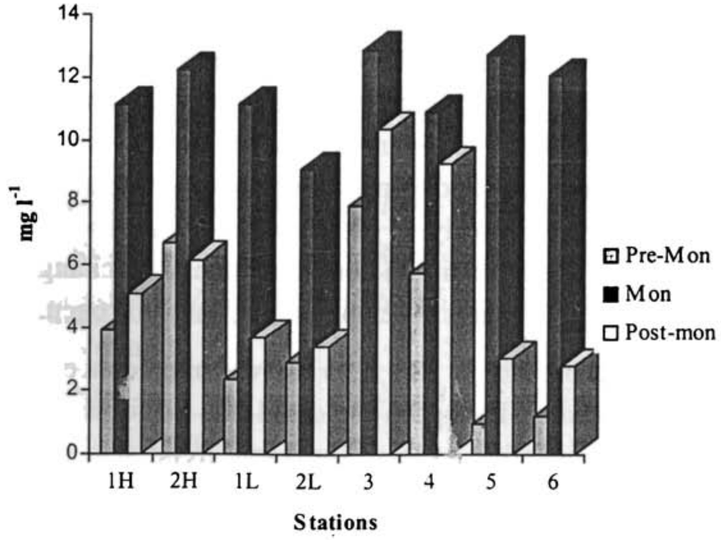

Fig 3.6 Seasonal variation of Protein (mg l^{-1})

3.5 Carbohydrate

The carbohydrates, which are made up of carbon, hydrogen and oxygen range in complexity from simple sugars to the celluloses. Nearly 60% of the plant biomass is constituted of carbohydrates of which cellulose is the main fraction. (20-50%). These are the easily decomposed part of dead and decaying plants. Thus they form the most abundant class of compounds in the biosphere. They exist as several classes; monosaccharides, oligosaccharides, polysaccharides and saccharides bound to humic substances. They are linked together to form polymers. These polymers decompose and enter into the aquatic system. Thus an important source of the carbohydrates in water is the leachates of plant matter. Although carbohydrates are the important constituents of DOM (usually 10- 20%), relatively little is known about them in estuarine and coastal ecosystems. Leaf material from vascular plants is an important source of organic carbon in a variety of coastal and estuarine ecosystems (Valeila et al 1984) and a potentially important source of dissolved and particulate carbohydrates.

Table 3.7 Seasonal variation of Carbohydrates (mg l^{1})

Stations	Pre-mon	Mon	Post-mon
1H	2.77	56.79	4.17
2H	3.01	30.15	4.23
1L	37.62	39.99	8.47
2L	4.16	25.74	12.27
3	4.07	21.66	16.44
4	3.97	16.08	19.39
5	5.04	24.45	11.02
6	2.41	11.58	10.79

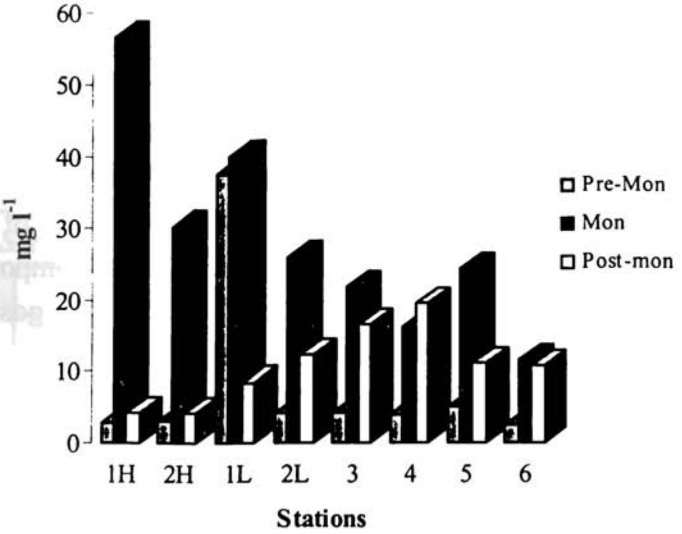

Fig 3.7 Seasonal variation of Carbohydrates (mg l^{-1})

Fig 3.7 shows seasonal changes in the distribution of dissolved carbohydrates and its monthly variation is included in the appendix. High concentrations were observed in all stations during monsoon. But comparatively higher values were noted in the forests than in the canals. The maximum concentration was noted in the forest of station 1 during high tide. The value varied between 21.66mg l $^{-1}$ - 56.79mg l $^{-1}$ among the forests 3 &1H. The concentration of carbohydrates decreased during pre-monsoon and post monsoon. But during post monsoon, the amount of carbohydrate was high in the canals than in the forests except in the station 5. In the forests, the concentration varied between 4.17mg l^{-1} - 16.44mg l^{-1}. Maximum was observed in the forest 1L during low tide and minimum in 1H. Higher concentration was observed in the forests than in the canals in this season also except in 1H.

Table 3.7a ***Earlier reported values of Carbohydrates ($\mu g\ l^{-1}$)***

No	System	Range	Reference
1.	Elron estuary	90- 1080	William et al, 1991.
2.	Narragansett Bay	122-156	Jhonson et al, 1977.
3.	Coastal waters of Goa	0.5-29	S.B.Kamat, 1976.

The concentration of carbohydrates in this area is not comparable with reported values given in the Table 3.7a. The observed peaks in the monsoon in the forests may be mainly due to the leaching of dead and decayed leaf litter. Partly of it might have been contributed by land drainage. It is also possible that in water some of it must have been contributed by bacterial action on particulate carbohydrate of planktonic origin (S. B. Kamat, 1976). Lowest values were observed in the premonsoon except in the station 1L. The concentration of dissolved components which is discharged from the decay process of sediments to the water column is high during low tide. Due to the reduced tidal flow, the leaf litter remain accumulated in the forest itself which will lead to an increase in the concentration of soluble leachates. According to Benner et al.(1986b) a significant fraction of the polysaccharide loss from a variety of vascular plant tissues occurs due to solubilization rather than the microbial mineralization. Compositionally, glucose was the most abundant sugar. In the hydrolyzate mixtures from the attached and submerged leaves (Benner et al, 1990).

3.6 Tannin and Lignin

Nonwoody vascular plant tissues are important sources of organic matter to terrestrial and coastal marine environments and often are rich in tannins and polymethylene type polymers that are likely precursors of geopolymers such as humic substances and kerogens. Lignin and the polysaccharides, cellulose and hemicellulose, typically comprise the bulk of woody plant tissues (Sjostrom, 1981). Polysaccharides are typically found to be more reactive than lignins, resulting in the gradual enrichment of the remaining detritus in lignin derived carbon (Spiker & Hatcher, 1987).

Mangrove swamps are examples of estuarine ecosystems that receive large quantities of senscent leaf material that are important source of carbon and other nutrients to food webs and to pools ~~and to pools~~ of dissolved and particulate organic matter (Odum & Heald, 1972; Twilley, 1985). The decomposition of mangrove leaf material occurs primarily through microbial action and leaching of water soluble compounds (Cundell et al., 1979; Benner et al., 1986c). During the initial stages of decomposition large quantities of dissolved organic matter leach from decaying leaves resulting in a rapid mass loss (Benner et al., 1988) Waters in the vicinity of decaying leaves are often tea- colored due to the relatively high concentrations of DOM that contain tannins and other phenolic compounds. Vanillyl and syringyl phenols were the dominant components of mangrove lignin. Lignin was a minor component of all leaf tissues. As with the leaf material, the high aro~~p~~matic and low lignin contents (Benner et al., 1990) indicate that tannins are the major constituents of the leachate·Polysaccharides and lignin, which typically account for >90% of the biomass of most woods, accounted for only 30% of the biomass of mangrove leaves (Benner et al., 1990). During early diagenesis of leaves, leaching produces relatively large quantities of dissolved organic matter, and the lignin component, in particular, may provide a convenient tracer for studying the distribution and fate of mangrove derived DOM in coastal and estuarine waters.

Table 3.8 Seasonal variation of Tannin and Lignin (mg l^{-1})

Stations	Pre-mon	Mon	Post mon
1H	0.55	0.31	0.10
2H	0.90	0.03	0.10
1L	0.53	0.34	0.92
2L	1.01	0.27	0.56
3	0.11	0.02	0.18
4	0.02	0.03	0.16
5	0.11	0.03	0.07
6	0.02	0.01	0.16

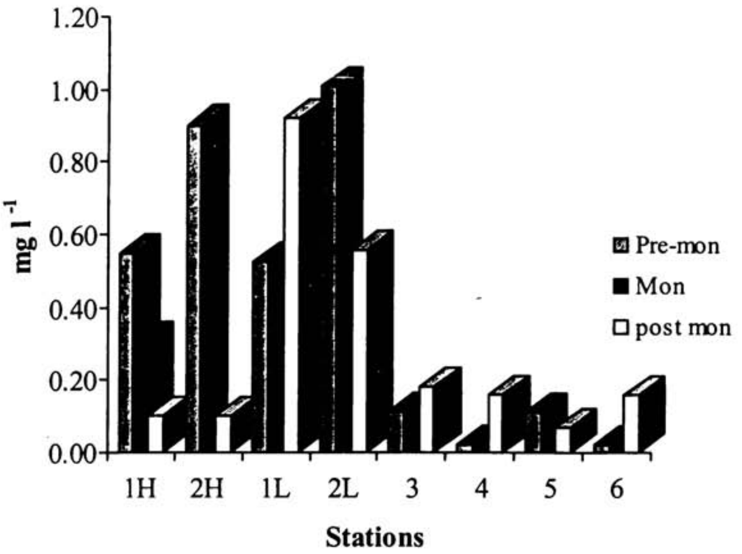

Fig 3.8 Seasonal variation of Tannin & Lignin (mg l^{-1})

The monthly distribution of tannin and lignin in the three mangroves are given as appendix. Seasonal variation is exhibited in Fig 3.8. Among the forests high concentrations were noted in stations 3 & 5 during pre monsoon. Comparatively lower values were noted in all stations during monsoon. Maximum amount of tannin and lignin was observed in all forests except in canal 4. During post monsoon season higher amount was noted in canals except in forests 1L and 3. Majority of the species of mangrove leaves contained greater amount of tannin and lignin during pre monsoon (Katherisan et al., 1990). Since these leaves are the main source its concentration was maximum in the system during this season. This is again evidenced by the high low tide value of the canal. This is again evidenced by the high low tide value of the canal. Even though there is considerable amount of tannin & lignin in the mangrove leaves, the concentration is very low in water. This may be due to the low solubility of the species in water and the net release to the water will be negligible. Higher concentration of this in the deep sediments supports this. Values are comparable with that reported in Cochin mangroves (Table 3.8a).

Table 3.8 a. Earlier reported values of Tannin and Lignin (mg l^{-1})

No	System	Range	Reference
1.	Mangroves in Kochi	0.187 - 1.1676	Nisha 2002
2.	Mangrove leaves	3.28-20.02 mg g^{-1}	Kathiresan et al,1990.
3.	West coast of Arabian Sea	0.08 - 0.147	Kalesh et al 2001

3.7 Tidal Variations

Intertidal sediments are subject to diurnal drying and flooding which leads to major changes in the local transport of material to and from the sediments. Clearly when the tide has ebbed there is no overlying water present and there can be no dissolved output from the sediment. This may result in increasing concentrations of dissolved substances that have a source within the sediments, such as ammonium.. This pool of high concentration may then be released when the water returns to flood the sediment. In contrast, a substance whose source is the water and is consumed in the sediment may become depleted when the water is not present. Thus the sediments are both the sinks and sources of different nutrients and organic compounds and that the behavior changes with the tide.

During the tidal cycle the hydraulic regime in the sediments changes and advective flow along pressure gradients may occur. Muddy intertidal sediments have a high porosity but have a low permeability limiting transport. Sandy sediments have a permeability great enough to allow drainage of the sediments at low water and subsequent saturation as the tide advances the impact of advection and resultant changes, such as increased penetration of oxygen into the sediments, has yet to be fully addressed but will have a major impact on redox sensitive processes such as coupled nitrification and denitrification (Rysgaard et al., 1994).

Superimposed on the diurnal cycles, the tides exhibit a spring /neap cycle of changing tidal range which has two effects. Firstly, the area of the sediment exposed and the length of exposure changes as the tide range alters and secondly, the velocity of the ebb and flood current changes. The sediment source /sink term is area related and the current velocity will have an impact on the disturbance and transport of sediment and on flushing characteristics (Vorosmarty& Lorder, 1994). Therefore, the export and the import of material from intertidal areas like mangroves is influenced by spring / neap cycles.

Variations of various parameters with the tidal cycle are given in the Fig 3.9, 3.10 and 3.11. Diurnal changes in the oxygen concentrations and other parameters were followed at the forest and canal of station 1. To obtain a complete tidal cycle, sampling was begun in the morning and was continued at 3 hour intervals during the night until the next morning. Oxygen value fluctuated with the tides in both forest and canal. Oxygen was not detected in the forest in the early stages and gradually became oxygen rich as the water brought in by the tide increased. But in the canal, even though water is always oxygen rich the values fluctuated with tides. Seasonal variations of salinity of this system was very large, changing from high saline to low saline according to rain fall and evaporation. However, only very small variation according to the tide was noted, due to the negligible concentration of the fresh water when compared with the total volume in cooperated in each tidal cycle, since the sampling was done during pre- monsoon. pH was in the alkaline range during all the stages of tide both in the canal and forest. Not wide fluctuations were noted in the values except in the canal at 5 p.m when the pH rose to 9.3 which may be due to any pollutant that entered the water column. Wide fluctuations were shown in the alkalinity values of the forest and not in the canal. In the case of chlorophyll and POC higher concentrations were noted in the forest than in the canal. Variations in these values of the forest with the tidal changes were not predominant. This indicated that the main sources of these parameters are the leaf litter and the dead and decayed remains of the plant parts of the system.

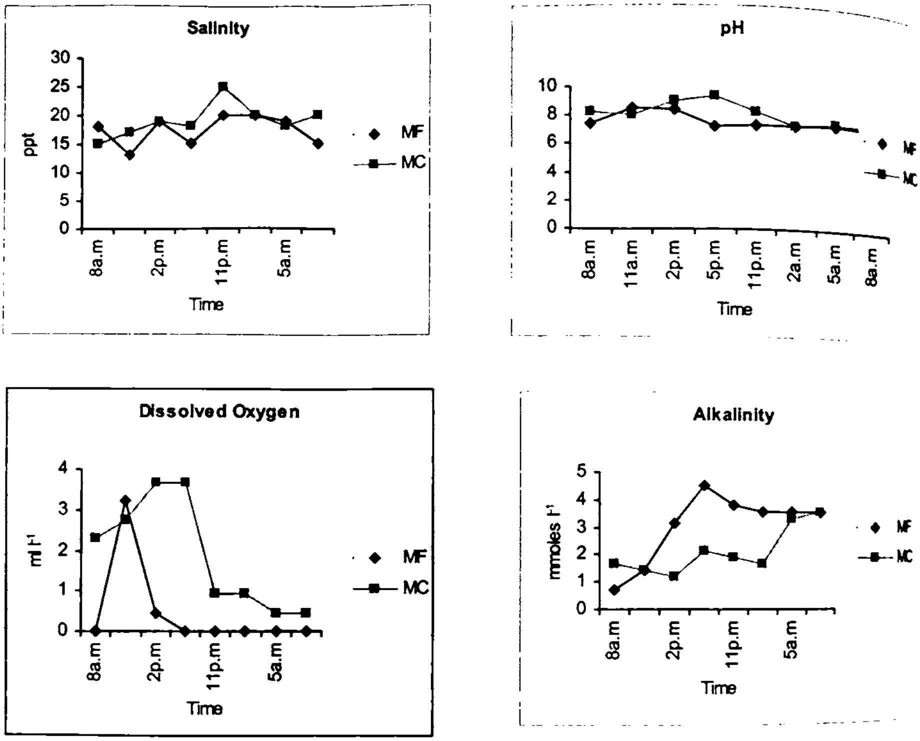

Fig. 3.9 Tidal variation of General hydrographic parameters

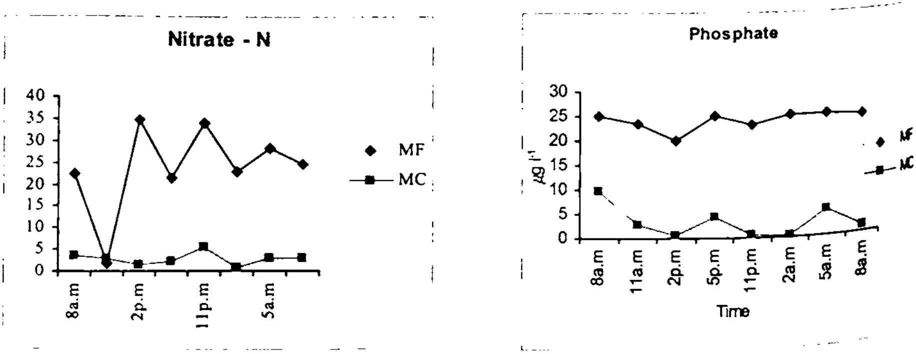

Fig. 3.10 Tidal variation of Nutrients

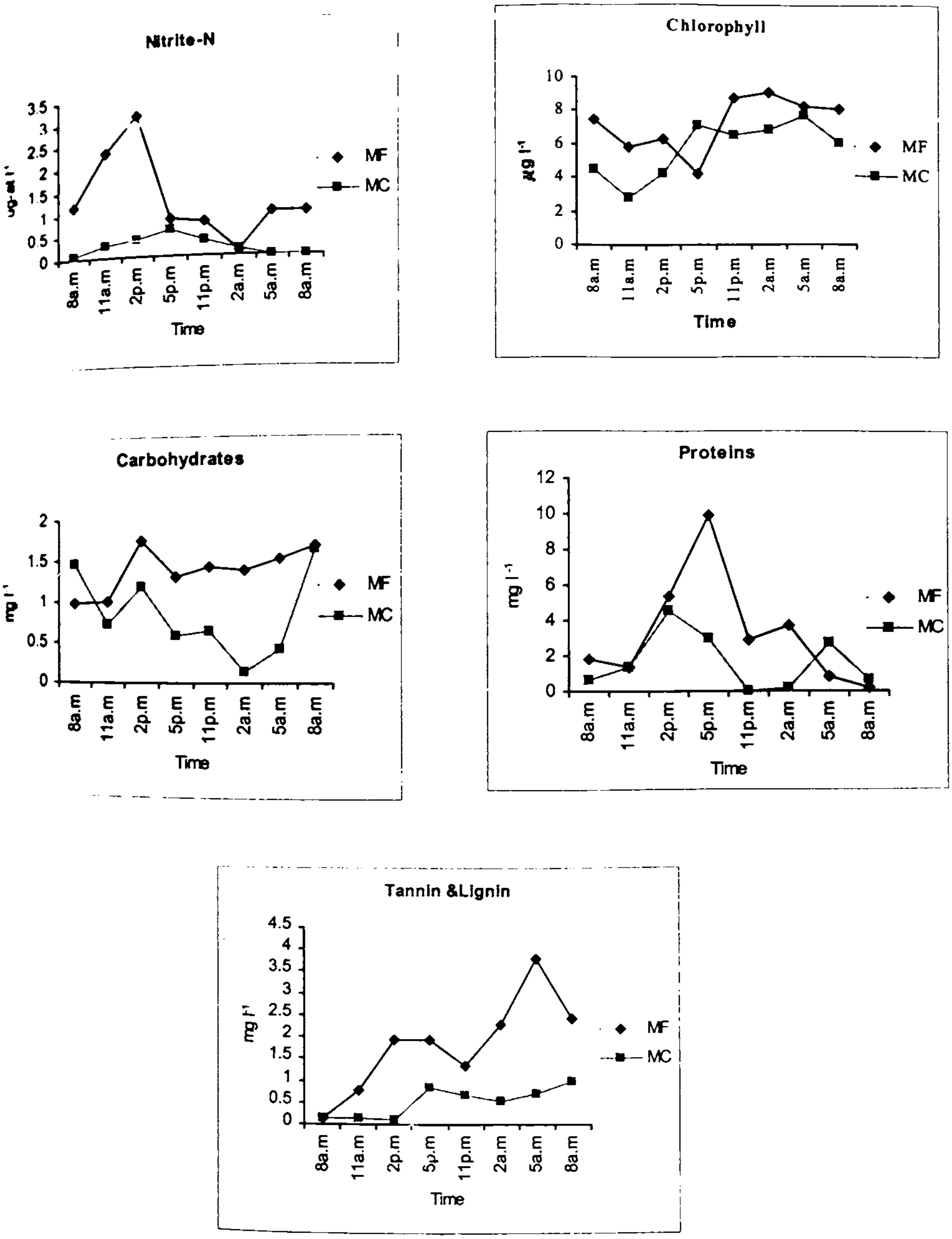

Fig. 3.11 Tidal variation of Nutrients and Organic compounds

The concentration of nutrients in the forest was high when compared to that in the canals. Very wide fluctuations in the concentration of nitrate with the tidal cycle were observed in the forest. Even though high values for phosphate were noted in the forest, wide variation with tidal cycle was not observed. These observations clearly indicated that the nitrate concentration of the system is influenced by the river run off and the phosphate by land run off.

The concentration of organic compounds was higher in the forest than in the canal. The concentration of carbohydrates in the forest did not vary much with the tidal cycle. But the value of proteins and the tannin and lignin fluctuated widely with the tidal discharge which indicate the influence of the tidal water.

Alvarez- Borrego et al (1977a) and Alvarez- Borrego et al.(1977b) generated a 26-h time series of salinity, temperature, oxygen, nutrients, chlorophylls and meteorological variables at the mouth of a bay. However, these investigators realized that sampling for such short periods was like looking at reality through slits, and general conditions could not easily be separated from irregular or episodic events. They emphasised the necessity of taking longer time series, so that the ocean-lagoon relationships could be assessed more rigorously. Due to limitations only one tidal cycle was sampled during this study. So the distributions revealed cannot fully reflect the diurnal changes as well as the tidal character of the ecosystem and its adjacent water body. Therefore no discussion on the observed values is offered.

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Chapter 4

THE MODEL

A system is a part of the universe, which will have interaction with its surroundings and contains a collection of objects that are interrelated in many ways. An object is some elemental unit upon which observations can be made, but whose internal structure either does not exist or is ignored. Finally, for completeness, a description is a signal that can be decoded or interpreted by humans. "Models are cartoons of reality". This is one important perspective to hold on models, because one should realize that predictions of real - world behaviour are not possible. There are many approximations and assumptions that have to be made to model a process or an event in the environment. Only the dominant processes affecting the event can be included. Thus, there will be always some difference between model results and natural occurrences, even if the processes being modelled exposure assessments can be conducted. The soundness of model predictions is highly user -dependant. Models are not like radios in that anyone can plug them in and get beautiful music. Rather, they are like violins- tools that require practice and experience before one can obtain beautiful music. The development of sound and tested models in an aquatic system is a long -term effort. For example the modelling of dissolved oxygen began some 50 years ago with the Streeter-phelps equation. Through successive comparisons of predictions with field and laboratory data, it was found that certain phenomena were being ignored. This discovery led to the addition of nitrogen cycling and algal interactions to existing models. More recently, an improved description of water/ sediment interactions has also improved our ability to model dissolved oxygen. Models offer a unique way of asking the question "What if?". They are ideal ways of evaluating potential impacts a priori. They provide an excellent framework for sorting through massive quantities of environmental data in a logical way. The use of a model in this way can help to identify cause- effect relationships that are not apparent when one simply reviews data. When used in this manner, models can act as repositories for the current state of the art. Another way of gaining understanding with a model involves parameter variation, sometimes called sensitivity analysis. The final way in which models improve one's understanding is in their application. Differences between observed chemical concentrations and predicted concentrations force the user to seek an improved understanding of both the model and the real world. It can also be used as a focal point for the clarification of issues and uncertainties This is a very subtle but powerful use for modelling, especially in the area of hazard assessment. There are different forms of models:

1. Conceptual or Verbal
2. Diagrammatic
3. Physical
4. Formal- Mathematical.

4.1 Modelling of Environmental Problems

Organic compounds and heavy metals are present in varying degrees in all phases of the environment- air, water and land. They are transferred between and among these media, undergo transformation within each, and accumulate in viable and non-viable constituents. The magnitude and significance of the problem has become increasingly evident, particularly in the accumulation of toxic substances in food chains and in contaminating water supplies. An understanding is therefore required of transport, transformation and exchange of these substances in and between the various media of the environment. The various phenomena that affect transport, transformation and accumulation of organic compounds and heavy metals in the various phases are to be identified. The exchange of these materials between water and other phases of the environment are to be taken into account. However, the primary emphasis is directed to aquatic systems, specifically to the spatial and temporal distribution of these materials in the various types of natural bodies, ie rivers, lakes, estuaries and the coastal zone. The distribution of substances that are natural components of biochemical and ecological cycles of oxygen, nutrients, minerals, dissolved and suspended solids and the basic elements of the food chain are also to be defined. Models for the analyses of organics and heavy metals are similar to those developed for constituents that are natural components of ecological cycles. The terms relating to the particulate form and its interaction with the dissolved component are the additional components to be incorporated. Further more, the exchange between the suspended and the bed constituents must be taken into account.

Modelling has now become a standard tool in environmental analysis as well as its management. Large scale use of models for environmental regulation is just now beginning. The equation describing the spatial and temporal distribution of organic compounds is developed using the principle of mass conservation, including the inputs with the transport, transfer and reactions components. The general equation for the mass-balance equation about a specific volume V

$$V\, dc/dt = J_I + \sum R_I + \sum T_I + \sum W \qquad (1)$$

Where c_I - concentration of the compound under consideration in the compartment I

J - Transport through the system.
R - reactions within the system
T - Transfer from one phase to another
W - inputs

This equation describes the mass rate of change of the substances because of the net effect of the various fluxes and transformations

The general term compartment refers to each phase of the physico chemical regime ie dissolved and particulate solids in the water, atmosphere and bed, as well as to each element of the food chain. The transport, reaction and transfer terms may be positive or negative, depending on the direction of kinetic routes between the hemicals in the compartment I and its concentration in the other compartments with which it reacts or exchanges. The pathways are determined by the hydrodynamic, geophysical, chemical and biological characteristics of both the system and the components. The hydrodynamic components transport material from one spatial location to another by dispersion and advection. The physical factors transfer from onc phase to another, such as exchange with the atmosphere, adsorption to and desorption from the suspended and bed solids and settling and scouring of these solids. The chemical factors transform the substance by the processes such as photooxidation, hydrolysis and oxidation /reduction reactions. The biological phenomena affect transference and transformation: the latter primarily by microorganisms that may metabolize the chemical, and the former by assimilation and excretion by the various aquatic organisms. Accumulation in the food chain is brought about by ingestion of the chemical from the water and by predation on contaminated prey.

Let the concentration Cd to be the dissolved component of the chemical in the water. It interacts with the particulate concentration Cp. The interaction may be an adsorption / desorption process with the solids or an assimilation / depuration process with the aquatic organisms. In either case the particulate concentration is defined as;

$C_{pi} = r_I mi$

Where c_p = particulate concentration in compartment I

r_I = mass of chemical/ unit of interaction

m_I = concentration of the interacting species

The mass- balance equation for the particulate component, similar to Equation 1, is then

$$d_{cpi}/dt = r_I\, d_{mi}/dt + m_I\, d_{ri}/dt$$

$$= J + \Sigma R + \Sigma T + \Sigma W \qquad (2)$$

Equation (2) is more generally expressed as a summation of the individual components of the interacting substances:

$$C_{pi} = \Sigma\, r_i m_i$$

The receiving water models for lakes and streams include the mechanisms illustrated in Figure1 (Dominic & John.1982)

MECHANISMS

INFLOW	OUTFLOW	LOADING
$\downarrow Q_1$	$\uparrow Q_1$	$\downarrow W_T$
WATER COLUMN REACTIONS	K_1	
ADSORPTION- DESORPTION	$m_1 \Pi_1$	
SETTLING	RESUSPENSION	DIFFUSION
$\downarrow W_s$	$\uparrow W_{rs}$	$\downarrow\uparrow K_L$
SEDIMENT REACTIONS	K_2	
ADSORPTION-DESORPTION	$m_2 \Pi_2$	
SEDIMENTATION		

Steady state (with respect to the sediment- water interface) occurs when both concentration and the parameter functions (diffusion coefficients, burial velocities, etc) are independent of time. Nevertheless, a steady state may exist in at least two situations. First, if the fluctuations have a mean period very much shorter than the other time scales for diffusion, advection and reaction, then it is possible to time- average over the variability. An example is the derivation of biodiffusion from the biologically induced motions of sediment grains. Given no other time-dependant forcings, the time-derivative term may then disappear, and a steady state can exist. In this comparison, the time scale for diffusion is defined by the Einstein-Smoluchowski relations, which tells that this scale is dependent on the square of the size of the system being modelled. The advective time scale is important only where advection is the dominant transport process, and it is given by dividing the size of the system by the advective velocity. Finally, the reactive time scale is given by the inverse of the apparent first-order reactive time-scale is given by the apparent first-order reaction rate constant. Secondly, pseudo-steady state can be assumed when the time between fluctuations is much longer than the other process time scales. In this situation, the perturbation decays long before the next disruptiuon to the system. Similarly, if the forcing is continuous, but has a very long relative time scale, then the sediment can be described by a series of steady states. (Berner, 1980)

If C_{T1} is the concentration of a chemical compound in the water column and C_{T2} is the concentration in the sediment then according to the steady state conditions,

$$dC_{T1}/dT = 0$$

$$dC_{T2}/dT = 0$$

The differential equations for C_{T1} and C_{T2} specify the response of the water column and sediment segment concentrations of the concerned chemical compounds. Steady state approximations can be applied to the diagenesis also. Steady state diagenesis relative to the sediment-water interface, occurs if the concentration always has the same value at the same depth.

4.2 Application of Modelling in Different Systems

Emerson et al (1985) developed a flux model to study the dynamics and preservation of organic carbon in the deep-sea sediments. Two types of sediment traps were used for particulate organic carbon measurements. The sediment portion of the model deals only with the region of the sediments that contain oxygen. In the formulation of a model describing the interaction between pore-water chemistry and organic carbon concentration at the sediment interface of the deep sea, it is assumed that oxygen is the only important electron -acceptor. The contribution from other oxidants has shown to be minor. Further assumed that particulate organic carbon is the only significant reduced substance, that enter the sediments. Since there is no information about organic matter degradation between the sediment traps and the sediment -water interface, it is assumed that the particulate carbon rain into the traps is equal to that immediately above the interface. This is supported by the observation that there is not a great difference in carbon flux in any of the traps below 1000m. A less constrained assumption is that the carbon that reaches the sediment -water interface is degraded within the sediments rather than at the interface. Together the above assumptions imply that the measured sediment trap flux equals the flux into the sediments ie

$R_c = F_c$

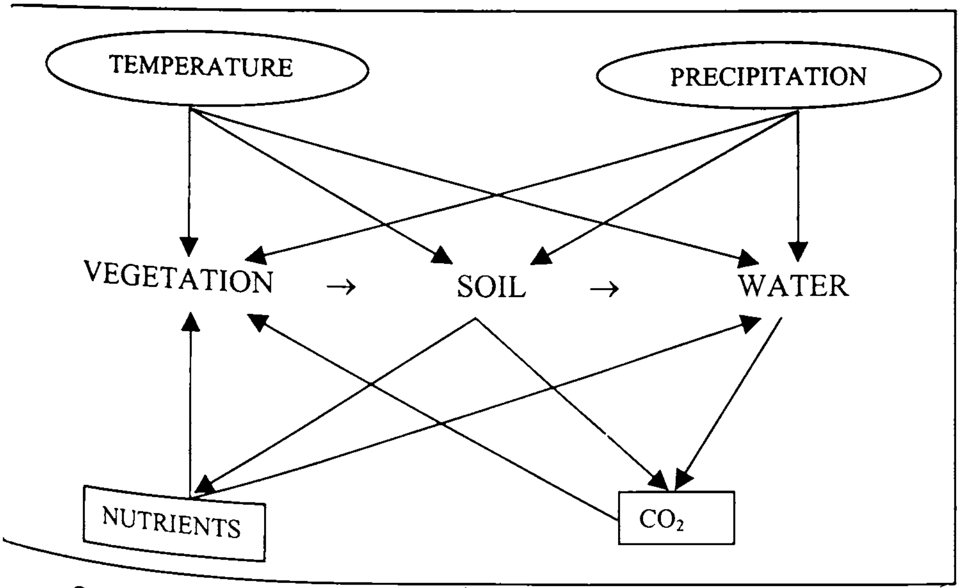
Two general cases for the oxygen and carbon distribution in the sediments are considered. In the carbon limiting case oxygen is not totally consumed and carbon reaches a low but non-zero level representing the refractory carbon concentration. If oxygen is consumed in the pore waters, residual carbon will be buried below the $O_2 = 0$ horizon. The mass balance relationship between carbon and oxygen formed the basis of the model. When oxygen is limiting

$$F_c - F_{c,z} = \int_0^z C \, dz = \gamma F_{oi.}$$

Which simply states that the particulate flux across the sediment-water interface minus the burial flux of organic carbon ($F_{c,z}$) must be equal to the integrated degradation rate of organic carbon. The model derived relationship among C, F_c, F and k. Within the constraints of the model, the three main variables influencing the sedimentary carbon content are the particulate carbon flux across the sediment water interface (F_c), the degradation rate constant (k) and the bioturbation constant (K) An increase in particulate organic flux Fc by 10 - 20%, an increase in the bioturbation rate K by about a factor of five or a decrease in the organic matter degradation rate k brought about an increase of 1.1% in the organic carbon.

Interface Carbon Fluxes
↓ R_c ↓
Sediment
Trap
Water
sediment

The degradation of organic matter in sediments is presumed to occur through a first order process with respect to labile organic carbon. This formulation assumes no dependency on the size of the bacterial population or reactivity of different carbon fractions. The model constructed suggests that the extent of preservation of organic matter and the different characters of the pore waters are controlled by the bioturbation and the rate of organic matter degradation in addition to the particulate organic carbon flux. Further more, these interface processes appear to be independent on factors other than the flux of particulate organic carbon to the sediments. This analysis suggests that the reconstruction of surface water paleoproductivity estimates based solely on the organic carbon content of ancient marine sediments may be misleading. The residence time of organic carbon with respect to microbial decay in the top few centimeters of sediments is on the order of 15y to 150y. This value is 10 to 100 times slower than present estimates for water column decay rates, but it is of the same magnitude as C^{14} estimates of the age material that is eaten up by deep sea benthos.



Clair& Erhman (1996) predicted how the basin exports of dissolved organic nitrogen would be affected by changes in climatic conditions using a conceptual model. They collected data from a number of river basins to simulate discharge and DOC and DON export from river basins. According to this model, modification in precipitation will lead to changes in run off that will then change the rate of organic matter transport from soils. Higher temperatures should lead to increased plant production and thus higher humus production but also to higher soil organic matter decomposition and mineralization rates which will cause lower amounts of Carbon to be for export to the steams and rivers. Increased temperature will also be responsible for more evapotranspiration, which would reduce the amount of water available for transporting soil organic matter to watercourses. Through this model they generated hypotheses concerning the relative effects of climatic - forcing functions that affect runoff and dissolved organic matter export from drainage basins. The total precipitation and maximum temperature have roughly similar importance in controlling discharge and DOC export. They estimated the magnitude of the changes in water and nutrient exports that would be expected with climatic change. A 6^0 increase in temperature with a concurrent 20% decrease in precipitation led to a predicted 34% reduction in export, most likely because more plant matter would decompose in soils under drier conditions and there would be less organic matter left to export with less runoff.

The dependence of sulphate reduction rate in sediments on organic matter was studied by Westrich & Berner (1984). The oxic decomposition of planktonic organic carbon in the laboratory over a period of 2 years was modeled in terms of the first order decay of two reactive organic fractions. A simple first order model was the first kinetic model developed to describe the dependence of sulfate reduction rate in sediments on organic matter. An important assumption of this model is that rates of sulfate reduction can be related to overall rates of organic carbon decomposition according to the reaction

$$2CH_2O + SO_4^{2-} \longrightarrow H_2S + 2HCO_3^-$$

The material CH_2O refers to the solid phase organic detritus undergoing decomposition, and it is assumed to have a bulk oxidation state similar to that of carbohydrate. The fermentative microorganisms hydrolize the initial detritus and produce low molecular weight species, which are then used by sulfate reducing bacteria. In the simple first order model, the material denoted as CH_2O is assumed to be decomposed at an overall rate directly proportional to its own concentration. This can be expressed as
$dG/dT = - kG$

Where G is the metabolizable organic carbon that can be decomposed by the sulfate reducing community of micro organisms, k is the first order decay constant for decomposition via sulfate reduction and t is time. Integrating this equation for the boundary conditions $t = 0, G = G_0, t \rightarrow \alpha, G \rightarrow 0$,

$$G_{(t)} = G_{(0)} [\exp - kt]$$

This equation shows that the rate of sulfate reduction decreases exponentially with time because of the exponential decrease of metabolizable organic carbon with time. The pool of decomposable, sedimentary organic material is actually composed of various groups of compounds that have different reactivities with regard to decomposition. According to this formulation, each group is assumed to degrade via first - order kinetics. This can be expressed as

$$G_T = \Sigma G_I$$

$$dG/dT = k_I G_I$$

$$-dG/dt = \Sigma k_I G_I$$

where k_I and G_I refer to individual fractions, each with different reactivity, and G_T represents total decomposable organic matter. The amount of total decomposable organic matter as a function of time is then equal to a sum of numerous terms, with each term being a single exponential function. To simulate natural organic matter decomposition and bacterial sulfate reduction in the marine environment, a large amount of freshly collected planktonic material was degraded oxically in sea water for a long period time and variously aged fraction were used as a source of organic matter studying bacterial sulfate reduction in marine sediments. Weighed portions ot each freeze dried sample was added to the unaltered sedime and the sediment homogenized anoxically in a glove bag flushed with N TOC and POC were measured. A refractory organic matter fraction that wa not reactive also appears to be present. Based on this formulation, the TO and POC data as a function of time can be represented by an equation

$$G_T(t) = G_{01}\,[\exp(-k_1t)\,] + G_{02}\,[\,\exp(-k_2t)\,] + G_{NR}$$

Where $G_T(t)$ is the concentration of total POC or TOC, G_{01} the initi concentration of the highly reactive POC or TOC,G_{02} the initi concentration of the less reactive POC or TOC, G_{NR} the concentration of the non reactive POC or TOC, k_1 is the first order decay constant of the high reactive POC or TOC, k_2 is the first order decay constant of the less reacti POC or TOC, t is the time of decomposition. The kinetic model based o this equation assumes that the material denoted as G_1 and G_2 is converted t CO_2 and that G_{NR} remains constant throughout the experiment. Anothe potential problem is that most resistant material may not have been derive from the planktonic decomposition at all but instead may prese resuspended from bottom sediment. From the experiments, calculated deca constants were in good agreement with those determined in other ov decompositions. To determine the decay constants for the fresh plankton material under anoxic conditions, some data manipulations are made. Firs the rates of sulfate reduction are converted to rates of organic carbo decomposition using the stoichiometric conversion factor of two. th measured sediment porosity of 70% and a sediment particle density of 2 were assumed. Nrext, the organic carbon added is corrected for material used by the bacteria.

An essentially non reactive fraction is also present which at the end of the experiments made up about 35% of the particulate organic carbon seems to be decomposable only on a much longer time scale. The additio of both fresh and degraded planktonic particulate material to buried anoxic sediment increased the rate of sulphate reduction occurring in the sediment. This proved that sulfate reducing community of microorganisms was originally organic carbon limited in the unaltered sediment. Further more, the stimulated rate of sulphate reduction is linearly related to the amount of particulate organic carbon that is added to the sediment. These results were in good agreement with the assumption that the rate of sulphate reduction is proportional to the concentration of the metabolizable organic carbon. These experiments are also consistent with the multi G model in which the organic material decomposed by sulfate reducing bacteria is assumed to be composed of a number of fractions, each of which undergoes first order decomposition.

Colombo et al in 1996 applied a diagenetic model to explain the high variability observed in the bioturbated top few cm of the core sediment. The basic equation is

$$G_Z = G_u + (G_s - G_u)\, e^{-\lambda z}$$

Where G_Z is the concentration of organic matter at a specified depth z, G_u is the concentration of unreactive organic matter i.e. that of the bottom of the core, G_s - G_u is the concentration of reactive organic matter, with G_s as the concentration in the top 0-3cm, and λ is the attenuation factor.

$$\lambda = \omega/2D_b - [(\omega/2D_b)^2 + k/D_b]^{1/2}$$

where D_b is the biological mixing coefficient ω is the sedimentation rate assumed to be 0.6cm /year and k is the decay constant of the species. The values of Gs and G_u were obtained experimentally. The model was applied to the data assuming D_b, ω and k, by a non linear regre3ssion procedure which obtains least square s estimates of the unknown parameter λ. The high value of R^2 values indicate a good agreement between the model and the data.

Estuarine salt marshes of the world share the characteristics of being invaded more or less frequently by salty water. The tidal frequency and salinity vary, but must be often enough or high enough to produce a discernable effect on the floral and faunal composition. Explanatory models of salt marshes must be based on realistic interactions between structure and functions. These interactions produce behaviour. Such models may be used for 1. Management 2. Predictions 3. Development of testable hypotheses.

A photograph of a salt marsh is a model in the sense of portraying as ecosystem. But the picture is a static model. The static model has the structure but cannot simulate behaviour and thus cannot be used to predict. The dynamic model by Weigert et al (1975) consists of 14 compartments. The theme is carbon flow. This model had its sole major objective the investigation of hydrological effects on carbon transport and mass balance. Simulation run with the model predicted a net accumulation ogf somewhat more than $200gC\times m^{-2} \times yr^{-1}$. Because this was still much more than the measured accumulation in the marsh, they used the model to help develop and test three hypotheses.

1. Bedload transport could account for the additional carbon, but only if carbon transport by the shifting sediments at the mouth far greater than the existing measurements.
2. Two additional rainstorms falling on the marsh at high tide could also account for the loss of excess carbon.
3. The excess carbon could be lost via motile organisms leaving the marsh and not returning. Such trophic transfer would depend on carbon transformations originating with bacterial degradation of DOC and POC. The model was used to evaluate the reasonableness of this hypothesis by predicting the rate of predation on bacteria by detritovores that would be needed to use up less than $200gC*m^{-2} * yr$ The answer, 3% of the standing stockof bacteria per day, seemed well within the productive ability of the bacteria. Quantitative data on the migration of fish, shrimp and crabs are non existent for the marshes.

although it is common knowledge that such organisms do in fact emigrate offshore. This carbon transport mechanism is not in the model, nor have respiration measurements made on the water column taken into account the CO_2 loss from the macroheterotrophs

4.3 Our System

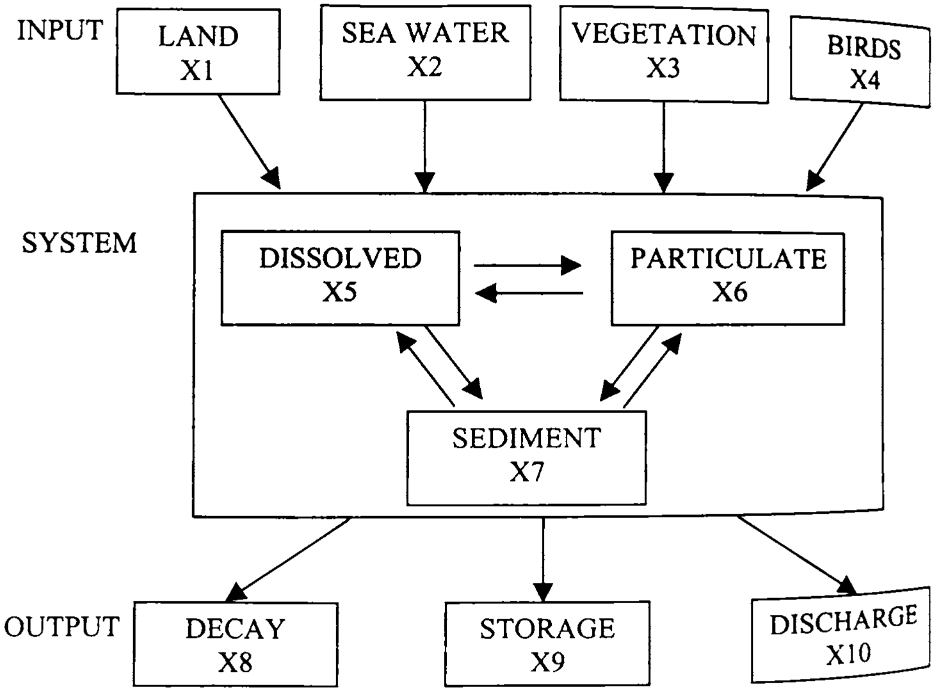
The modelling of the environment systems are based on the analysis of the inflow and out flow of the components in consideration. The system is defined on the basis of the variables which contribute to the inflow and outflow. Now, the sources which contribute to the input of the present system are the land, sea water, the vegetation and birds and the outflow will be through the deca, storage and discharge. The movement of carbon is the theme of the model. The carbon is represented by the total organic carbon in the different compartments as well as the protein, carbohydrates, and lignin fractions. Steady state approximation is the approach. The data generated from the system is used for the evaluation of the model.

a. *Observations*

1. Against the expectations of stable trend in the deep sediments, the analysis of the data indicates seasonal variation and irregular trend.
2. The bulk density was considerably low and the moisture content was high indicating a high porosity.
3. The retention time of water over the sediment is considerably low and in pre monsoon the surface sediment is exposed to atmospheric variability.
4. Organic load reaching the surface during post monsoon is considerably high
5. Major fraction of the organic matter is refractory substances and of the reactive species protein shows the higher %
6. Compared to protein a higher concentration of carbohydrate is present in the overlying water.

Based on these observations, we can prepare a flux model to identify the exchange character of the organic carbon between the system and the adjacent water body.

The components of the system which contribute to the dynamicity has to be defined in terms of assessable variables or parameters. Generally, a balancing of the inflow and outflow is the technique used to evaluate the model. The physical picture of the system in terms of the inflow and the outflow can be given as



X values indicate the concentration of total organic carbon available in each compartment. The general flow pattern of the carbon can be represented by a differential equation,

$$dx = dx_1 + dx_2 + dx_3 + dx_4 - dx_8 - dx_9 - dx_{10}$$

where dx is the change in concentration in the system and dx_1,dx_2, dx_3 & dx_4 each of the compartments. As the concentration of the carbon within the system is always will be the net result of the processes operating in the system between the compartments, the registration of individual compartments within the system was considered as not much significant except in the partitioning within the system.

The dx_1, dx_2 can be represented as a rate function of the concentration of carbon in the compartment or

$$dx_1 = k_1x_1,\ dx_2 = k_2x_2 \ldots\ldots\ldots \text{ etc or}$$

$$dx = k_1x_1 + k_2x_2 + k_3x_3 + k_4x_4 - k_8x_8 - k_9x_9 - k_{10}x_{10}.$$

The steady state treatment of computing dx =0, approximates the relation to a mass balance or flux relation. As the general driving force in the water flow characteristics, the k values can be considered as a function of the water balance and so for all practical purposes can be replaced by water balance

One major difficulty in computing the data is to evaluate the significant contribution of the seasons towards the individual components. In the present system, the addition from the land or terrestrial input is considered to be negligible only because the contribution of water through the terrestrial discharge is negligible. The monsoon and postmonsoon season delivers a high load of freshwater to the system leading to domination of fresh water character in the annual cycle. But the premonsoon is having a domination of saline water. The net balancing, the annual balancing is still in favour of a slight saline structure. The contributions from the vegetation and birds are also seasonal in character, but the demarcation between the seasons requires continuous monitoring of the system and so the annual values are considered as the significant component. Similarly in the case of decay, storage and discharge also, the contribution of the seasons are significantly high. During the premonsoon, the low tide more or less lead to direct contact between the sediment and the atmosphere. The high ventilation due to this will lead to aerobic decay patterns or processes. So the system generally will be having a mixed diagenetic conditions, oxic and anoxic. The development of the model is done in three steps based on the experimental observations. The first step is used to study the system characteristics. The second step is used to study the decay character of the sediments and the third step is the assessment of the budget of particulate organic carbon. The foundation of the model is laid by the salt balance, water balance and POC balances. Tidal influx is the main source.

a. Step 1 Salt balance & Water balance.

The system characteristics are identified by assessing the water balance and salt balance of the system (Simpson et al 1997) The principal source of salt is the tidal water. The volume of the water present in the system is also influenced by the tidal discharge. The differnce between the water discharged during high tide and that of low tide gives the amount of water losts by evaporation and percolation.

$Q_{sw(HT)} = Q_{sw(LT)} + dQ$

$Q_{sw(HT)}$ - water discharged during high tide.

$Q_{sw(LT)}$ - water discharged during low tide

dQ - water losts by evaporation and percolation in the tidal cycle.

The water balance and salt balance data indicate a net retention of the salt and water in the forest

$Q_{swtHT)} \times \text{salinity}_{(HT)} = Q_{sw(LT)} \times \text{salinity}_{(LT)} + ds$

salinity$_{(HT)}$ - Salinity of the forest during high tide.

salinity$_{(LT)}$ - Salinity of the canal during low tide.

ds - Amount of salt retained in the system in a tidalcycle.

In the case of system 1. from the water balance and salt balance a rough estimate of the amount of evaporation can be obtained. As the major reason for the increase in salinity during low tide is the evaporation, it is assumed that during the percolation, the salinity is more or less maintained. The amount of evaporation can be obtained from

$$dv = dQ - (dS / Salinity_{(HT)})$$

The data indicate that the amount of vaporization from the system is considerably small and insignificant compared to the inflow of water in the pre monsoon period. The conditions for vaporization is most favourable during the pre monsoon as the season indicates highest temperature and less humidity. It is therefore is a logical conclusion that the contribution of the evaporation to the water balance in the system is insignificant during all seasons.

Table 4.1 Water balance in three systems.

	Premon	Mon	Post mon	Mean	Annual turn over
System 1	3375000	2700000	3000000	3025000	147216.67
System 2	450	360	400	403.33	147216.67
System 3	450	360	400	403.33	147216.67

Table 4.2 Salt balance in three systems.

	Premon	Mon	Post mon	Mean	Annual turn over
System 1	3375000	-1215000	3600000	1920000	93440
System 2	900	540	-1360	26.67	9733.33
System 3	-450	-2772	-184	-1135.33	-414396.67

Table 4.1 and 4.2 give the values of salt balance and water balance in three systems. In the case of the system 2 & 3, no significant variations in the salinity was observed with the tidal cycle and so the salt balance gives no significant information about the evaporation and percolation. Monsoon and postmonsoon periods due to the high fresh water discharge exhibit no regular feature. and so the system characteristics in terms of the salt balance and water balance infact has to be restricted to the pre-monsoon period. Still

the annual baiance has been taken in the case of all the three systems. In order to identify the net values which can be considered to an annual turnover of the various components, the annual turn over of sea water and salinity calculated from the data are given in the Table 4.1.A close examination of the data further reveals that there is a net concentrating effect in the case of the salt which can be due to evaporation of water. So this indicates that amount of vaporisation from the system is considerably small insignificant compared to the inflow of water.

b. Step 11 Degradation of surface sediments.

The major contribution to the C- budget is the diagenetic processes operating in the sediment. As continuous resuspension is possible for the surface sediment, the degradation will be at its maximum in this layer. The demarcation of the surface to deep sediments is more or less flexible and depends on the character of the system. In the shallow waters, and in the case of deep waters the sediment upto 3 cm is treated as the surface sediment. But where there is regular turbulence or flushing sediments upto 5 cm can be considered as surface sediment. In the systems under consideration, due to the very low water column and due to the regular tidal activity, the first 5cm can be considered as the surface sediment with possibility of direct exchange with overlying water. The occasional exposure of the sediment to the atmosphere and also the significantly low water column during low tide can lead to a ventilation of the sediment and the oxygen can take part in the diagenesis. This occasional in co-operation of oxygen in the diagenesis or the decay as pointed out earlier will lead to a mixed path and also an enhanced bioturbation.

The detailed analysis of the decay was not the intention here but the attempts were made for the eestimation of the decay process or the decay rate. The earlier work in the diagenesis of organic matter especially in the case of surface sediments indicated that the decay rate can be expressed in terms of first order kinetics. The time related decay rate is an impossible task in the environment system and so the ratio of the organic matter at the different depths is considered as the index of the decay. The differential conditions available in the system can lead to a differential decay processes and in the present study to identify the diagenetic character, the ratios of carbon and nitrogen are utilized. The obtained degradation rate is given in the Table 4.3. It can be seen from the data that the monsoon season is having the lowest decay and postmonsoon having the highest in terms of both C & N. The decay rate of N_2 is comparatively lower to that of C. The similar trend is observed in the decay rate of carbohydrates and protein as estimated (chapter 5). Due to the shallowness of the system, sediment decaying by trap is not possible. So the nature of the particulate flux is used to assess the budget. Particulate flux which reaches the system is not completely retained in the system, a part of it is transported to the sea water, a part degraded before it is attached to the sediment. The particulate flux that has been transferred to the sediment can be obtained from the amount that is left after disintegration. The surface organic matter decay rate is the only tool, which can be applied in this condition. Due to the low lying water column, the first 5cm is considered to be the surface sediment which is having the possibility of exchange with the overlying water.

Table 4.3 Decay rate of Carbon & Nitrogen in three systems

	dc5/dc0			dN5/dN0		
	Premon	Mon	Post	Premon	Mon	Post
System 1	0.50	0.93	0.32	0.88	1.10	0.28
System 2	1.04	1.07	0.26	0.85	1.07	0.26
System 3	0.28	0.47	0.58	0.20	0.60	0.33

c. *Step 111 Particulate organic carbon budgeting.*

The contributions to the POC flux in the system are the inflow through the seawater, vegetation and land drain and in situ generation and the outflow in the form of sedimentation, decay and the discharge to the seawater. Of these the contribution from in situ generation is considered to be negligible because; During the pre monsoon, the chlorophyll content of the water is negligible, and during the monsoon and post monsoon periods, the water flushing pattern does not allow any significant growth of the phytoplankton in the system and the chlorophyll content observed is mainly due to the contributions from the vegetative matter reaching the system. This is clearly indicated by the POC/Chlorophyll ratio. Now the outflow will be through three parts: a. Sea water b. Bioturbation & degradation c. storage of the carbon to the sediment.

The amount of transfer of POC to the sediment is generally determined by sediment trapping techniques. Due to the shallowness of the system, such methods cannot be applied. The mass balance relation of the distribution of POC in the different compartments along with the decay rate of the surface sediment is utilized to evaluate the POC flux (Jeffry et al 1990)

$$\text{Inflow} = \text{Outflow.}$$

$$Y_{\mathrm{poc(HT)}} + Y_{\mathrm{poc(Veg+land)}} + Y_{\mathrm{(insitu)}} = Y_{\mathrm{(sediment)}} + Y_{\mathrm{poc(LT)}} + Y_{\mathrm{(Degradation)}} + Y_{\mathrm{(Bioturbation)}} + dY$$

$$Y_{\mathrm{poc(HT)}} = Q_{\mathrm{sw\,(HT)}} \times \mathrm{POC}_{\mathrm{(HT)}}$$

$$Y_{\mathrm{poc(Veg+land)}} + Y_{\mathrm{(insitu)}} = \text{Lateral addition}$$

$$= \mathrm{POC}_{\mathrm{(ForestHT)}} \times Q_{\mathrm{sw\,(HT)}} -- \mathrm{POC}_{\mathrm{(canalHT)}} \times Q_{\mathrm{sw\,(HT)}}$$

$$Y_{\mathrm{(sediment)}} = \mathrm{POC}_{\mathrm{(ForestHT)}} \times Q_{\mathrm{sw\,(HT)}} - \mathrm{POC}_{\mathrm{(canal\,LT}}$$

$$Y_{\mathrm{(Degradation)}} = \mathrm{POC}_{\mathrm{(ForestHT)}} \times Q_{\mathrm{sw\,(HT)}} \times dc5/dc0.$$

$$dY = \text{Amount that has been volatilized}$$

$Y_{\mathrm{poc(HT)}}$ - Amount of POC brought to the system by the tidal water

$Y_{\mathrm{poc(Veg+land)}}$ - lateral input in the system through vegetation and land addition. This is obtained by the difference between the amount of total POC present in the system and the amount that is brought in by the tidal water.

$Y_{(insitu)}$ - Amount of POC generated in situ.

$Y_{(sediment)}$ - Amount of POC processed in the sediment and it is calculated by the difference between the amount of POC present in the system and the amount lost to the canal

$Y_{poc(LT)}$ - Amount of POC lost to canal.

$Y_{(Degradation)}$ - Amount of POC lost by degradation which is obtained by the product of total amount of POC present in the system and the ratio of carbon in the 5cm and 0cm.

dy - Amount POC lost by volatilization

$Y_{(Bioturbation)}$ - Amount that is lost by bioturbation.

Table 4.4 Percentage of Inflow & outflow in three systems.

System 1

	Input	Decay	Lateral input	Processed	Output	Actual sediment
Pre	14.7%	15.44%	85.50%	84.60%	82.14%	42.4
Post	89.70%	83.01%	10.20%	16.90%	201.5%	5.40%
Mon	6.08%	10.98%	93.91%	89.01%	10.69%	83.12%
Annual	18.57%	20.52%	81.42%	79.84%	98.12%	57.07%

System 2

	Input	Lateral input	Processed	Actual sediment	Decay	Output
Pre	75.65%	24.35%	24.35%	25.26%	75.65%	75.65%
Post	97.41%	2.59%	2.59%	1.84%	97.41%	97.41%
Mon	42.03%	57.97%	57.97%	70.05%	42.03%	42.03%
Annual	63.31%	36.69 %	36.69 %	42.71%	63.31%	63.31%

System 3

	Input	Lateral input	Processed	Actual sediment	Decay	Output
Pre	0 %	100 %	100%	27.59 %	0 %	0 %
Post	71.43 %	28.57%	-42.86 %	-42.82 %	142.86 %	71.43 %
Mon	229.08 %	-129.08%	-358.16%	-167.65%	458.16 %	229.08 %
Annual	150.26 %	-0.17 %	-100.34%	-60.96%	300.51%	150.26 %

The balancing of inflow and outflow is represented as:

POC Budget

System 1

Sea water input	18.57 %	Sea water out put 98.12 %
Lateral input	81.42 %	Storage 57.07 %
		Decay 20.52 %

Inflow – Outflow = (18.57 + 81.42) - (57.07 + 20.52 +98.12) = -75. 72 %

System 2

Sea water input	63.31 %	Sea water out put 63.31 %
Lateral input	36.69 %	Storage 42.71 %
		Decay 63.31 %

Inflow- out flow = (63.31+ 36.69) - (63.31 + 42.71 +63.31) = -69.33 %

The assessment of the budget revealed that in the system 1, 75. 72 % of the POC formed is exported to the adjacent water body and in system 2. an export of 69.93% is assessed

System 3

This is an almost small island and the concentrations observed need not be completely due to the mangrove system. The surrounding environment showed higher POC than the system, and the direcyt application of the model as such will not be possible. Still as it trepresents an open system, for comparison the data have been worked and given in the table.

Sea water input	150.26 %	Sea water out put150.26 %
Lateral input	-0.17 %	Storage -60.96 %
		Decay 300.51 %

Inflow- Outflow = (150.26 - 0.17) + (150.26 -60.96 +300.51) = 239.38 %

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Chapter 5

GEOCHEMISTRY OF SEDIMENTS

5.1 Organic Carbon, Total Nitrogen & Total Phosphorus

5.2. Protein

5.3 Carbohydrates

5.4 Tannin & Lignin

5.5 Discussion

5.6 Reactivity of the Sediments

The global cycles of carbon (Berner, 1982,) and oxygen offer a variety of useful perspectives on the extent and mechanisms of sedimentary organic matter burial, as well as intriguing contradictions. Inventories and stable carbon isotope mass balances indicate that essentially all carbon in sedimentary rocks where approximately one of five C atoms is organic. About 90% of the preserved organic material ($15,000 \times 10^{18}$ g C) now resides as amorphous, highly insoluble kerogen macromolecules disseminated in shales and other sedimentary rocks. In addition to providing a molecular record of life, organic materials in sedimentary rocks include economically important coals and petroleum. Sedimentary burial of organic matter and pyrite also is essentially the only source of atmospheric oxygen, and intimately links the global cycles of C,S and O over geologic time (Berner, 1982).

About 0.1% of the carbon in the Earth's crust cycles in active surface pools. The greatest active reservoir is inorganic carbon dissolved in sea water. Other dynamic pools are 1-2 orders of magnitude smaller and include atmospheric CO_2, soil carbonate, soil humus, land plant biomass, dissolved organic matter in sea water, carbon preserved in surface sediments. With the exception of terrestrial biomass, the active organic reservoirs contain complex mixtures of heavily degraded which are poor in recognizable biochemicals.

Rivers carry about 1 % of terrestrial productivity to the ocean in comparable fluxes of particulate and dissolved organic materials. Total organic carbon burial in the marine sediments is less than one third of the river discharge. This indicates that riverine POM and DOM are rapidly and extensively mineralised within seawater or surficial marine sediments. The boundary between the land and sea is in the form of abrupt and often spectacular cliffs, but elsewhere, the boundary can take the form of a complex environment of intertidal sediments. These environments include shingle banks, sandy beaches, mud flats, saltmarsh and mangrove communities. The total global area indicates the significance of inter tidal sediments. The total area of intertidal sediments is likely to be similar to that adjacent saltmarshes and mangals. Inter tidal sediments offer an important habitat for wildlife, food and recreation. The very nature of intertidal areas has left them relatively undistributed by human activity compared to inland areas. The chemistry of these systems is modulated by interacting with the geological and biological environment. The plant detritus together with decomposing below-ground plant material and organic carbon associated with imported fine sediment, provides the sediments with a rich supply of organic matter. It is the decomposition of this organic matter which provides one of the unifying biogeochemical concepts in all these intertidal environments. This organic matter is subsequently oxidised by bacteria using a variety of oxidising agents or terminal electron acceptors or TEA which are themselves reduced, hence the term redox reactions. These different TEAs yield different amounts of energy from their reactions with organic carbon, so the microbial community using the highest energy yielding system always dominates, assuming there is significant amount of that TEA present. Thus as long as there is oxygen present, this will always be the oxidising agent used, but once this is exhausted, alternative oxidants are used in a fixed sequence beginning with nitrate (Coleman, 1985). It is for this reason that these intertidal sediments can consume large amounts of nitrate very quickly. In many systems nitrate levels are naturally low, but increasing concentrations of nitrate in rivers arising from human activity can mean nitrate is an important electron acceptor in some coastal systems today. Once nitrate is exhausted in the sediments the readily available oxidised iron and manganese are reduced to their more soluble reduced form. Since phosphate in the sediments is usually strongly associated with iron, this iron mobilisation can also result in phosphorus mobilisation (Sundby et al 1992). These reactions involving the important nutrients, nitrate and phosphorus, illustrate the ways in which intertidal sediment processes can influence the productivity of the intertidal ecosystems and potentially the adjacent coastal waters.

5.1 Organic Carbon, Total Nitrogen & Total Phosphorus

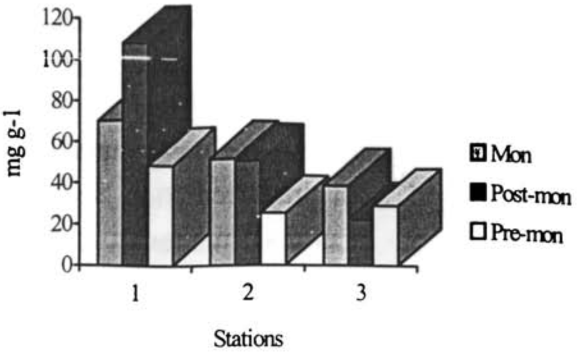


Fig5.1 Distribution of Carbon in the surface sediment (mg g^{-1})

Fig 5.1 shows the seasonal distribution of organic carbon in the surfa sediments of three ecosystems and Fig 5.1a shows its depth profile in sediment and Table 5.1 its amount in both the surface sediment and core.

Table 5.1 Distribution of Organic Carbon in the surface and core sediments

System 1

Organic Carbon (mg g^{-1})			
Depth (cm)	Mon	Post- mon	Pre-mon
0	69.61	107.2	48.2
5	65	34.5	24.2
10	60.7	33.6	23.3
15	36.1	26.4	20.4

System 2

Organic Carbon (mg g^{-1})			
Depth (cm)	Mon	Post- mon	Pre-mon
0	51.1	50	25.2
5	61.75	35.4	26.14
10	52.25	35.13	26.02
15	45.37	49.94	28.88

System 3

Depth (cm)	Organic Carbon (mg g^{-1})		
	Mon	Post- mon	Pre-mon
0	38.71	22.51	29.18
5	18.12	13	8.05
10	12.5	13.5	9.5
15	6.4	5.46	9.9

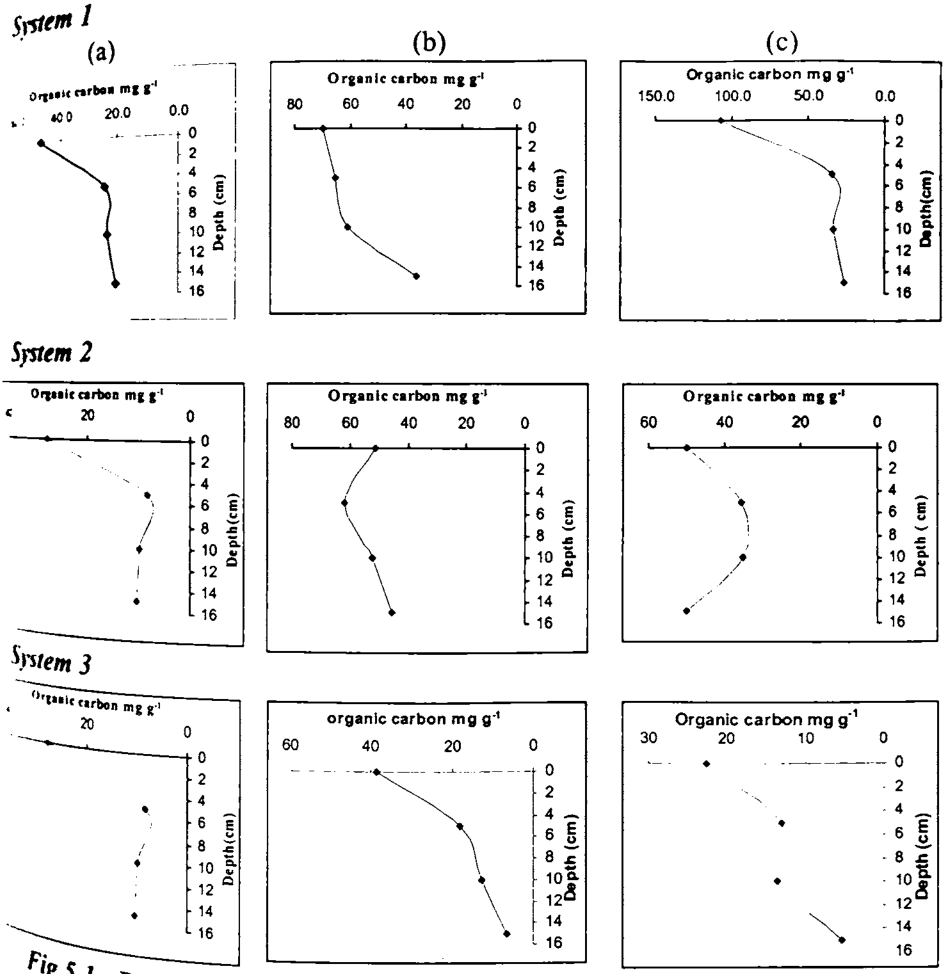


Fig 5.1a Depth profile of Organic carbon in the sediment during three seasons a) Pre-mon b) Mon c) Post-mon

Comparatively higher values for carbon were observed in station 1 in all seasons. During all the three seasons, maximum amount was noted in station 1 and minimum in station 3. In the case of core sediments, the amount of carbon gradually decreased towards the depth except in station 3 during post monsoon. The values were fluctuated between 38.71mg/g-69.61mg/g in the surface during monsoon. The amount of carbon in the sediments increased in the post monsoon. In this season, the sediments are rich in carbon and the values were in the range of 22.51 mg/g - 107.2 mg/g. Lower values were observed during pre monsoon. The percentage of sand silt and clay are given in the Tables 5.2, 5.3 & 5.4 respectively. High percentage of clay in the sediment during monsoon and postmonsoon also supports the high amount of carbon during these seasons.

Table 5.2 Sand%

	Pre	Mon	Post
System 1	16.47	23.03	33.06
System2	16.19	2.84	39.32
System 3	63.41	91.87	85.13

Table 5.3 Slit %

	Pre	Mon	Post
System 1	38.62	32.98	16.56
System 2	44.12	47.56	24.65
System 3	8.53	1.32	6.72

Table 5.4 Clay %

	Pre	Mon	Post
System 1	44.77	43.56	49.83
System 2	40.81	49.13	34.81
System 3	27.92	6.31	7.57

The distribution of nitrogen and phosphorus in the surface and core sediments is given in the Table 5.5

Table 5.5 Distribution of nitrogen and phosphorus in the surface and core sediments.

System 1

Depth (cm)	Total N (mg g^{-1})			Total P (mg g^{-1})		
	Mon	Post- mon	Pre-mon	Mon	Post- mon	Pre-mon
0	4.5	9.39	7.4	0.89	11.17	9.5
5	4.9	2.6	6.5	0.48	0.5	0.48
10	7.1	4.3	3.5	0.1	0.25	0.1
15	3.6	0.98	2.6	ND	ND	ND

System 2

Depth (cm)	Total N (mg g^{-1})			Total P (mg g^{-1})		
	Mon	Post- mon	Pre-mon	Mon	Post- mon	Pre-mon
0	4.2	4.42	3.84	ND	0.86	0.83
5	4.48	1.14	3.25	2.25	5.91	ND
10	3.6	2.26	6.83	2.21	0.46	1.78
15	2.85	2.48	5.36	7.09	0.45	0.62

System 3

Depth (cm)	Total N (mg g^{-1})			Total P (mg g^{-1})		
	Mon	Post- mon	Pre-mon	Mon	Post- mon	Pre-mon
0	0.81	2.18	3.33	0.66	0.26	0.98
5	0.49	0.71	0.67	0.16	ND	0.51
10	1.88	1.03	1.12	0.46	0.93	ND
15	ND	1.17	1.12	ND	ND	0.11

Lower values of nitrogen were observed in system 3 and higher in System 1 during all seasons. The values observed were in the range of 0.81mg g^{-1}-4.5 mg g^{-1} during monsoon. In the core sediments, the amount gradually decreased in system 2. But in system 1 & 3, higher amount was noted in the 10cm layer than 5cm. In the post monsoon, the amount of nitrogen increased in all systems and maximum was noted in system1. In this season, the concentration in the 10cm layer was more than in the 5cm in all systems. The depth profile during premonsoon in system 1 showed a gradual decrease, but in System 1 & 3 an increase was observed towards 10cm layer.

The amount of phosphorus observed in these systems was less than nitrogen during all seasons. Maximum was noted in system1 and minimum in system 3 during all seasons. Phosphorus was not detected in system 1 during monsoon and the values were in the range of 0.66mg g^{-1}- 0.89 mg g^{-1} in systems 1&3. Concentrations gradually decreased towards 10cm in system 1 and not detected in the 15cm layer. But in system 2, even though the surface sediment is devoid of phosphorus, its amount gradually increased towards the depth and maximum was noted in the 15 cm layer. In system 3, phosphorus was not detected in the 15cm layer. During pre monsoon, the surface values were in the range of 0.83 mg g^{-1} -9.5mg g^{-1} The maximum was observed in system 1 and minimum in 2. Gradual decrease was noted towards the depth and not detected in system1.But in system 2, phosphorus was not detected in the 5cm and then a gradual decrease was noted. In system 3, 10 cm layer was devoid of phosphorus. The amount increased during post monsoon except in system 3. In this season, a gradual decrease leading to a not detected state was observed in the system 1. But in the system 2, a maximum amount of 5.91 mg g^{-1} was noted in the 5cm layer and then a gradual decrease. In system 3, this was not detected in the alternate layers and a gradual increase was observed. Fig 5.2 & 5.2a exhibits the seasonal distribution of proteins in the surface and in the core table 5.6 shows its values

5.2. Protein

The seasonal variation of protein in the surface and in the core is given in the Table 5.2 & 5.2a and its values in the Table 5.6. During monsoon maximum amount of protein was noted in System 2 and minimum in system 3. The values were in the range of 0.2 mg g^{-1} -1.24 mg g^{-1}.

Gradual decrease towards the depth upto 15cm was observed in system 3. But in systems 1&2 an increase was noted in the 10cm layer and then a decrease. In the pre monsoon, maximum amount was observed in the surface in systems 1& 3, but in system 2, maximum was noted in the 15cm layer. There was a gradual decrease in 1, but in 2& 3 an increase was noted at 10cm depth.

Table 5.6 Distribution of proteins in the surface and the core sediments

System 1

Depth (cm)	Mon	Pre mon	Post mon
0	0.84	29.54	6.7
5	0.52	6.8	2.29
10	0.45	3.55	2.26
15	0.23	1.04	2.52

System 2

Depth (cm)	Mon	Pre mon	Post mon
0	1.24	15.62	6.42
5	1.23	7.41	7.23
10	1.93	9.45	4.92
15	2.96	7.04	4.81

System 3

Depth (cm)	Mon	Pre mon	Post mon
0	0.2	12.5	19.14
5	0.95	4.35	16.32
10	0.13	4.51	7.53
15	0.62	21.09	14.29

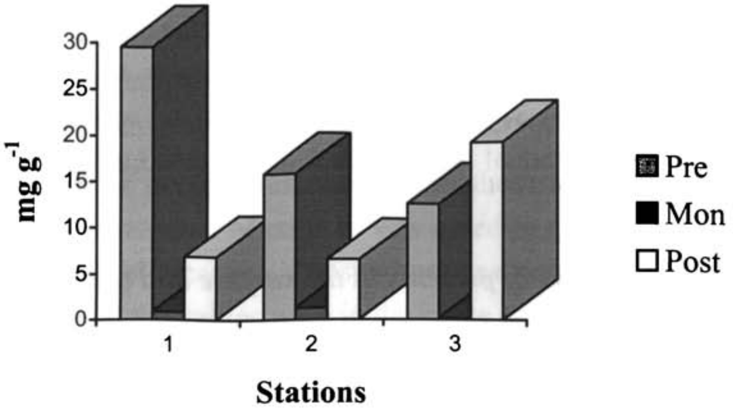
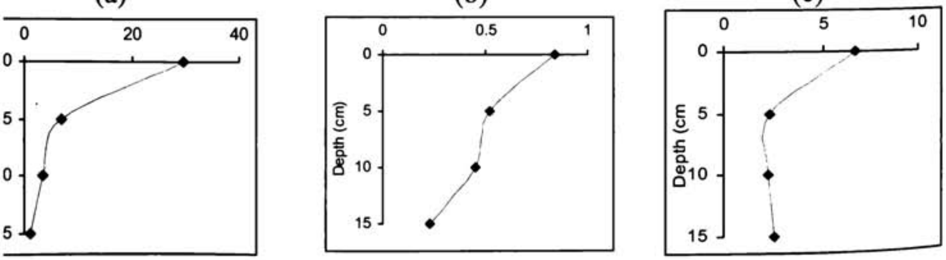


Fig 5.2 Distribution of Protein in the surface sediment (mg g^{-1})

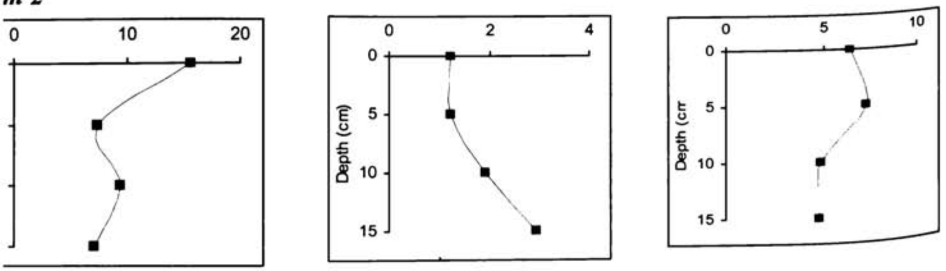
In the post monsoon, The values were in the range of 6.42 mg g^{-1} - 4 mg g^{-1}, maximum in system3 and minimum in system 2. In system 1, adual decrease was noted, but in 2 an increase was observed at h10cm and in 3 an increase at 15cm.

em 1

(a) (b) (c)



m 2



System 3

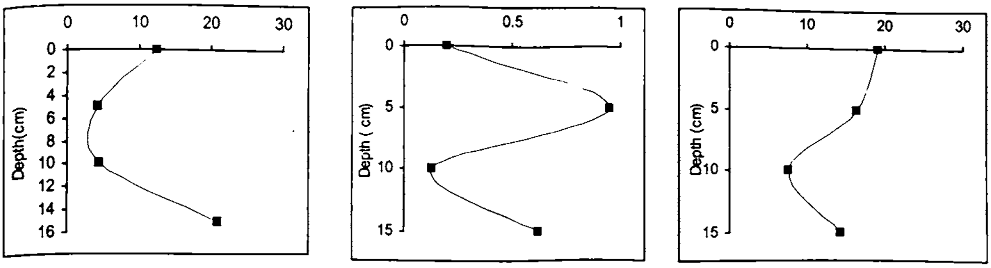


Fig 5.2aDepth Profiles of Protein during different season (a) Pre-monsoon (b) Monsoon (c) Post-monson

5.3 Carbohydrates

Table 5.7 shows the seasonal variation of carbohydrates in the surface and core sediments and Fig 5.3 & Fig 5.3a exhibits its graphical representation.

Table 5.7. Distribution of carbohydrates in the surface and core sediments.

System 1

Depth (cm)	Mon	Pre mon	Post mon
0	5.27	2.07	7.86
5	3.81	2.41	2.35
10	3.18	1.42	1.62
15	3.18	1.74	1.5

System 2

	Mon	Pre mon	Post mon
0	6.51	2.39	17.15
5	10.25	2.15	2.11
10	10.39	2.53	2.93
15	6.13	2.56	2.53

System 3

Depth (cm)	Mon	Pre mon	Post mon
0	1.55	1.55	17.5
5	1.36	0.72	0.66
10	1.54	0.98	1.52
15	3.86	0.62	1.62

Maximum amount of carbohydrates was observed in all systems during post monsoon. During this season, the values were in the range of 7.86 mg g^{-1}- 17.5 mg g^{-1}. The highest amount was noted in 3 and the lowest in 1. A gradual decrease towards depth was noted in system1. But in 2&3 an increase was observed in 10cm layer. During monsoon, highest was concentration was noted in 2 and the lowest in 3. The values were in the range of 1.55mg g^{-1}- 6.51mg g^{-1}. In system 3, a gradual increase was noted towards the depth and reached a maximum at 15cm depth. There was a gradual decrease towards depth in 1, but in 2 an increase was noted at 10cm. In the pre monsoon season maximum concentration was observed in 2 and minimum in 3. Towards the depth, a gradual decrease was noted in 1, but an increase at 10cm was noted in 2 &3.

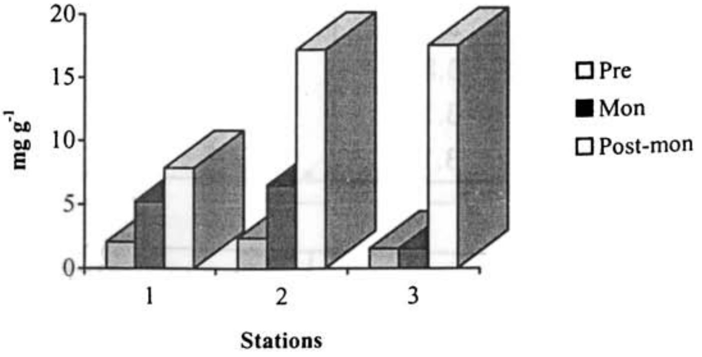
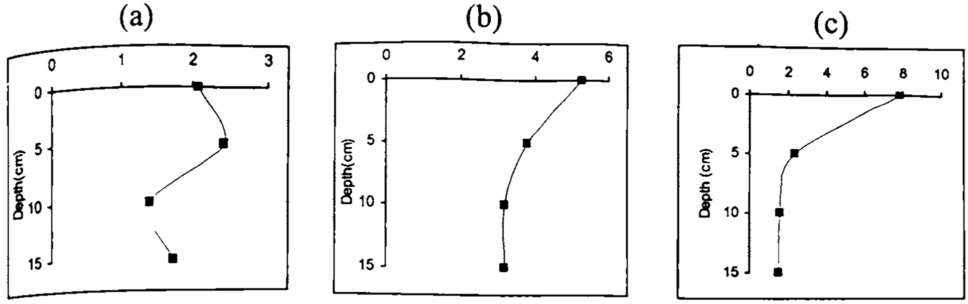
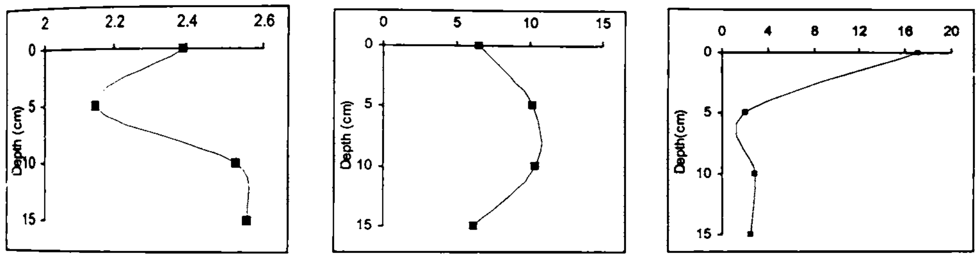


Fig 5.3 Distribution of Carbohydrates in the surface sediment (mg g^{-1})

System 1



System 2



System 3

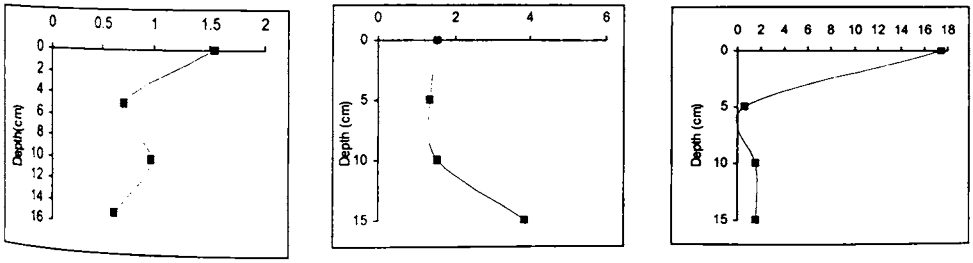


Fig 5.3a Depth Profiles of Carbohydrates during different season (a) Pre-monsoon (b) Monsoon (c) Post-monsoon

5.4 Tannin & Lignin

Fig 5.4 & 5.4a shows the seasonal distribution of Tannin and lignin in the surface and core and Table 5.8 its values.

Table 5.8 Distribution of Tannin & Lignin in the surface and core sediments

System 1

Depth (cm)	Mon	Pre-mon	Post-mon
0	3.95	7.15	1.71
5	2.94	4.74	4.91
10	2.91	2.87	3
15	2.42	4.92	1.72

System 2

Depth (cm)	Mon	Pre-mon	Post-mon
0	0.97	6.25	0.56
5	1.36	2.23	3.33
10	1.44	2.43	3.03
15	2.66	4.17	5.37

System 3

Depth (cm)	Mon	Pre-mon	Post-mon
0	1.6	3.45	0.70
5	1.45	1.72	1.38
10	1.66	1.47	2.62
15	3.54	2.8	1.55

Maximum amount of tannin and lignin was noted during pre monsoon in all systems. The values were in the range of 3.45 mg g^{-1}-7.15 mg g^{-1}. Highest was observed in 1 and the lowest in 3. A gradual decrease was noted upto 10cm depth and then an increase at the lowest layer in all systems. In the monsoon, the values were in the range 0.97mg g^{-1} -3.95mg g^{-1}. Maximum was observed in system1 and minimum in system 2. There was a decrease towards the depth in 1. But in systems 2& 3, the same trend was observed in this season also. Comparatively lower amount was observed during this season in all stations. The values fluctuated between 0.56 mg g^{-1} - 1.71 mg g^{-1} with a maximum in system1 and minimum in system 3. In the system 2, the concentration of tannin & lignin increased towards the depth and reached a maximum at 15cm. But in system 1, a gradual increase was increase was noted upto 10cm and then a decrease. Similar trend was observed in system 3 also.

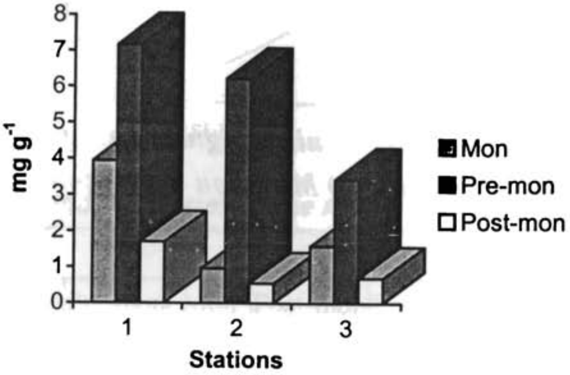
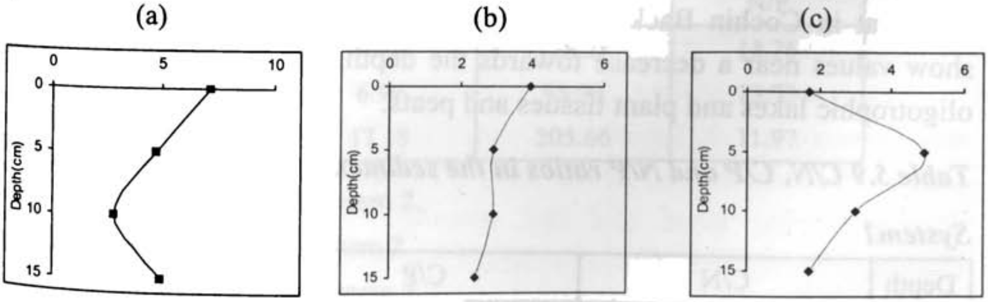
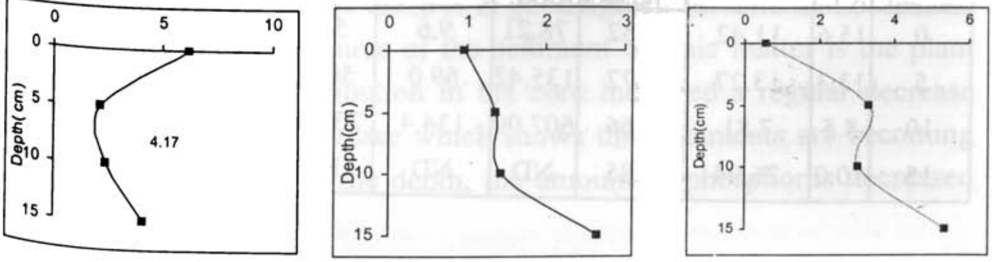


Fig 5.4 Distribution of Tannin and lignin in the surface sediments (mg g^{-1})

System 1



System 2



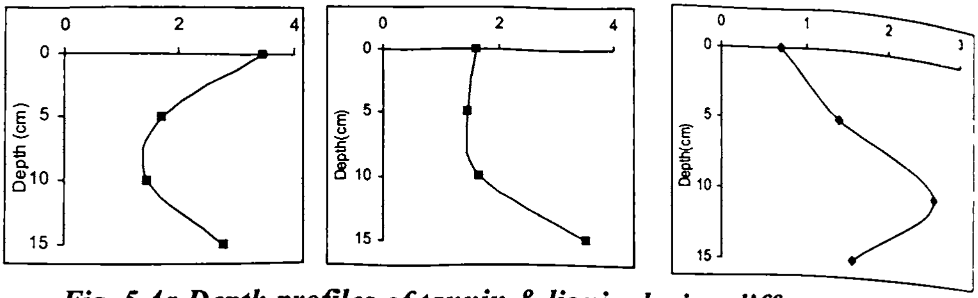


Fig. 5.4a Depth profiles of tannin & lignin during different seasons (a) Pre-Monsoon (b) Monsoon (c) Post-monsoon

5.5 Discussion

1. C/N, C/P ratio

The C/N and C/P ratios of the sediment and the leaves are given in the Table 5.9, 10, 11. The C/N and C/P of the leaves in this system is in good agreement with that of the sediment. Slight variations are noted in the pre-monsoon which could be due to the mineralisation of organic matter in the sediments. The observed value of C/N in this system is in close agreement with that in Cochin Back waters (Table 5.12). The profile of C/N ratios show values near a decrease towards the depth, but lies within that of the oligotrophic lakes and plant tissues and peats.

Table 5.9 C/N, C/P and N/P ratios in the sediments and leaves of system I

System I

Depth (cm)	C/N			C/P			N/P		
	Mon	Post- mon	Pre-mon	Mon	Post-mon	Pre-mon	Mon	Post-mon	Pre-mon
0	15.6	11.42	6.52	78.21	9.6	5.08	5.01	0.84064	0.78
5	13.3	13.27	3.72	135.42	69.0	50.42	10.21	5.2	13.54
10	8.5	7.81	6.66	607.00	134.4	233.00	71.10	17.2	35.00
15	10.0	26.94	7.85	ND	ND	ND	ND	ND	ND

	C/N	C/P	N/P
Mav	11.57	143.85	12.43
Mac	9.38	93.37	9.95
Mrh	15.30	138.35	9.04

Mav - Avicennia in system 1
Mac - Acanthus in system 1
Mrh - Rhizophora in System 1

Table 5.10 C/N, C/P and N/P ratios in the sediments and leaves of system II

Depth (cm)	C/N			C/P			N/P		
	Mon	Post- mon	Pre-mon	Mon	Post-mon	Pre-mon	Mon	Post-mon	Pre-mon
0	12.17	11.31	6.56	ND	58.14	30.36	ND	5.14	5.14
5	13.78	31.05	8.04	27.44	5.99	ND	1.99	0.19	0.19
10	14.51	15.54	3.81	23.64	76.37	14.62	1.63	4.91	4.91
15	15.92	20.14	5.39	6.40	110.98	46.58	0.40	5.51	5.51

Leaf	C/N	C/P	N/P
Vav	9.32	128.28	13.76
Vac	6.99	95.94	13.73
Vrh	17.18	205.66	11.97

Vav - Avicennia in system 2.
Vac - Acanthus in system 2
Vrh - Rhizopora in system 2.

In this system also, the value is in good agreement with that of leaves. This indicated the main source of the sediment organic matter is the plant remains. The vertical distribution in the core indicated a regular decrease upto 10cm and then an increase which shows that sediments are becoming poor in nitrogen. Towards the depth, the amount of phosphorus decreased indicating preferential phosphorus removal occurs prior to deposition and burial of the organic matter.

Table 5.11 C/N, C/P and N/P ratios in the sediments and leaves of system III

Depth (cm)	C/N			C/P			N/P		
	Mon	Post- mon	Pre-mon	Mon	Post-mon	Pre-mon	Mon	Post-mon	Pre-mon
0	47.79	10.33	8.76	58.65	86.58	29.78	1.23	8.38	3.40
5	36.98	18.31	12.01	113.25	ND	15.78	3.06	ND	1.31
10	6.65	13.11	8.48	27.17	14.52	ND	4.09	1.11	ND
15	ND	4.67	8.84	ND	ND	90	ND	ND	10.18

Leaf	C/N	C/P	N/P
Nav	21.04	305.46	14.52
Nac	14.60	180.61	12.37
Nrh	20.52	221.04	10.77

In this system the value of C/N is high, but is in agreement that of plant remains and peats (Waksmann, 1933; Brenner et al., 1978). The high value indicated poor protein in sediments than in leaves.

Comparison of the C/P and N/P values with the earlier works indicate that, the system 2 & 3 is having comparable values of C/P in the surface as well as deep sediments. In the case of system 1, the postmonsoon values showed similar trend and the monsoon value was found to have considerably high value. The phosphorus content was low compared to the carbon in all the cases where a high C/P was observed. Rather than the amount of nitrogen, the phosphorus content was found to be the governing factor in the N/P ratio also. The trend given in the N/P ratio when it is compared with the C/N in fact should have attracted a different interpretation for the geochemistry of sediments of these systems, but for the value of the phosphorus and C/P, it is comparable.

Table 5. 12. Comparative values of C/N, C/P, and N/P ratios from a variety of investigations.

Region	Ratios	References
India:		
-Cochin Backwaters	C/P 2.25:1 to 37.5:1 C/N 2.3: 1 to 16.9:1 N/P 1.2:1 to 4.07:1	SANKARANARAYANAN & PANAMPUNNAYIL (1979)
-Cochin Backwaters	C/P 22.6:1 to 60.4:1 C/N 5:1 to 10.5:1	QASIM & SANKARANARAYANAN (1972)
-Cochin wetland Sediments	C/P 15.37:1 to 36.77:1 C/N 1.22:1 to 5.27:1 N/P 3.69:1 to 17.23:1	LIZEN MATHEWS (2000)
-Natural Plankton	N/P 13.8:1	SEN GUPTA et al. (1976)
-Culture Plankton	N/P 18.2:1	
-Sediments of Mandovi Estuary, Goa	C/P 1.53:1 to 38.5:1 C/N 0.21:1 to 2.0:1 N/P 2.92:1 to 37.51:1	NASNOLKAR et al. (1996)
USA (California):		
-Sediments of Catalina	N/P 5.8:1(average)	RITTENBERG et al. (1955)
-Sediments of Santa Barbara	N/P 3.3:1(average)	
-Sediments of Santa Monica	N/P 1.4:1(average)	
Pacific ocean:		
-Completely oxidized Sediments	C/N 2.2:1 to 5.0:1	MULLER (1977)
Arabian Sea:		
-Shelf Sediments	C/N 2.48:1 to 37.5:1 C/P 1.0:1 to 8.0:1	BHOSLE et al. (1977)
Finland:		
-Coastal Waters of the Archipelago Region	C/N 7.4 C/P 42 N/P 72	HEISKANEN and TALLBERG (1999)

5.6 Reactivity of the Sediments

The decay rate of C and N indicate that the main reactivity is in the first 5cm. It has already been mentioned that the first 5cm is subjected to resuspension and significant bioturbation moreover the availability of the molecular oxygen due to the depth characteristics of the overlying water also may be a reason for the enhanced reactivity.

Table 5.13 Decay Ratio of sediments in three systems

	dc15/dc10			dn15/dn10		
	Premon	Mon	Post	Premon	Mon	Post
System 1	0.88	0.59	0.79	0.74	0.51	0.23
System 2	1.11	0.87	1.42	0.78	0.79	1.10
System 3	1.04	0.51	0.40	1.00	Nd	1.14

The decay ratio at 10 and 15cm are comparable to each other suggesting a uniform decay pattern. The 15cm data in the case of monsoon and postmonsoon exhibit a random character, which can be attributed to the effective release of OM from that depth zone. It is to be noted that attempts to differentiate between the sediment and pore water contributions haven't been done here primarily because the intention was to identify the actual amount of OC and nitrogen (the total available OC) and also the sediment characteristics. Semi solid or colloidal nature shown by the sediments didn't permit the clear separation of pore water from the sediment. Studies to identify the pore water contribution in this geochemical zone are in vogue.

As it can be seen from the data (Table 3.8), the refractive substances including Tannin and lignin constitute the major fraction of the organic matter in the sediment. Even though no attempt has been made to isolate the reactive organic component or matter from the total content, the observed values of the tannin and lignin indicate a substantial accumulating tendency of the refractory substances. This would definitely contribute or modify the reactivity calculations and the randomness observed in the geochemical reactivity in fact supports this argument.

To assess the reactivity of the systems, the classic one G model (Berner, 1989) with slight modifications to suit to the system was employed here. The equation quoted by Colombo et al (1996) is given as:

$$Gz = Gu + (Gs-Gu)\, e^{-\lambda z.}$$

where Gz is the concentration of organic matter at a specified depth Z, Gu is the concentration of unreactive organic matter, i.e the bottom of the core, Gs-Gu is the concentration of reactive organic matter, with Gs as the concentration in the top 0-3 cm and λ is the attenuation factor.

$$\lambda = \omega/2Db - [\ (\omega/2Db)^2 + k/Db]^{1/2}$$

where Db is the biological mixing coefficient, ω is the sedimentation rate and k is the apparent first order decay of the species in question. The values of Gs and Gu were obtained from the profiles. The model was applied to the data assuming constant Db,ω and k.

While adopting the model to the present study, the biological mixing coefficient is replaced by the average flushing time. In the present systems, the tidal action is the major contributor to the flushing processes. So the average time for a tidal cycle has been taken as the flushing time. As it has already been mentioned, the first 5cm of the sediment is considered as the surface sediment which will be subjected to maximum diagenetic processes. This part of the sediment in fact takes part in the geological processes like sedimental resuspansion and also to the bioturbation. So the decay constant was evaluated from the ratio of organic carbon in the surface and 5cm depth of the sediment. The decay constant is given as

$$\text{Decay constant} = G_5 - G_0 / G_0$$

Due to the low depth characteristics of the over lying water and the shallowness of the water column, a direct estimation of the sedimentation rate is impossible in the present systems. As the sedimentation rate is proportional to the POC flux in the present calculations, the POC flux /area has been utilized to replace the sedimentation rate in the equation. The values corresponding to these parameters are subject to modifications due to the seasonal contributions. The attenuation factor was so calculated independently for the three seasons.

Table 5.14. Comparison of Calculated & Observed value of various organic compounds in system 1

	10		15	
Carbon	Cal	Obs	Cal	Obs
Mon	61.78	52.25	61.80	45.37
Pre	26.14	28.88	26.14	28.88
Post	35.69	26.02	35.83	49.94
Nitrogen				
Mon	4.48	3.6	4.48	2.85
Pre	3.25	6.83	3.25	5.36
Post	1.20	2.26	1.24	2.48
Carbohydrates				
Mon	10.25	10.39	10.261	6.13
Pre	2.1498	2.53	2.1498	2.56
Post	2.11	2.93	20.901	2.53
Protein				
Pre	7.40	9.45	7.40	7.04
Mon	1.23	1.93	2.03	2.96
Post	7.21	4.92	6.41	4.81
	Attenuation factor (y)			
	pre	0.00001		
	post	-0.0002		
	mon	0.001		

The parameters as well as the attenuation: factor from the calculations is given in the Table 5.13, 14 &15.The amount of organic carbon, nitrogen, carbohydrate, protein at different depths of the sediment was calculated using the attenuation factor. The calculated results are given in table 1,2,3.The comparison of these values indicate that in all the systems, the observed value at low depth is in good agree with the calculated value. But this agreement id observed only for the premonsoon period in the case of 15cm depth. The monsoon and post monsoon observed values considerably vary with calculated value. The difference may be due to the difference in the affect of the seasons at depths. The close agreement between the observed and calculated approved the considerations put forth for the computation of the data. Significant seasonal contribute to the OC in the different depths of the sediment with earlier reported work (Klump et al 1980). Here also, no concrete explanation is offered expect that the system characteristics above the sediment is significantly different for three reasons.

Table 5.15 Comparison of Calculated & Observed value of various organic compounds in system 2

Carbon	obs	cal	obs	cal
Post	13.5	13.03	5.46	13.04
Pre	9.5	8.10	9.90	8.12
Mon	12.5	18.23	6.40	18.29
Nitrogen				
Post	1.03	0.71	1.17	0.72
Pre	1.12	0.68	1.12	0.69
Mon	1.88	0.49	ND	0.49
Carbohydrate				
Post	1.52	0.71	1.62	0.74
Pre	0.98	0.72	0.62	0.72
Mon	1.54	1.36	3.86	1.36
Protein				
Post	7.53	16.33	14.29	16.33
Pre	4.51	4.37	21.09	4.38
Mon	0.13	0.95	0.62	0.95
	Attenuation factor (y)			
	Post	-0.0003		
	Pre	-0.00023		
	Mon	-0.00056		

Table 5.16 Comparison of Calculated & Observed value of various organic compounds in system 3

	10		15	
Carbon	Obs	Cal	Obs	Cal
Post	33.60	45.18	26.40	46.32
Pre	23.30	25.28	20.40	25.15
Mon	60.70	55.69	36.10	60.14
Nitrogen				
Post	4.30	9.99	0.98	6.18
Pre	3.50	6.85	2.60	7.03
Mon	7.11	4.86	3.60	4.84
Carbohydrates				
Post	1.62	4.52	1.5	5.26
Pre	1.42	2.26	1.74	2.21
Mon	3.18	3.95	3.18	4.01
Protein				
Post	2.26	4.03	2.52	4.62
Pre	3.55	17.06	1.04	20.29
Mon	0.45	0.55	0.23	0.56
	Attenuation factor (y)			
	Pre	-0.06		
	Post	-0.05		
	Mon	-0.01		

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Summary

Intertidal sedimentary environments are important areas for scientists to study, and there is along history of such works. But this has often focused on the geomorphology of these areas and how this can interpret the geological record and the ecology of these areas. But it does not focus on the chemistry of these systems. The primary productivity of these areas is highly linked to offshore communities. This high productivity is supported in part by high rates of nitrogen fixation Very little of the productivity of marshes and mangroves appears to be grazed while alive, but is rather decomposed by micro organisms partly in or on the sediments, together with the products of benthic algal production and partly after export to adjacent coastal waters. Thus these sediments are rich in organic matter. The present study revealed higher concentration of carbon in the surface sediments.

In the mangroves, tidal flushing causes exchange of different materials such as organic carbon, nutrients, pesticides and radionuclieds with the adjacent water masses. When the tide has ebbed there is no overlying water present and there can be no dissolved output from the sediments which result in increasing the concentrations of dissolved substances which have a source within the sediments. In the present study, higher values for dissolved nutrients, POC, and carbohydrates were observed during low tide.

The area of sediment exposed and the length of exposure changes as the tide range alters. As a result the intertidal areas are subjected to sufficient ventilation of oxygen at times. This leads to a mixed aerobic and anaerobic diagensis of the sediments. When the water is not present, a substance whose source is the water and is consumed in the sediment may become depleted. When the water returns to flood the sediment, a high concentration of various substances may then be released. Thus the sediments can act as both the sinks and sources of different nutrients and different compounds and there is material exchange between the ecosystem and the adjacent water body. Even though there is much practical difficulty in the assessment of budget for these exchanges in these areas, an attempt is done in the case of particulate carbon. The assessment revealed an outflow of POC in the 1st and 2nd systems.and an inflow in the 3rd system.

The major temporary or ultimate sink for various pollutants in estuaries is the sedimentary reservoir, including intertidal areas. The historic record of the sedimentation as well as its diagenetic behavior can be obtained from the depth profile study. Due to the complex root system in these ecosystems, the study could be extended only upto 15cm. A gradual decrease in the amount of carbon towards the depth is observed in this area. The biomixing of labile organic carbon downwards will result in a convex up profile in this zone. Here the sedimentation rate and the carbon burial rate are sufficiently low, relative to diffusion, to extend the processes of early diagenesis over tens of meters. In the upper muddy sediments the vertical variation in degree of anaerobic activity is probably controlled by the balance between organic carbon content and oxygen availability, both of which decline with depth. Seasonality in the distribution of organic compounds such as carbohydrates, proteins, tannin and lignin in the core and in the microbial content of the surface sediment is observed. Many of these processes are biologically mediated which have a marked seasonality in temperate regions. The redox reactions in sediments also show a seasonality through the seasonal input of organic matter from the growth cycle of marsh plants. Redox and pH conditions can also change on short time scales as a result of tidal pumping and intrusion of air during the tidal drying of tidal flats. Variation of the estimated compounds between the 5 and 10cm layer is observed in this area. A gradual decrease towards the depth is expected, but an increase in the 5 and 10 cm layer is noted. But in the case of tannin and lignina storage towards the depth is noted in the post monsoon.

Appendix

Variation of pH in Water

Month	1H	2H	1L	2L	3	4	5	6
Nov	7.4	7.4	7.2	7.1	7.4	7.1	6.9	6.9
Dec	7.6	0.6	7.2	7.2	7.3	7.1	6.6	7.4
Feb	7.9	7.6	7.3	7.1	7.4	7.3	7.8	8
Apr	8.4	8.9	7.4	8.2	7.9	8.2	8.2	8.6
Jul	8.1	8.1	8.1	7.8	7.7	7.8	7.8	8.2
Aug	7.8	7.7	8	7.4	7.5	7.6	7.3	7.4
Nov	7.5	7.6	7.7	8.2	8	8.1	8.1	8.6

Variation of Dissolved Oxygen (ml l^{-1})

Month	1H	2H	1L	2L	3	4	5	6
Nov	4.11	4.11	7.2	7.1	2.46	0.82	3.29	3.29
Dec	2.05	4.1	7.2	7.2	0.82	1.62	3.29	5.76
Feb	2.05	3.07	7.3	7.1	1.02	1.02	3.07	4.11
Apr	0.46	3.68	7.4	8.2	1.84	1.38	3.68	3.22
Jul	1.3	5.23	8.1	7.8	1.96	3.92	5.88	6.5
Aug	4.62	4.97	8	7.4	1.42	1.42	6.04	3.55
Nov	3.25	3.54	7.7	8.2	2.07	0.59	3.25	2.95

Variation of Salinity (ppt)

Month	1H	2H	1L	2L	3	4	5	6
Nov	6	10	5	5	13	10	2	3
Dec	13	13	12	10	23	14	8	9
Feb	18	17	20	20	27	24	15	17
Apr	19	19	18	15	23	22	13	13
Jul	0.05	0.07	1.67	0.74	4.55	2.08	0.43	0.98
Aug	0.61	0.33	0.94	0.82	2.97	2.61	0.74	1.01
Nov	12	14	16	13	29	26	9	16

Variation of Alkalinity (mmoles l^{-1})

Month	1H	2H	1L	2L	3	4	5	6
Nov	0.23	0.11	0.7	0.7	0.73	0	0	0
Dec	0.19	0	0.96	0	0.8	0.42	0.4	0.2
Feb	0.54	0.54	0.23	0.54	0.41	0.63	0.54	0.57
Apr	3.1	1.19	0.72	1.67	2.38	2.62	2.62	3.57
Jul	8.19	4.21	8.36	3.32	6.15	3.4	11.8	3.99
Aug	3.12	2.12	2.09	10.8	8.13	8.55	1.11	6.67
Nov	1.82	1.67	1.47	2.14	2.69	2.09	0.90	1.19

Variation of Chlorophyll (μg l^{-1})

Month	1H	2H	1L	2L	3	4	5	6
Nov	4.9	4.9	2.4	4.8	2.6	5.2	0.46	2.6
Dec	5.9	8	12	10	2.5	2.5	1	2.5
Feb	12	4.4	15.7	3.9	4.6	4.9	1.2	4.6
Apr	6.3	6.87	7.5	4.45	6.1	4.06	5.09	4.23
Jul	90.01	171.48	107.16	69.15	71.8	91.41	41.51	90.02
Aug	59.01	11.79	58.46	20.25	51.96	54.32	35.76	34.1
Nov	6.32	5.67	5.87	5.32	3.9	8.41	7.42	8.14

Variation of POC (mg g $^{-1}$)

Month	1H	2H	1L	2L	3	4	5	6
Nov	3.18	3.18	3.18	3.18	6.36	6.36	3.18	3.18
Dec	20.71	5.18	49.2	2.6	2.59	2.59	0	0
Feb	11.5	4.8	33.6	2.7	8.18	7.58	11.6	0
Apr	34.69	1.58	22.19	2.86	3.32	1.12	2.6	0
Jul	38.18	0.91	50.15	4.09	19.38	8.77	2.54	6.15
Aug	10.12	2.04	24.25	6.94	1.31	2.31	1.29	2.84
Nov	3.82	1.82	5.31	4.82	8.09	4.24	3.83	1.82

Variation of Nitrate (µg-at l^{-1})

Month	1H	2H	1L	2L	3	4	5	6
Nov	73	123.5	96	103.5	18.1	21	8.5	4
Dec	2.1	3.36	0.63	1.12	6.71	2.21	16.6	7.82
Feb	12.8	10.26	0.72	23.43	4.13	5.96	22.2	3.37
Apr	56.65	12.75	16.6	16.49	2.76	4.1	6.72	24.81
Jul	29.7	27.85	29	24.24	10.33	23.22	34.79	29.37
Aug	42.87	30.77	23.46	18.57	6.44	5.47	22.57	18.16
Nov	23.14	28.89	17.98	11.38	11.78	16.32	7.23	2.84

Variation of Nitrite (ug-at l $^{-1}$)

Month	1H	2H	1L	2L	3	4	5	6
Nov	1.05	0.85	1.05	0.85	0.867	2.96	1.44	1.4
Dec	0.11	0.48	0.11	0.48	0.17	0.08	0.51	0.65
Feb	2.06	1.76	2.06	1.76	4.69	4.88	1.07	6.27
Apr	3.09	0.36	3.09	0.36	0	0.47	0.81	0
Jul	1.27	0.81	1.27	0.81	0.73	1.3	0.85	0.49
Aug	30.35	2.66	30.35	2.66	1.22	1.02	2.01	1.89
Nov	3.65	0.68	3.65	0.68	0.46	1.68	2.08	0.67

Variation of Phosphate (µg- at l^{1})

Month	1H	2H	1L	2L	3	4	5	6
Nov	0.48	0.85	3.73	0.19	0.19	5.2	0.037	0.01
Dec	0.22	0.48	0.66	0.2	0.2	2.5	0.09	0.01
Feb	0.11	1.76	0.28	0.46	0.21	4.9	0.18	0.5
Apr	23.56	20.01	24.89	2.88	2.82	4.06	4.03	7.17
Jul	6.48	27.9	15.93	24.37	18.71	91.41	4.45	5.45
Aug	5.88	6.22	21.58	20.89	11.17	54.32	4.88	2.75
Nov	15.62	5.76	78.29	25.44	5.46	8.41	3.02	1.37

Variation of Protein (mg l^{1})

Month	1H	2H	1L	2L	3	4	5	6
Nov	5.09	7.45	3.91	3.45	8.55	8.09	2.27	2.18
Dec	3.81	4.9	5.09	3.81	11.72	10.63	4.27	4.27
Feb	7.59	8.94	2.93	5.84	11.34	10.39	0.06	1.25
Apr	0.18	4.55	1.79	0.08	4.41	0.18	1.93	0
Jul	8.91	8.95	13.53	8.58	11.51	7.98	11.7	11.29
Aug	13.35	15.55	13.16	9.57	14.26	13.81	13.71	12.8
Nov	6.43	6.32	2.17	2.98	10.43	8.47	2.65	1.97

Variation of Carbohydrate (mg l^{-1})

Month	1H	2H	1L	2L	3	4	5	6
Nov	4.15	6.53	8.81	7.45	15.08	20.25	8.81	10.34
Dec	0.93	1.86	5.16	11.53	0	7.71	ND	ND
Feb	2.79	4.83	10.59	6.86	7.03	6.36	10.59	3.05
Apr	1.75	1.19	0.98	1.47	1.12	1.59	0.49	0.77
Jul	88.63	37.53	64.65	50.9	31.24	23.3	4.9	7.26
Aug	24.95	23.77	15.13	0.58	11.98	19.05	45	15.91
Nov	7.43	4.32	11.45	5.36	17.8	20.21	13.23	11.25

Variation of Tannin and Lignin(mg l^{-1})

Month	1H	2H	1L	2L	3	4	5	6
Nov	0.09	0.07	0.37	0.09	0.09	0.07	0.057	0.054
Dec	0.35	0.19	2.07	0.35	0.32	0.17	0.11	0.091
Feb	0.12	0.07	0.08	0.12	0.07	0.01	0.17	0.046
Apr	0.97	0.12	0.97	0.97	0.15	0.03	0.05	0.023
Jul	0.32	0.05	0.36	0.32	0.06	0.03	0.03	0.01
Aug	0.302	0.026	0.32	0.302	0.054	0.023	0.02	0.01
Nov	0.072	0.049	0.31	0.072	0.13	0.085	0.042	0.186

Distribution of protein in the surface sediment (mg g^{-1})

Month	1	2	3
Nov	11.66	9.84	28.05
Dec	0.91	1.8	8.44
Feb	14.02	9.8	11.74
Apr	45.07	21.45	13.24
Jul	1.37	0.87	0.18
Aug	0.31	1.72	0.16
Nov	7.53	7.63	21.93

Depth profile of protein in the core sediment (mg g^{-1})

Month	1			2			3		
	5cm	10cm	15cm	5cm	10cm	15cm	5cm	10cm	15cm
Nov	2.29	2.8	2.09	7.16	2.12	3.24	5.87	6.65	15.46
Dec	2.37	1.58	3.43	7.8	9.73	8.45	38.98	10.18	14.17
Feb	2.01	2.13	2.25	8.85	8.35	3.54	8.03	7.08	17.1
Apr	11.9	4.98	0.84	5.97	10.55	10.55	0.68	1.94	25.08
Jul	0.73	0.84	0.21	1.09	2.27	2.68	0.5	0.25	0.62
Aug	0.31	0.05	0.25	1.37	1.6	3.25	1.4	0.012	ND
Nov	2.21	2.35	2.16	6.83	1.98	2.76	4.32	5.73	13.24

Distribution of Carbohydrate in the sediment (mg g^{-1})

Month	1	2	3
Nov	9.31	17.06	13.33
Dec	3.95	6.03	9.78
Feb	0.18	0.37	0.533
Apr	3.96	4.42	2.58
Jul	4.84	6.18	2.05
Aug	5.71	6.84	0.86
Nov	10.32	11.36	11.4

Depth profile of Carbohydrate in the core sediment (mg g^{-1})

Month	1			2			3		
	5cm	10cm	15cm	5cm	10cm	15cm	5cm	10cm	15cm
Nov	1.38	1.14	1.03	0.67	1.89	1.7	5.87	6.65	15.46
Dec	4.13	2.7	2.59	4.43	4.76	3.81	38.98	10.18	14.17
Feb	3.62	2.09	2.63	2.82	2.97	1.52	8.03	7.08	17.1
Apr	1.19	0.75	0.86	1.48	2.09	3.6	0.68	1.94	25.08
Jul	3.51	2.18	2.88	9.71	10.15	5.78	0.5	0.25	0.62
Aug	4.12	4.38	3.68	10.8	10.64	6.49	1.4	0.012	ND
Nov	1.26	1.02	0.98	1.23	2.12	2.06	4.32	5.73	13.24

Distribution of Organic carbon in the sediment (mg g^{-1})

Month	1	2	3
Nov	78	40.32	30.08
Dec	120.2	34.53	30.14
Feb	36	20.93	15.09
Apr	60.44	29.55	28.2
Jul	56.66	41.59	5.93
Aug	82.57	60.64	65.55
Nov	123.4	75.25	7.33

Depth profile of Organic carbon in the core sediment (mg g-1)

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

Distribution of Tannin &Lignin in the sediment (mg g^{-1})

Month	1	2	3
Nov	1.45	0.63	0.57
Dec	1.45	0.33	1.32
Feb	6.25	5.32	2.45
Apr	8.05	7.17	4.48
Jul	2.98	0.86	2.32
Aug	4.82	1.08	0.96
Nov	1.98	0.72	0.37

Depth profile of Tannin & Lignin in the core sediment (mg g^{-1})

Month	1			2			3		
	5cm	10cm	15cm	5cm	10cm	15cm	5cm	10cm	15cm
Nov	3.63	3.63	1.55	3.92	2.96	6.8	1.59	2.69	1.65
Dec	7.98	2.52	2.21	4.39	4.21	5.35	1.19	2.65	2.05
Feb	3.91	2.21	2.98	1.86	4.13	6.6	1.89	0.92	3.95
Apr	5.58	3.4	4.72	2.59	0.73	1.73	1.55	2.02	1.66
Jul	2.64	2.89	2.09	1.04	0.96	1.38	1.23	0.95	3.54
Aug	3.25	2.93	2.76	1.68	1.92	3.95	1.68	2.41	ND
Nov	3.24	2.86	1.42	1.68	1.92	3.95	1.37	2.53	0.94