SURFACE ACTIVE SUBSTANCES IN THE COCHIN ESTUARINE SYSTEM

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PREFACE

The hydrosphere which constitutes about 71% of the earth's crust contains more than 70% life on earth. Though the estuaries and inshore waters are only a minor fraction in the hydrosphere, these water bodies are the most productive areas in the aquatic realm. The ultimate sink of solid and liquid pollutants is the ocean but almost all of them exhibit their reactivity mainly in these land adjacent water bodies. The impact of human activities is at its maximum in these aquatic systems. A large variety of chemical entities are discharged in to these waters regularly making these the most polluted system. Being the nursery for many fishes, shrimps, bivalves etc., these waters warrants immediate attention for the proper management and the protection of this invaluable treasure.

The Cochin Estuarine System (CES) is a tropical complex positive tidal system, which has been seriously affected by the heavy load of pollutants dumped from the industrial conglomorate on the banks. This system along with the coastal waters of Kerala constitutes the most productive zones in the southwest coast of India. The components of untreated sewage, which most adversely affect the receiving waters, include suspended solids, floatable, plastic bags, bacteria, organic matter, nutrients, trace metal and other toxicants etc. These constituents are also present in varying degrees in water treatment plant effluents, industrial effluents, urban runoff, riverine inputs, and atmospheric deposition.

Organic matter in an estuary, comprising of a complex mixture of different dissolved, colloidal and particulate organic compounds, originates from several sources. The synthetic detergents, the major constituent of which is anionic surfactants represent the most significant surface active compounds entering the estuarine and riverine environment. Humic/ fulvic acids and phenols are the major natural surface active substances in the aquatic systems. Surface active substances influence the structure and physico chemical properties of natural interfaces and mediate the processes of mass and energy transfer between different phases. An increased concentration of surfactants in natural waters affects the exchange processes of gases and ions, as well as colloid stability and the formation of solid phase in natural aquatic systems. As a consequence of their complex structure, these surfactants are able to interact both with heavy metal ions and with many organic substances, which are considered as pollutants.

This thesis contains the results of the investigations on Surface active substances in the Cochin Estuarine System. The thesis is divided in to five chapters. Chapter 1 gives general introduction to the surface active substances, anionic surfactants and phenols with special reference to their behaviour in aquatic systems. This chapter contains a brief description on the estuarine system and character and properties of the organic matter in the system. This chapter also includes the aim and scope of the study.

Chapter 2, Location, materials and methods. This chapter gives the location of the study area and techniques used for sampling and preservation. Analytical procedure for the determination of anionic surfactants, phenols, chlorophenols, boron, hydrographic parameters and sediment characteristics are also incorporated. The results of hydrographic parameter temperature, salinity, dissolved oxygen and pH and sediment characteristics such as grain size and organic carbon also forms part of this chapter.

Chapter 3 gives the results of the analysis of the samples of various surface active substances, which includes anionic surfactants (MBAS) and phenols (4- AAP method), in the water and sediment samples of the CES. The geographical distribution pattern, seasonal variations and their relations with other parameters are also discussed in this chapter.

Chapter.4 deals with the distribution and seasonal variation of o-chloro, m-chloro, p-chloro and other seven fractions of chlorophenols present in the water and sediment samples of CES. The chapter contains a brief report on the seasonal characteristics of these compounds also.

Chapter.5, the modeling of the CES using boron as a tool. A kinetic approach utilising the distribution pattern of boron to define the reactivity of the CES is attempted here. The model is used to explain the trends given by MBAS and Phenol.

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Chapter 1

Introduction

The recent trends in scientific scenario demand an educational and research program, which promotes a sustainable development and promotion of biodiversity. The hydrosphere, being the prime supporter of life on the earth, requires a special attention because of the high human interactions. Coastal lines, estuaries and inland water are the most susceptible in their [illegible]. These regions are the most productive and dynamic systems of the hydrosphere and the zones of direct human intervention. The advancement of technology and industry resulted in an increased input of a large variety of contaminants into these systems. The environmental variabilities being maximum in the estuarine and coastal systems, these waters are considered to be the most vulnerable to the impact of contaminants.

Generally environmental contamination is considered to be synonymy with environmental toxicity. In the aquatic system, the manifestation of the effects need not be completely attributed to toxicity. In many cases indirect involvement in the modification of life parameters is also observed. The best examples are the depletion of oxygen, nutrients, blocking of breathing by organic compounds etc. The estuaries being semi-enclosed restricted water bodies, such effects are very common along with the toxicity.

Estuarine and coastal marine environments are susceptible to a multitude of human wastes from a burgeoning population in the coastal zone. These highly sensitive ecosystems serve as reservoirs for dredged spoils, sewage sludge, industrial and municipal effluents and other types of pollution.

1.1 Estuarine System

Cameron and Pritchard (1963) defined an estuary as a semi-enclosed coastal body of water, which has free connection with the open sea, and, with in which, seawater is measurably diluted with freshwater derived from land drainage. Fairbridge (1980) defined it as an inlet of the sea reaching in to river valley as far at the upper limit of tidal rise, normally being divided into three sections: the lower estuary, maintaining free connection with the sea; the middle estuary, subject to strong salt and freshwater mixing; upper estuary, dominated by freshwater but exposed to tidal movements.

Estuarine environments are amongst the most productive and sensitive ecosystems. Their importance in terms of carbon fixation, fisheries habitat, nutrient assimilation, water storage and sediment stabilisation has been recognised for a long time (Odum, 1983).

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Historically, marine sediment is considered to be the ultimate sink for many classes of anthropogenic contaminants. However, the studies by Loganathan and Kannan, (1991) have demonstrated that during the last decade environmental regulation has resulted in a reduction in the loading of waste from terrestrial sources, but the marine sediment reservoir could act as a non-point source, and has the potential to release the `in place contaminants' causing adverse effects to organisms and human health through tropic transfer.

Organic pollutants can be found in diverse environments and their properties indicate that they have long term deleterious effects and are of potential threat to human health. However, due to their chemical complexity and trace levels of presence in the environment, organic pollutants in water and sediment have not been studied as extensively as metals.

Estuarine water has a natural ability to accept and assimilate limited amount of organic matter and other pollutants without visible harm and damage. Given sufficient time and dilution (Topping, 1976; Kennish, 1990; Nedwell *et al.*, 1990), the estuarine water can assimilate degradable organic and inorganic substances, but unassimilated materials, such as long life radioactive wastes and synthetic organic compounds, will accumulate and remain essentially unaltered in the marine environment(Park and O'Conner., 198

Park *et al.*, 1983, Eisenbud, 1988, Gage & Tayler., 1991). The persistence of these hazardous wastes in the marine environments may pose a long-term danger to marine food webs. Physical, chemical and biological processes taken together therefore, not only govern the distribution of anthropogenic wastes, but also their fate and overall effect on the marine environment by altering the concentration, chemical form, bioavailability or toxicological strength of contaminants.

The principal environmental concerns of waste disposal in the marine environment are the following (1). The accumulation and transfer of metals and xenobiotic compounds in marine food webs, including accumulation in commercial resources. (2). The toxic effects of such contaminants on the survival and reproduction of marine organisms and the resulting impact on ecosystem. (3). The uptake and accumulation of pathogenic organisms in commercially harvested species destined for human consumption. (4). The release of degradable organic matter and nutrients to the marine environment was resulting in localised eutrophication and organic enrichment (Cupuzzo *et al.*, 1985).

Our geological understanding is further tempered by Schubel and Hirscheberg (1978) who note that "estuarine deposit rarely can be delimited unequivocally from other shallow water marine deposits in the geological record because of their limited area extent, their ephemeral character and their lack of distinctive features". It is believed that estuaries figure significantly in the sedimentary make up of a coastal system, or frame work of estuarine environments: lagoon-bay-inlet-total tidal flat and marsh. The physiology of organism with in estuarine habitats depends on suspended solids, turbidity, temperature, salinity, chlorophyll a, nutrients, trace metals, toxic organic chemicals concentrations.

1.2 Organic matter in Estuaries

Organic matter present in estuarine water comprises of a wide spectrum of natural and anthropogenic compounds, which includes carbohydrates, proteins, lipids, pesticides, hydrocarbons, phenolic compounds, surfactants, fatty acids, amino acids, humic substances, etc. Surface active substances are those compounds, which lower the surface tension of liquids. The synthetic detergents represent the most significant surface-active compounds entering the estuarine and riverine environment, the major constituent of which is anionic surfactants. Humic/ fulvic acids and phenols are the major natural surface-active substances in the aquatic systems.

Riverine dissolved organic carbon (DOC) is an important yet poorly defined and highly dynamic component of the global carbon cycle (Likens *et al.*, 1981). Riverine DOC has a weighted world wide concentration of 5.75 mg C/litre and a global flux averaging 1.25 times that of particulate organic carbon (Meybeck 1981, 1982). Riverine transport of organic carbon appears to be related to the annual production in the drainage basin (Moeller *et al.*, 1979; Mantoura and Woodward, 1983) and yields a total export to the oceans of around 6(± 4) X 10^{14}g C/year (Meybeck, 1982). Although most riverine suspended sediments are deposited at river mouths or in the coastal zones (Wangersky, 1981), riverine DOC behaves conservatively in estuaries (Manoura and Woodward, 1983) and thus has the potential to contribute significantly to offshore marine environments.

A major fraction of the DOM in natural water is composed of refractory humic compounds, three-dimensional polymers of variable composition. Although their overall structure may be complicated and ill defined, humic compounds appear to contain reasonably simple and consistent functional groups for coordination such as carbonyl, alcoholic and phenolic groups. The major fraction of the photochemical reaction in aquatic systems must be ultimately oxidative. The more suitable reductive role of these reactions may also be important in the geo-chemical cycle of trace elements.

Surfactant properties of a molecule depend on its lipophilic and hydrophilic characteristics. At interfaces (*e.g.* fat and water or water and air), the surfactant molecules assemble leading to a lowering of surface tension. At these interfaces, the development of foams leads to the production of large additional areas of interface and results in the accumulation of surfactants leading to a reduction in the concentration of surfactant in the water mass.

1.2.1 Anionic Surfactant

Surfactants are active ingredients in many consumer-cleaning products and are discharged in high volumes to domestic sewage. Typically, consumer products are discarded down the drain and surfactants are removed by a combination of sorption and biodegradation during sewage treatment. Commonly used surfactants include LAS, BAS, linear alcohol ethoxylates and monoalkyl quarternary ammonium compounds. Synthetic detergents, the active ingredients of household washing powders, contribute the major amount of surface active agents which forms part of natural aquatic systems as urban waste waters.

The surfactant end use market in 1982 was household 30% (laundry/dish washing), personal care 16% (toilet soap, shampoo) and industrial 54% (industrial and institutional process aid, etc) covering 30 million metric tons worldwide. Among the major synthetic surfactants used in the household product market are the linear alkylbenzene sulfonates, alcohol ether sulfates, whereas alkylphenol ethoxylates are used almost exclusively in industrial applications such as tanning and textile processing. Surfactants have been reported in natural waters that receive municipal wastes in the US, Japan, and the Western Europe (Maltulova, 1964; Nyberg, 1976; Margaritis and Creese, 1979; Fisher, 1980; Siva et al, 1982; Kikuchi et al., 1986; and Tarazona and Nunez, 1987). Several surfactants and their break down products also have been measured in varying degrees in drinking water (Crawthorne *et al.*, 1984; Ventura *et al.*, 1989), sewage sludge's, sludge-amended soils, and sediments (Lewis, 1990).

Surface active substances influence the structure and physico-chemical properties of natural interfaces and mediate the processes of mass and energy transfer between different phases. They are involved in the processes such as bubble flotation of particles and microlayer enrichment (Hunter, 1980; Wallace and Duce, 1987; Cosovic and Vojvodic, 1989). MacIntyre (1970) and Blanchard (1975) suggest that surfactant matter affect the properties of the sea surface and the aerosolization process. Natural surfactant matter is constituted mainly (estimated about 50-70%) by marine humic substances (HS). The fulvic acid fraction is one of the most important soluble components involved in the marine aerosol process (Loglio *et al.*, 1989; Cini *et al.*, 1994). From a chemical point of view, the fulvic acids show the characteristics of wet surfactants.

Although the Alkyl Benzene Sulphonate (ABS) surfactants are used mainly in the form of the sodium salt, these substances occur in natural waterways as the calcium salt. This salt has low water solubility and exists as an unstable suspension. It first assembles at interfaces such as air-water, fat waters and bottom sediments-water, but ultimately it gets associated with the bottom sediments as deposits. Building up of a high concentration of surfactants in sediments in areas receiving surfactant containing wastewater is a general observation.

In sea water the time required for the biodegradation of LAS seems to be rather long. At room temperature and 35 salinity, Hon-nami and Hanya (1980) found that, the half-life of 10 ppm of LAS was about 15 days, and Dalla Vanezia *et al.,* (1980) did find significant degradation in 48 hour. Cosovic (1982) found concentrations up to 0.62 ppm of anionic detergents in Rovinj Harbor (Yugoslavia). Yaramaz and Tuncer (1988) found up to 4.53 ppm of anionic detergents, mainly represented by LAS, in Izmir Bay (Turkey).

LC_{50} values of intact LAS to aquatic organisms are in the range of 0.1 to 8.2 mg/l, (Kimerle and Swisher, 1977; Brown *et al.,* 1978; Stephen *et al.,* 1986; Reif *et al.,* 1979). It is generally accepted that LAS does not give significant ecotoxicological threats, due to its easy biodegradability in waste treatment plants or in aquatic habitats, and the reduced toxicity of the intermediate biodegradation compounds (Brown, 1978: Gledhill, 1974, 1975; Larson, 1983; Vives-Rego, 1987; Martein *et al.,* 1991). Effect of LAS on marine fauna, especially in its first stage of development has been reported earlier by several authors (Hidu, 1965; Walne, 1978; Granmo, 1972).

Most of the studies made in fresh water conclude that biodegradation follows a first order kinetics (Sales *et al.,* 1987). However in saline water, the differences in number of type of microorganisms can reflect on the biodegradation processes. Sales *et al.,* (1987) studied primary biodegradation of five anionic surfactants. The degradation of LAS at temperature below 15°C, and Isohexyl-isopentyl- sulfosuccinate (HPS) 25 °C occurs with a zero order kinetic. In the first case, the observation can be attributed to the decreased bacterial activity at the lower temperatures leading to a fall in the rate of surfactant- activity making the process independent of the amount of surfactant in the medium. In the case of HPS, along with the temperature effect the scant biodegradability of the surfactant as a consequence of its highly branched aliphatic chain may be the reason for the observed kinetics (Reckman, 1975). Sales *et al.,* (1987) conducted the experiments in the presence of sediments, and it has been established that there was substantial increase in the processes of surfactant degradation.

In general, surfactants interact with membranes and enzymes. The effects can be moderated in plants by adsorption of surfactants and immobilization on cell walls (Fujita and Koga, 1976). The surfactants can cause an alteration to cellular ultra structure (Healey *et. al.,* 1971). Lundhal and Cabridenic (1974), after investigation of a range of organisms, have suggested that toxicity arises from inhibition of enzymes or the selected transmission of ions through membranes. Sublethal effects such as inhibition of growth in plants and fish (Mitrovic, 1972) budding in hydra (Bode *et al.*, 1978) and damage of respiratory epithelium of fish gills (Mitrovic, 1972) have been observed with surfactants.

1.2.2 Phenolics

Phenolics, the weak acids of aromatic hydrocarbons, due to their broad pesticidal efficiency at low cost, have been used as algaecides, bactericides, fungicides, herbicides, insecticides and molluscicides with a variety of applications in industrial, agricultural and domestic fields. The discharges of phenols from these operations find their way into water resources. A large variety of phenols are produced as byproducts also, by natural decomposition of various allochthonous and autochthonous materials (Adelman *et al.,* 1976). Due to high volatility and water solubility, phenols impart taste and odor problems to the drinking water supplies even at ppb levels (Thomas, 1973). Phenols pose a serious pollution problem adversely affecting the food chain and fish population by interfering with carbohydrate, protein and lipid metabolism, ions transport, nerve conduction and the energy production at biomolecular levels due to uncoupling of oxidative phosphorylation (Desaiah, 1978; Gupta, 1985a).

The major sources of phenolic compounds are the distillation of coal and wood; oil refineries, chemical plants; livestock dips; human and other organic wastes and hydrolyse, chemical oxidation, and microbial degradation of pesticides. Phenol is one of the most versatile and important industrial organic chemicals. It is the starting material for diverse products used in the home and industry. A partial list includes nylon, epoxy resins, surface active agents, synthetic detergents, plasticizers, antioxidants, lube oil additives, resins, polyurethane's, aspirin, dyes, wood preservatives, herbicides, drugs, fungicides, gasoline additives, inhibitors, explosives and pesticides. Some compounds are refractory to biological degradation and can be transported long distance in water.

Anthropogenic sources of phenolic compounds in marine waters include the effluents of oil refineries, chemical plants, gas works, pesticide plants, paper and pulp mills (Buikemia *et al.,* 1979), and human and other organic wastes (Babich and Davis, 1981) which includes agricultural effluents from animal husbandry and drainage of irrigation water, and urban run-off. Naturally occurring sources include seaweed secondary metabolites (Fenical, 1975; Ragan and Glombitza 1986; Gennings and Steinberg 1994) and Humic materials (Hedges and Parker 1976).

Industrial phenols are monomers and its halogenated derivatives, as well as cresols and xylenols. Phenol and substituted phenols are very common contaminants in water. For phenols, the USEPA (1986) criteria are <200 µg/l to protect organism and 1µg/l to prevent tainting of fish flesh. For chlorinated phenols, the quality levels to protect aquatic life are lower, down to, 0.5 µg/l for pentachlorophenol. Trace amounts of (<1 mg/l) phenolic compounds can have significant detrimental effects on water quality. Phenols are toxic to aquatic life and mammals and can impart objectionable taste and odors to water and fish. United States physical and chemical drinking water standards recommended a limit of 0.001 ppm for phenol in drinking water (Goldberg, & Weiner., 1980).

Phenolic compounds are frequently found as contaminants in surface waters, including riverine, estuarine and coastal waters (Krajnovic *et al.*, 1988). Phenols are generally classified as nonspecific metabolic inhibitors, and the main toxic effects are manifested on the nervous system due to the dissolution of lipids, whereas in the circulatory system phenols act as hemolysing agents of erythrocytes. In fresh water fish species exposed to phenol, the number of erythrocytes and the serum proteins were decreased. Leision of gill filaments with edema and blood infiltration with degenerative changes in liver were also observed (Waluga, 1966; Mitrovic et al., 1982, 1968). Simple phenolic compounds are common microbial degradation products of lignin (Kirk, 1984) and occurs in other substances such as tannin (Hedges, 1982), both lignin and tannin are major class of the secondary products of plant metabolism and are ecologically important

Phenols and chlorinated phenols are readily accumulated into biological tissue (Kobayashi and Akitake, 1975; Call, 1980; Makela, 1991; Tichikawa, 1991). Bioaccumulation may result in physiological effects such as reduced reproductive success and physical defects such as gill necrosis (Buikemia, 1979; Gupta, 1985). In fish a very broad spectrum of toxic effects of phenol has been reported, ranging from disturbances in behavior to impairment of growth and reproduction or even serious organic damage (Jones, 1951; DeGrave, 1980; Mitrovic, 1968; Reichenbach-Klinke, 1965). It has also been observed that previous exposure to phenol confers a certain degree of resistance (Flerov, 1971).

Oxidative coupling involves a free radical reaction in which an electron and a proton are lost from the electron donating molecules (Cookson, 1995). Electron rich molecules, such as phenols or anilines, participate in these reactions more readily than those that lack transferable electrons. The resonance -stabilised free radical generated in this processes can react with either another phenolic free radical or a phenolic sub unit of humic macromolecule (Bollag *et al.,* 1980). This results in the polymerisation of phenols or incorporation of the phenolic structure in to SOM (Sarkar *et al.,* 1988). It is believed that the coupled compounds are stable and may be considered detoxified due to reduced availability to soil biota (Khan, 1982; Berry and Boyd, 1985b; Dec and Bollag 1992, 1990; Brenzny *et al.,* 1993; Barr and Aust, 1994).

Either soil enzymes or metal oxides may mediate oxidative coupling. The role of soil enzymes such as peroxidases and phenoloxidases in catalysing oxidative coupling of phenols has been studied in model systems (Bollag *et al.,* 1980, Sarkar, et al., 1988), in wastewater (Sun *et al.,* 1992), and in soils (Berry and Boyd, 1985b). Metal cations (Fe, Al, Zn and Cu) associated with clays have been shown to participate in electron-transfer reactions that yield hydroperoxyl or hydroxyl radicals capable of producing phenol radicals either by direct addition to phenols or by abstraction of hydrogen atoms Larson and Hufnal, 1980). Once generated these radicals can polymerise or form covalent linkages with other organic molecules. Polymerisation of aromatic molecules may also be catalysed by smectite (Mortland and Halloran 1986) or Mn, Fe, Al and Si Oxides (Mc Bride 1989). Oxidative coupling of phenols catalyzed by manganese oxide surfaces in aqueous systems has been illustrated (Ulrich and Stone, 1989). Enhanced adsorption and irreversible binding of phenols in the presence of atmospheric oxygen has been observed for sediment fractions (Isaacson and Frink, 1984), activated charcoal (Nakhala *et al.,* 1990) and activated carbon (Grant and King, 1990; Vidic and Suidan, 1991; Sorial *et al.,* 1993 a, b).

Many phenolic compounds may be derived from natural products. For example, seven hydroxy derivatives of benzene were found from degradative substances of color macromolecules (Christman Glassen ~~*et al.,*~~ 1966). These compounds were catechol, resorcinol, vanillin, vanillic acid, syringic acid, protocatechuic acid and 3, 5 - dihydroxybenzoic acid. In natural waters, there is the possibility that these compounds may have derived from the microbial catalysed degradation of color molecules. Many of these phenols have been recovered and identified in two rivers in Japan (Matsumoto et al., 1977).

The tainting of fish flesh occurs at much lower phenolic concentration than does toxic activity. In fact, o-chlorophenol has caused tainting at a level of 0.001 mg/l (Fetterolf, 1964). Taste of certain fish has been affected by 2, 4 dichlorophenol at the 0.001 mg/l level and by 2 methyl 6 chlorophenol at a concentration of 0.003 mg/l (Delfino et al., 1976). An EPA sponsored study on the effect of water pollutants on flavor of fish showed that of 27 organic compounds, a chlorophenol has the greatest effect, with a threshold concentration of only 0.0004 mg/l (Fetterolf, 1964). A study of fish taken from the Rine and Elbe Rivers considered the low levels of phenol present (0.02 - 0.07 mg/l) to be damaging to fish (Reichenbach-Klinke, 1965). Considerable pathological lesions were found in fish.

Humic acids according to [illegible], [illegible]) [illegible] Kleinhempel (1970) consist of polymers of polyhydroxybenzenes, polyhydroxy benzoic acids, sugars and small amounts of N-bases. Humic acid and Fulvic acids both give identical monomeric byproducts in various degradable methods surveyed by Schnitzer and Khan, (1972). Example of degradation products generally found are resorcinol, chloroglucinol, pyrogallol, catechol, orcinol, 2, 6-dihydroxytoluene, o and m- phthalic acids and 3, 5 dihydroxybenzoic acids. Phenolic components are abundant in soil and water of eutrophic environments and are the main components of soil and aquatic humic substances (Haslam, 1989; Jorge *et. al.*, 1996).

1.2.3 Chlorophenols

The chlorinated phenols consist of a group of 19 different isomers that include mono, di, tri, tetra and one pentachlorophenol. Chlorophenols are of environmental interest because of their wide spread distribution in fresh water habitats. All these compounds are toxic to aquatic species, but to varying degrees depending on the number and the position of the chlorine substituent on the benzene ring (Buikema *et al.,* 1979; Olli-Pekka Penttinen, 1995).

Chlorophenols have been used extensively since the 1930s as fungicides, mold inhibitors, antiseptics, disinfectants, and insecticides. The annual world production volume is estimated to be on the order of 150 000 tons (Christoffer Rappe, 1984). The most important use of 2, 4, 6 tri-, 2, 3, 4, 6, tetra-, and PCP (or their sodium or potassium salt) is for wood preservation. PCP and its salts are also used for slime control in the manufacture of pulp, for tanning leather, and in synthetic cutting fluids, paints, glues, and textiles (Christoffer Rappe, 1984).

Penta and tetra chlorinated phenols are effective fungicides and are used as antiblue stain and antisap stain agents and are used to prevent fungal biodeterioration of wood material. As a result contamination of soil and ground water around areas where industrial wood preservations activities are taking place (Valo *et al*, 1984; Kitunen *et al*., 1985, 1987; Goerlitz *et al*., 1985).

High PCP concentration was observed near timber industries/ saw mills (Valo *et al.,* 1990) in the soils, surface water, and ground water in the vicinity of the sawmills. In samples of the ground water, PCP concentrations up to the range 100-200 mg/l were reported. Significant levels of PCP has been found in cattle living with in corrals constructed of PCP-treated wood (Kinzell *et al.,* 1979) and in persons living in PCP treated log homes (McConnachie and Zahalsky, 1991).

PCP is often associated with toxic polycyclic aromatic hydrocarbons (PAH) in cresolate PCP mixtures. It is also a threat to the human environment because of its toxicity to human and aquatic life (EPA, 1986). PCP is corrosive to the skin causing burns and blisters. It is also highly irritating to the nose and throat. In mammals, acute exposure leads to elevated body temperature, increased respiratory rates, elevated blood pressure, hyperglycemia, and cardiovascular distress (EPA, 1978).

PCP is soluble in most organic solvents, but its aqueous solubility is dependent on pH. Since PCP is a week acid, its solubility increases with increasing pH (Ramaprasad, 1994). Therefore, leaching of PCP can be of important environmental significance, depending on the pH of the soil. As the pH of the soil decreases, volatility of PCP increases. Lamar and Dietrich (1990) reported that less than 4% of PCP was lost due to minerlisation and volatilisation of intermediate compounds in an alkaline soil.

Kuwatsuka and Igarashi (1975) found that PCP was degraded in both aerobic and anaerobic soils. The half-life of PCP was 30 days in flooded paddy soils and 50 days in upland soils, but almost no degradation occurred after 50 days in a forest soil low in organic matter, regardless of aeration. In addition to the aeration status of the soil, an important factor in PCP degradation is the presence of an acclimated bacterial population.

In rice paddy soils, degradation occurs under aerobic and anaerobic conditions; however, in nonagricultural soils no PCP degradation occurred. This difference can probably attributed to the fact that ~~that~~ the agricultural soils had been treated previous with PCP as a herbicide (Watanabe 1978, 1977). Watanabe (1977) also examined changes in the PCP degrading bacteria populations after PCP treatment, using the most probable number technique. He found that the bacterial populations increased early in the first year, and that the number remained high during the second and the third year of application, indicating that the population of PCP degrading bacteria was stable. Factors such as soil type, organic carbon content, moist~~er~~ure content, temperature and PCP formulations can affect the persistence of PCP in soils. Contrasting opinions exist on whether PCP degrades more rapidly in aerobic or flooded anaerobic soils (Kaufman, 1978).

Due to the polar nature of chlorophenols, toxicity is associated with the dissociation constant pKa (Saarikoski and Viluksela, 1982; Schultz, 1987; Kishino and Kobayashi, 1994, 1995). When acidic phenols are evaluated, pKa is a significant descriptor of toxicity. The pKa values of the lower chlorinated phenols are sufficiently high that dissociation is not significant over the pH range to which aquatic organisms are usually exposed (Saarikoski *et al.*, 1986). The current understanding of aquatic toxicity suggests that the non-ionised form of chemical is more toxic than the ionised form (Schultz, 1987). Further, the neutral and the ionised chlorophenols have entirely different modes of action (Saarikoski and Viluksela, 1981).

PCP is a general metabolic poison used extensively as a biocide in many industrial applications and as such is a contaminant in many bodies of water (Rao, 1978; Jones, 1981). The list of PCP degradation products detected in soils includes tetrachlorophenol, trichlorophenol and dichlorophenol isomers, as well as pentachloroanisole. Due to the high degree of halogenation, biodegradation of PCP in soil under aerobic conditions is often a slow process. At high concentration levels of PCP (266 mg/l), toxicity to microorganisms inhibited the biodegradation process (Ruckdeshel *et al.*, 1987). Crawford and Mohn (1985) showed that PCP concentrations of less than 100 mg/kg of soil were mineralised within one weak, but at concentrations of 500 mg/kg no mineralisation was observed.

Chlorophenolic compounds are formed through chlorine bleaching of soft wood pulp containing residual lignin and have been the subject of a number of studies of pollution in marine, river and Lake Environments. They have also been shown to be decomposition by-products of chlorolignins. Under laboratory conditions, Eriksson *et al.,* (1985) found that chlorolignins from extraction stages of bleaching of softwood could decompose slowly to products that include tri, and tetrachlorinated catechols and guaiacols. Chlorinated guaiacols and chlorinated phenols in effluent from pulp mills have been found to degrade slowly in recipient lake water, with chlorinated guaiacols being strongly preserved in sediments (Seppala and Kansanen, 1988). Chlorinated guaiacols, catechols and dimethoxyphenol were also found to be persistent in lake sediments by Paasivirta *et al.,* (1988).

Chlorinated phenols are also formed in the aquatic environment by the chlorination of humic substances (Quimby *et al.,* 1980; McCreary *et al.,* 1981). Chlorination of humic acids under the same condition identical with those used in the chlorination of lignin s, all types of chlorophenols, catechols, and guaiacols were generated (Knut P. Kringstad *et al.,* 1985).

Chlorophenols are formed also from the chlorination of naturally occurring organic compounds (Larson & Rockwell ~~*et al.,*~~ 1979). Hypochlorous acid was reacted with two natural compounds. p-hydroxybenzoic acid and vanillic acid under a variety of conditions. A mixture of 4-chlorophenol, 2, 4 dichlorophenol and 2, 4, 6-trichlorophenol was produced when p-hydroxybenzoic acid was chlorinated. These kinds of chlorination reactions presumably account for the occurrence of chlorophenols in such natural waters as the Rhine River, Delaware Estuary and Weser estuary (Eder & Weber ~~*et al.,*~~ 1980).

Halogenated organic compounds are ubiquitous in the biosphere. As a result, a wide variety of halometabolites have been isolated from marine organisms. There are about 550 naturally occurring halogenated compounds that are produced by 250 biological organisms (; Faulkner, 1978). The number of chlorinated compounds exceeds 150 including 50 brominated substances. On the other hand, fluorinated and iodinated compounds are few in numbers. Bromine compounds varies between 3 and 50 ppm (.

1.3 Cochin Estuary

Cochin Estuarine System (CES) is the part of the Vembanad backwaters around the Greater Cochin area comprising of the metropolis of Cochin and its satellite towns. The rivers enter in to the CES are Periyar, Moovattupuzha and Chitrapuzha. The Vembanad backwaters, extending between $9^0 29'$- $10^0 10'$N and $76^0 13'$ – $76^0 31'$E and with an area of 240 km^2 is the largest backwater system on the south west coast of India. Cochin is one of the most urbanised cities in West Coast of India, situated at the center of the Cochin Estuarine System.

The extensive population growth and industrial development in and around Cochin has led to the discharge of a heavy of urban wastes into the estuary, which invariably exceeds the assimilative capacity of the system. Cochin has an urban population of 1 million. The Cochin Port and oil terminals of petroleum refinery brings in more than a thousand medium and bulk sized cargo carriers in a year. The oil terminal pump out crude oil from the tankers and the refined oil is pumped back from the refinery through the terminals to the tankers for transportation to the other parts of India.

Angamally to Cochin is the most industrialised zone of river Periyar. There are over 50 large and medium industries and over 2500 small-scale industrial units. The industries of eloor-edayar region consumes around 1, 75000 m^3/d water from the river and discharge around 75 % of it as wastewater which contains a variety of industrial pollutants.

Considerable agricultural activities are present in the upper reaches of Periyar and Moovattupuzha River. The drains from these farmlands contain a wide spectrum of compounds of the vegetative matter and its degraded ones finally reach the estuary. The modern agricultural practices add a heavy load of anthropogenic pollutants like pesticides, insecticides and fertilizers.

A clear knowledge about the sources, the transport path ways and ultimate fate of pollutants is essential to assess, predict and manage the impact of human activity in this estuarine environment. Historically, estuarine sediment is considered to be the reservoir for many classes of anthropogenic contaminants. However, the studies by Loganathan and Kannan (1991) have demonstrated that during the last decade environmental regulation has resulted in a reduction of waste loading from terrestrial sources. But the marine sediment could act as a non-point source, and has the potential to release the `in place contaminants' causing adverse effects to organisms and human health through tropic transfer.

The estuarine waters of Cochin receives $11X10^9m^3$ of fresh water annually and the effluents from various industries and sewage discharge from the urban areas amounted to 1.4 X 10^6m^3 / day. Large quantities of wastewater are discharged from industrial units daily in to the estuary, which are not completely flushed out leading to stagnation and building up of the pollution level.

1.4 Aim and Scope

The West Coast of India is having a special significance in the marine research because of the contributions from the monsoon season to the productivity. The tropical Cochin Estuarine System is one of the most productive and positive estuary in the West Coast of India. This water body is considered to be the nursery of shrimps, which considerably support the Indian exports.

The prime importance of the Cochin Estuarine System in the national scenario can be seen from the research considerations it has attracted. For the last few decades the Cochin Estuarine System was subjected to thorough study in different deciplines and parameters. The works so far reported include the biological, physical, geological and chemical studies. The introduction of a multitude of industries on at the banks of the river and at estuary and exhaustive urbanisation has led to considerable contamination of the estuarine system because of the discharge of wastes in to this system. The focus of research, so, is now on the impact of these contaminants to the system.

The work on the chemical aspects so far reported include

1). The distribution, characterisation and dynamics of inorganic nutrients such as nitrate, nitrite, urea, phosphate, silicate, etc. and major ions (Sankaranarayanan *et al.*, 1984, 1979, 1969; Anirudhan, 1988; Saraladevi *et al.*, 1991; Nair, 1990).

2). The distribution, speciation and dynamics of trace metals (Sankaranarayanan *et al.*, 1986, 1978; Paul and Pillai., 1983a, 1983b: Ouseph, 1990, 1987; Shibu *et al.*, 1990; Nair *et al.*, 1990, 1991; Babukkutty., 1991; Shibu, 1992.

3). The distribution, charecterisation and identification of biogeo organics and pesticides (Sujatha, 1992; Vasudevan Nayar, 1992).

4). Chemodynamics of the sulphur cycle (Beenamma, 1993).

5) Ecotoxicological studies (Lakshmanan & Nambisan, 1989, 1985a, 1985b, 1983, 1980, 1979, 1977; Menon, 1986; Pillai &Silas., 1975; Sathyanathan et al., 1988; Sivadasan et al., 1986; Suresh., 1988; Prabhudeva, 1987; Krishnakumar *et al.,* 1990: Geetha., 1992.

These studies have identified that during the years this estuarine system have considerably got modified and a few of the biological species have become extinct. Significant concentrations of pollutants like pesticides, heavy metals etc. have been reported. The shrinking of this backwater system because of the reclamation activities and the load of pollutants is seriously affecting the fisheries resources as well.

Surface active substances being only a mild toxicant, the impact of these substances on the biological system especially the productivity as well as the chemical characteristics of the estuarine system is so far unattended. The industrial concerns and the Cochin metropolis are delivering a heavy load of these substances, which are integral part of the cleaning procedure. In the national scenario also, though this can act as a potential pollutant, no research attempts were made to characterise and quantify the load and impact. This work so can be considered as a first attempt in this direction in India.

This study focuses on (a) the fractionation and quantification of chlorophenols, the most important and potential pollutant in this category. (b) The distribution and seasonal dynamics of MBAS, phenols and chlorophenols and (c) development of a model to describe the chemical reactivity of the estuary are utilising the dynamics of boron.

A proper management of aquatic systems, especially the estuarine and the coastal systems, is need of the day because of the role they play in maintaining the life on the earth. A clear understanding of the chemical character and the dynamics can lead to the development of models, which can predict the requirements for such a management. The attempts have been to quantify a potential bioactive contaminant and bring it into a model for the sustainable maintenance of the system.

Chapter 2

Materials and Methods

2.1 Study Area

The study area and sampling sites are given in fig: 2. Based on the geographical pattern and salinity distribution the study area was divided into two: (1) northern part of the estuary along with Periyar river and (2) southern part of the estuary along with the Champakkara canal and the Barmouth. Water and sediment samples were collected from selected seven stations:

Station –1: Fact, near to the bund constructed for pumping water for industries and to block saline water intrusion into Periyar river during premonsoon season.
Station –2: Eloor, near to the ferry and down stream of Periyar, well mixed with various pollutants from various industries.
Station –3: Vaduthala, a retting zone.
Station –4: Tatapuram, an aquatic environment highly influenced by human activity such as transportation.
Station-5: Barmouth.
Station-6: Kundannur, an environment surrounded by mangroves.
Station-7: Champakkara, down stream of effluent discharge area of Cochin refinery and FACT Cochin division.

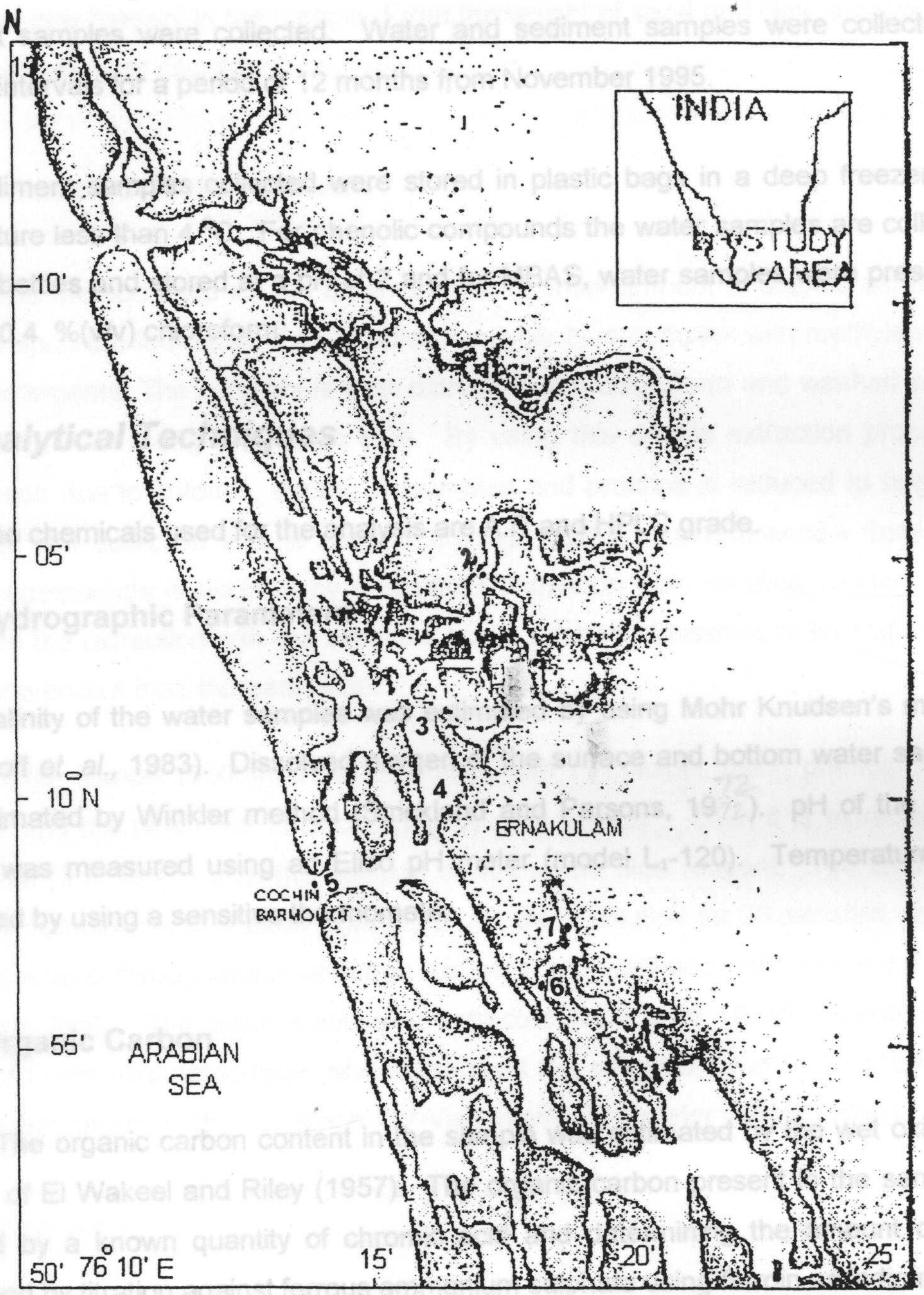


Fig. 2 Map of Cochin Estuary showing location of stations

2.2 Sampling and Storage

Surface samples were collected by using a clean plastic bucket and bottom samples with a high tech bottom water sampler. Using van-Veen grab (0.032m^3) sediment samples were collected. Water and sediment samples were collected at monthly intervals for a period of 12 months from November 1995.

Sediment samples collected were stored in plastic bags in a deep freezer at a temperature less than 4 ^{0}C. For phenolic compounds the water samples are collected in glass bottles and stored at a pH of 2 and for MBAS, water samples were preserved with 0.2-0.4 %(v/v) chloroform.

2.3 *Analytical Techniques*

The chemicals used for the analysis are A.R and HPLC grade.

2.3.1 Hydrographic Parameters

Salinity of the water samples was estimated by using Mohr Knudsen's method (Grasshoff *et. al.*, 1983). Dissolved oxygen of the surface and bottom water samples was estimated by Winkler method (Strickland and Parsons, 19$\overset{72}{72}$). pH of the water sample was measured using an Elico pH meter (model L$_1$-120). Temperature was measured by using a sensitive thermometer.

2.3.2 Organic Carbon

The organic carbon content in the sample was estimated by the wet oxidation method of El Wakeel and Riley (1957). The organic carbon present in the sample is oxidised by a known quantity of chromic acid and determining the amount of acid consumed by titration against ferrous ammonium sulphate using ferroin as indicator.

2.3.3 Texture

Grain Size Analysis of sediment sample was done by using pipette analysis (Krumbein & Pettijohn., 1938.). 10 gm sediment (dry wt.) and 7.5 gm sodium hexametaphosphate was taken in a 500ml beaker. Added 200ml distilled water and kept it over night. Dispersed the sediment uniformly by using a mechanical stirrer.

Sieved the samples using a sieve of mesh size 63-micron poring water through a funnel into a 1 litre measuring jar. Made the volume up to 1L. The residue gave the amount of sand and grains. Stirred the filtered portion for 2 minutes using a hand stirrer and pipette 20 ml of the sample after 2 hours and 2 minutes, and calculated the amount of clay present in the sample. From the weight of sand and clay, amount of silt in the sediment was calculated.

2.3.4 Anionic Surfactant (MBAS)

The method used for the determination of small amount of anionic surfactants is based upon the formation of a chloroform-soluble blue complex with methylene blue by the detergents. The complex is then extracted with chloroform and washed with an acid solution containing methylene blue. By using this double extraction procedure, interference due to chloride, nitrate, thiocynates and proteins is reduced to negligible amounts. The detection limit is about 0.002mg/l MBAS. Interferences from some organic compounds is avoided by chloroform extraction from alkaline solution (pH = 10), while the extraction with the aqueous acidic solution of methylene blue eliminates any interference's from inorganic salts.

Water sample (500ml) is made alkaline with 1 N NaOH, using phenolphthalein indicator and the pink color is discharged by 1 N H_2SO_4 . Then it is extracted with chloroform (3 X 10 ml) after the addition of methylene blue reagent. The chloroform extract is combined and shaken vigorously with wash solution for 30 seconds, drew off chloroform layer through glass wool that has been pre extracted with chloroform in to a volumetric flask. The wash solution is extracted twice with 10 ml chloroform and collected to the volumetric flask, and determined the absorbance at 652 nm against a blank of chloroform in 150-20 Hitachi UV-Vis spectrophotometer (APHA, 1995).

2.3.4.1 Reagents

a). Phenolphthalein indicator solution: Dissolve 0.5 g of phenolphthalein in 950 ml of ethyl alcohol and add 50 ml of water.

b). Sodium hydroxide: (1 M): Dissolve 40 g of NaOH in distilled water and dilute to 1 litre using distilled water.

c). Sulphuric acid, (0.5M): Dilute 27.8 ml of Concentrated H_2SO_4 (d=1.84) to 1 litre using distilled water.

d). Methylene blue reagent: Dissolve 100mg of methylene blue in 100ml of distilled water. Transfer 30 ml of this solution to a 1 litre volumetric flask. Add 500 ml of distilled water, 6.8 ml of concentrated sulphuric acid, and 50 gm of monosodium dihydrogen phosphate monohydrate. Shake until the dissolution is complete. Dilute to the 1-litre mark with distilled water.

e). Wash solution: Add, 6.8 ml of concentrated sulphuric acid to 500 ml distilled water in a 1-litre flask. Add 50 gm of monosodium dihydrogen phosphate monohydrate. Shake until the dissolution is complete. Make up the solution to 1-litre using distilled water.

f). Stock solution: The standard reference material is sodium lauryl sulphate. Dissolve 1 g of sodium lauryl sulphate in distilled water and dilute to 1 litre. Store in a refrigerator to minimise biodegradation. Prepare the solution weekly. 1ml = 1.0 mg of MBAS.

g). Methanol

h). Benzene

i). Chloroform

2.3.4.2 Extraction of MBAS from sediments

Ten grams of dried sediment sample was refluxed with 100 ml of methanol-benzene (1:1) solution for 1 hour at 80^{0}C on a water bath. The extraction was repeated three times with fresh solvent under the same conditions. All of the solvent used for these extractions mixed up and completely evaporated in a beaker on a water bath. The residue containing ABS was dissolved in 50 ml of hot distilled water (Yoshinari Ambe, 1973). ABS from water was estimated by the method used for water samples (APHA, 1995).

2.3.5 Phenol

Determination of total phenols in sea water is done by using 4- Amino antipyrene, Phenols form condensation reaction with 4 - AAP at pH 7.9 ± 0.1 in the presence of potassium ferricyanide to form a colored antipyrene dye. Efficiency of the method using external addition of phenol in the concentration range of 5 to 100 µg/l is 86.7 to 102.9%. Efficiency at the lowest detection limit of 1µg/l is 81 ± 18.5 %. The 4-AAP reacts with the phenolic group on each molecule but due to steric considerations, not with equal sensitivity for different phenols.

To 500ml water sample add 12 ml ammonium hydroxide, 10 ml phosphate buffer solution, 3 ml of 4 AAP and 3 ml potassium ferricyanide in sequence with stirring after each addition, pH of the solution was adjusted to 7.9 ± 0.1 by the addition of buffer solution. The orange color complex thus formed after standing 5 min was extracted using 25 ml of chloroform. The separated organic layer was dried over anhydrous sodium sulfate and its absorbance was measured at 460 nm (Kadam *et al.*, 1996) using UV-Vis Spectrophotometer (Hitachi 150-20).

2.3.5.1 Reagents

a). Phenol stock solution: Dissolve 1.0 gm of phenol in freshly boiled and cooled distilled water and dilute to 1 litre. 1 ml = 1.00 mg phenol.

b). Ammonium chloride solution: Dissolve 50 gm Ammonium chloride in distilled water and dilute to 1 Litre.

c). Ammonium hydroxide: (25%)

d). Aminophenazone solution: Dissolve 2 gm of 4-AAP (4-aminoantipyrine) in distilled water and dilute to 100ml. The solution must be prepared daily.

e). Potassium ferricyanide solution: Dissolve 8 gm of Potassium ferricyanide in distilled water and dilute to 100 ml. The solution must be prepared daily.

f). Potassium carbonate (0.01M): Dissolve 382.1 mg potassium carbonate in milli Q water and dilute to 1 litre.

g). Phosphate buffer: Dissolve 104.5 g of K_2HPO_4 and 72.3 g of KH_2PO_4 in water and dilute to 1 litre. The pH should be 6.8.

h). Sodium sulfate anhydrous

i). Chloroform

2.3.5.2 Extraction of phenol from sediment

25 gm sediment was shaken with 100ml (50, 50) 0.01M potassium carbonate for 2 hours, then the phenol present in the solution was extracted by using the method used for water samples (Kadam & Bhangale., 1996)

2.3.6 Boron

Boron in water samples was estimated by using curcumine method (APHA, 1995). Sample containing boron was acidified and heated in presence of curcumine, a red-colored product called rosocyanine was formed. The absorbance of the complex formed is measured at 540nm.

0.1 ml of water sample were pipette out in to a 50 ml conical flask which was precleaned with methanol and distilled water, and dried in the oven at 100^{0}C. Acetic anhydride (1ml) and concentrated Hydrochloric acid (0.1ml) were added successively. The contents were mixed by swirling and were allowed to react for 15 minutes. Acetic acid reagent (0.7 ml) and curcumin reagent (0.4 ml) were then added and the contents were mixed thoroughly. After keeping the conical flask immersed for 15 minutes in a water bath maintained at 40^{0}C, the buffer solution (5ml) was added and the contents were mixed well. The absorbance was measured at 540 nm on a Hitachi 150-20 UV-Vis spectrophotometer after cooling to room temperature.

2.3.6.1 Reagents

a). Curcumine reagent: 0.1 gm curcumine was dissolved in 20 ml of methyl isobutyl ketone.

b). Buffer solution: Ammonium acetate (180 g) and Isopropyl alcohol (90 ml) were mixed and made up to one litre with milli-Q water.

c). Acetic acid reagent: Equal volumes of glacial acetic acid and concentrated sulphuric acid were mixed thoroughly.

d). Methyl isobutyl ketone

e). Isopropyl alcohol

f). Acetic anhydride

g). Sulphuric acid

h). Hydrochloric acid

i). Boron stock solution: Dissolve 571.6 mg of anhydrous boric acid, H_3BO_3, in distilled water and dilute to 1 litre. 1.00ml = 100 μg B

j). Sodium chloride

2.3.6.2 Extraction of boron from sediment.

a) Water soluble boron

Five grams of the sediment sample was placed in a 100 ml beaker, add 25 ml of pure water, the beaker covered and placed in a hot plate and brought to gentle simmering (Wilfred W. Scott, 1958). After 15 minutes of heating, with occasional stirring, 1gm of NaCl crystals are added and the residue is allowed to clear. The solution is filtered and the extraction is repeated twice. Finally the residue is transferred to the filter by a 1% solution off NaCl. The extract is then made up to 100 ml and boron content was estimated by using curcumine method (APHA, 1995).

b) Water insoluble Boron (Acid extraction)

The residue on the filter from the water extraction is washed in to a beaker, 10 ml of 6 N HCl added, the beaker is covered and the mixture heated gently on a hot plate, just below the boiling for 15 minutes (Wilfred W. Scott, 1958). The solution is filtered and the extraction is repeated twice. The extract is then made up to 100 ml and boron content was estimated by using curcumine method (APHA, 1995).

2.3.7 Chlorophenolic Compounds

One litre of preserved water sample (acidified) was shaken thrice with 40,40 &20 ml of toluene for 10 min. The combined toluene extract was shaken with 3X 20 ml of 0.1 M potassium carbonate for 3 min. 0.5 ml of acetic anhydride and 10 ml of petroleum ether were added to the combined aqueous phases and thoroughly mixed at room temperature for 5 min. The petroleum ether phase was decanted and dried with anhydrous sodium sulphate (Wegman & Hofstee ~~*et al.*~~, 1979). 2 μl of the petroleum ether phase was injected in to the GC (PERKIN-ELMER Auto System XL).

2.3.7.1 Reagents

a). Potassium carbonate (0.1M): Dissolve 3.821 gm potassium carbonate in milli Q water and dilute to I litre.

b). Acetic anhydride

c). Petroleum ether

d). Sodium sulphate anhydrous

e). Hydrochloric acid

f). o-chlorophenol

g). p-chlorophenol

2.3.7.2 *Extraction from sediment*

Twenty five ml of 0.001 N HCl were added to 25 gm (dry) sediment , extract twice with 100 ml 0.1 m potassium carbonate for 2 hours (Wegman and Van Den Broek., 1983., Xie, 1983). Potassium carbonate layer separated and the chlorophenols contained were derivatised with acetic anhydride (Wegman and Hofstee., 1979) and injected to GC.

2.3.7.3 *Gas Chromatographic conditions*

Column: PE – 5 (30m X 0.53 mm, I.D.), Carrier gas: N_2, flow $\cong$ 5 ml/min (40cm/s), ECD make up 25 ml/min. Injector – 250^0C Split injection mode. Oven program: 50^0 C (hold 2 min), 50 - 250^0C at 5^0C/ min, 250^0c (hold 23 minute). Detector: ECD – 375^0C.

2.4 General Characteristics of Cochin Estuary

Hydrographic parameters of an estuary undergo considerable tidal and seasonal variations. As a consequence of marked seasonal fluctuations in meteorological features viz., temperature, rainfall etc., large scale variations of different physico-chemical properties are observed in estuarine ecosystems. Role of hydrographic features to the development of fishery in estuarine and coastal waters is well established.

2.4.1 Meteorological features

Atmospheric temperature, as well as rainfalls showed marked seasonal variation. The estuary experiences three seasons. Viz., monsoon with maximum rainfall, postmonsoon characterised by scarce rainfall and atmospheric cooling and premonsoon denoting warm weather season. The seasons are classifies as premonsoon (February to May), Monsoon (June to Sept.) and postmonsoon (October, to January).

2.4.2 *Water level variations*

The estuary is influenced by semidiurnal tides with two floods and two ebb periods of unequal heights within a tidal day. The highest high tide variations were also owing to the change in seawater ingress and freshwater discharges from the adjoining areas. The tidal height in CES was about one meter.

2.4.3 Temperature

Seasonal variation of temperature is given in fig: 2.1 a, b and table 2.1. Temperature shows maximum values in the surface and bottom water during premonsoon and low values during monsoon in the Cochin estuarine System.

Table. 2.1 Seasonal average of Temperature

Station	1	2	3	4	5	6	7
Postmonsoon.S	29.19	29.06	29.06	29.00	29.06	30.50	30.63
B	28.63	28.94	28.75	28.83	28.50	29.75	30.00
Premonsoon. S	31.31	31.63	31.50	30.81	30.50	31.69	32.13
B	31.13	31.88	31.25	30.69	30.06	31.38	31.56
Monsoon.S	27.17	27.17	27.50	27.83	29.50	30.33	30.00
B	27.00	26.92	27.33	27.75	25.75	30.00	29.67

S - surface; B - bottom

Influx of freshwater through the rivers and intrusion of sea water through the Barmouth reaches have profound influence on the distribution of temperature in back water system (Pillai *et al.*, 1975) apart from local phenomena such as mixing of heated waste water, heat production during biochemical oxidation *etc.*

There was a gradual rise in temperature from the downstream to upstream (from station 4 to station 1in the northern part and from station. 5 to station 7 in the southern part) along the estuarine system reaching the riverine system in both premonsoon and postmonsoon seasons but a reverse trend showing colder water along upstream regions of the estuary has been observed during monsoon. These findings are in general agreement with the observations of Day (1981).

2.4.4 Salinity

Salinity distribution provides information on the amount of seawater intrusion in to the estuary and also the distances up to which the seawater penetrates in to the rivers. Salinity in the present study showed seasonal variations (fig: 2.2 a, b). Higher salinity with minimum fluctuation was observed in the Barmouth during post and premonsoon. A constant decrease till the minimum value was obtained in the Barmouth surface and

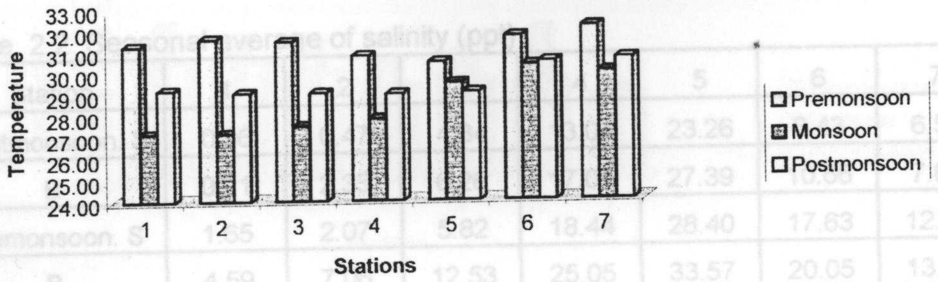
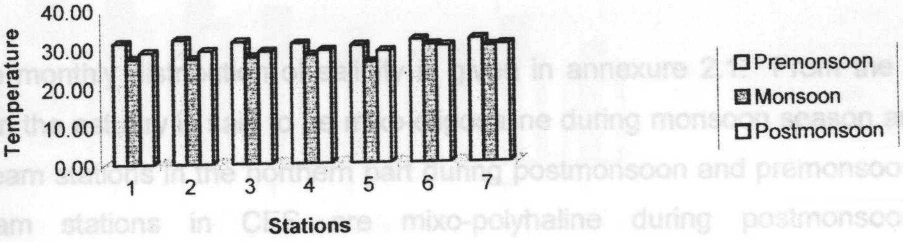
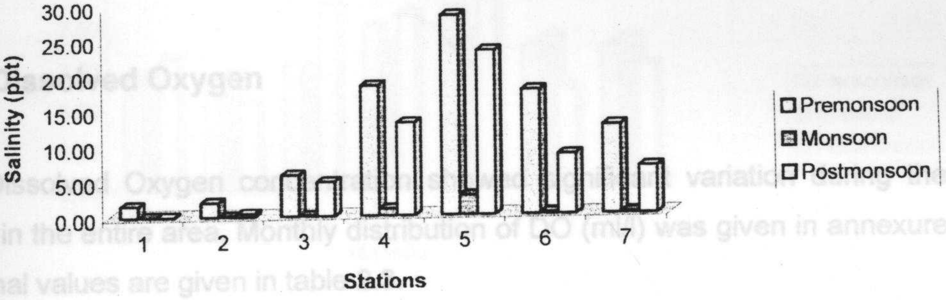


Fig: 2.1 a



Fig; 2.1 b



Fig; 2.2 a

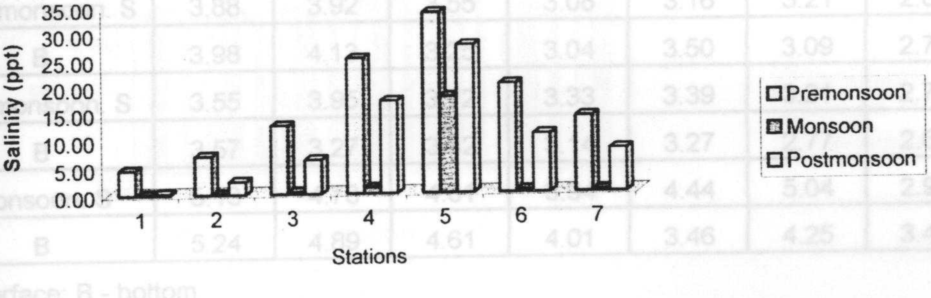


Fig: 2.2 b

Tatapuram during monsoon season and also in October. In monsoon season salinity value shows very low values, especially in the surface waters of the downstream stations. The seasonal values (ppt) were given in the table 2.2.

Table. 2.2 Seasonal average of salinity (ppt)

Station	1	2	3	4	5	6	7
Postmonsoon. S	0.06	0.47	4.84	13.04	23.26	8.43	6.58
B	0.21	2.35	6.26	17.01	27.39	10.66	7.82
Premonsoon. S	1.65	2.07	5.82	18.44	28.40	17.63	12.51
B	4.59	7.06	12.53	25.05	33.57	20.05	13.93
Monsoon. S	0.07	0.09	0.12	0.96	2.75	0.22	0.16
B	0.08	0.08	0.33	1.01	17.73	0.41	0.20

S - surface; B - bottom

The monthly distribution of salinity is given in annexure 2.1. From the salinity distribution the estuary is said to be mixo-oligosaline during monsoon season and also the upstream stations in the northern part during postmonsoon and premonsoon. The downstream stations in CES are mixo-polyhaline during postmonsoon and premonsoon seasons. Salinity showed a constant decrease in the CES from June till October can be attributed to steady dilution caused by massive ingress of freshwater from the rivers and land drainage.

2.4.5 Dissolved Oxygen

Dissolved Oxygen concentration showed significant variation during the study period in the entire area. Monthly distribution of DO (ml/l) was given in annexure-2 and seasonal values are given in table 2.3.

Table. 2.3 Seasonal average of DO (ml/l).

Station	1	2	3	4	5	6	7
Postmonsoon. S	3.88	3.92	3.55	3.08	3.16	3.21	2.83
B	3.98	4.13	3.25	3.04	3.50	3.09	2.79
Premonsoon. S	3.55	3.95	3.72	3.33	3.39	3.21	2.70
B	3.57	3.27	3.42	3.14	3.27	2.77	2.65
Monsoon. S	5.13	4.73	4.61	3.94	4.44	5.04	2.99
B	5.24	4.89	4.61	4.01	3.46	4.25	3.47

S - surface; B - bottom

Higher values for DO were observed during premonsoon and postmonsoon season in the Barmouth area compared to other stations (Station. 4,6 &7). During

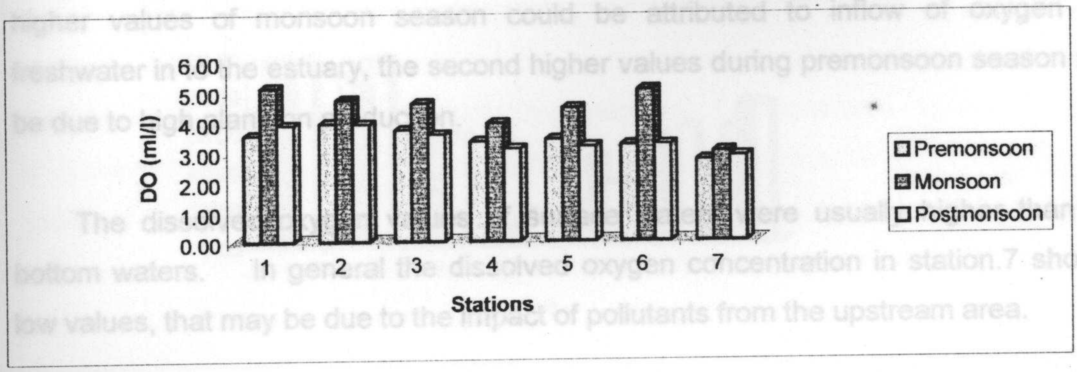


Fig: 2.3 a

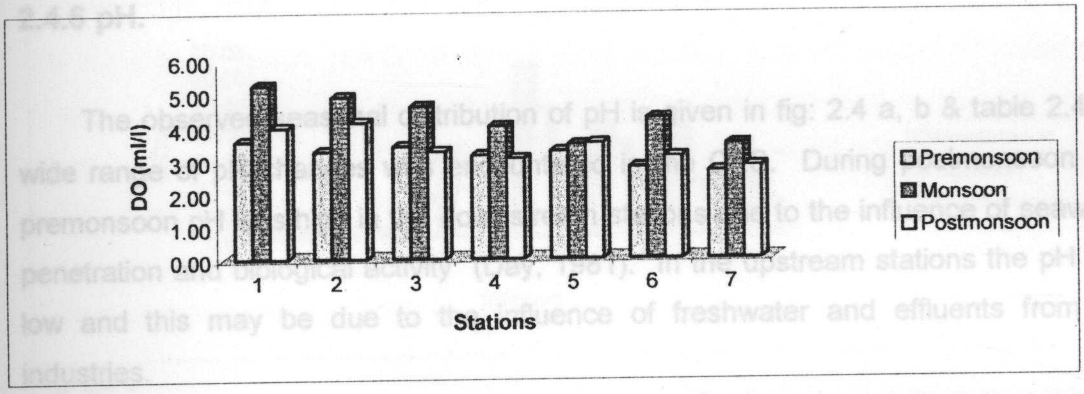


Fig: 2.3 b

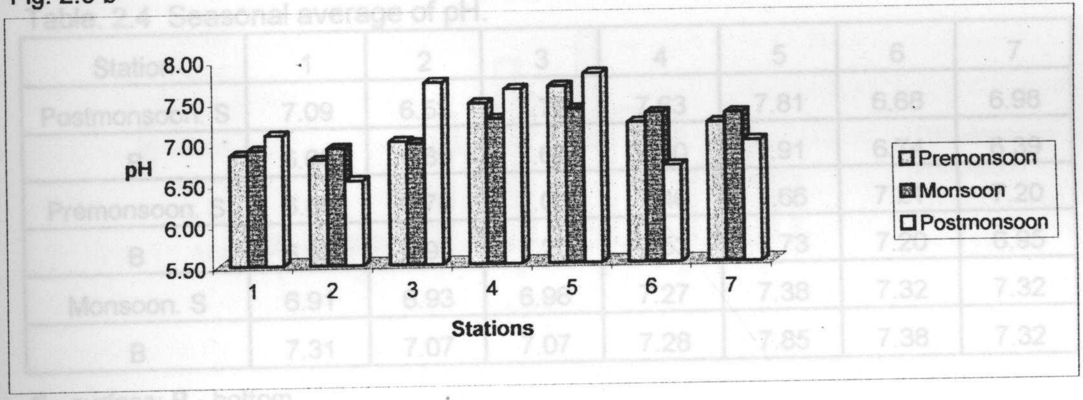


Fig: 2.4 a

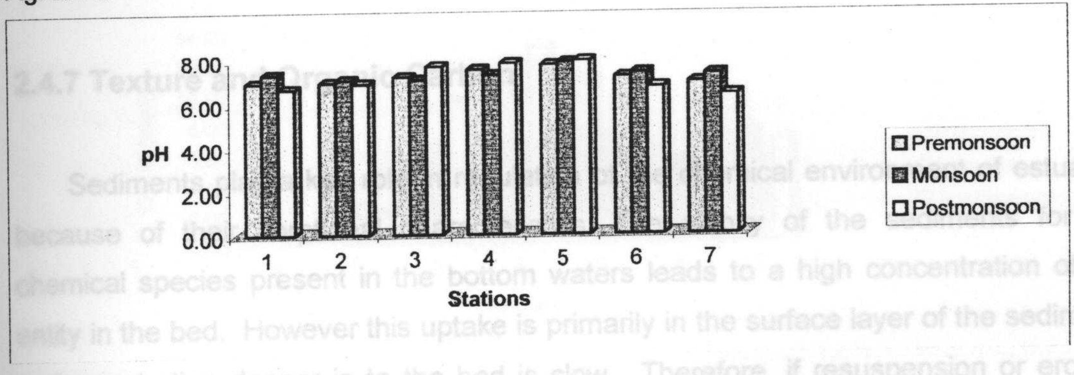


Fig: 2.4 b

monsoon, DO value showed higher values in the upstream stations and a decreasing trend towards downstream in the northern part of the estuary (fig: 2.3 a, b). While the higher values of monsoon season could be attributed to inflow of oxygen rich freshwater in to the estuary, the second higher values during premonsoon season may be due to high plankton production.

The dissolved oxygen values of surface waters were usually higher than the bottom waters. In general the dissolved oxygen concentration in station.7 showed low values, that may be due to the impact of pollutants from the upstream area.

2.4.6 pH.

The observed seasonal distribution of pH is given in fig: 2.4 a, b & table 2.4. A wide range of pH changes was encountered in the CES. During postmonsoon and premonsoon pH was high in the downstream stations due to the influence of seawater penetration and biological activity (Day, 1981). In the upstream stations the pH was low and this may be due to the influence of freshwater and effluents from the industries.

Table. 2.4 Seasonal average of pH.

Station	1	2	3	4	5	6	7
Postmonsoon. S	7.09	6.53	7.72	7.63	7.81	6.68	6.98
B	6.66	6.89	7.67	7.80	7.91	6.74	6.39
Premonsoon. S	6.85	6.78	7.00	7.46	7.66	7.21	7.20
B	6.93	6.95	7.20	7.53	7.73	7.20	6.95
Monsoon. S	6.91	6.93	6.98	7.27	7.38	7.32	7.32
B	7.31	7.07	7.07	7.28	7.85	7.38	7.32

S - surface; B - bottom

2.4.7 Texture and Organic Carbon

Sediments play a key role in regulation of the chemical environment of estuaries because of their sorptional characteristics. The affinity of the sediments for the chemical species present in the bottom waters leads to a high concentration of the entity in the bed. However this uptake is primarily in the surface layer of the sediment, and penetration deeper in to the bed is slow. Therefore, if resuspension or erosion occurs, the material will get resuspended in the water.

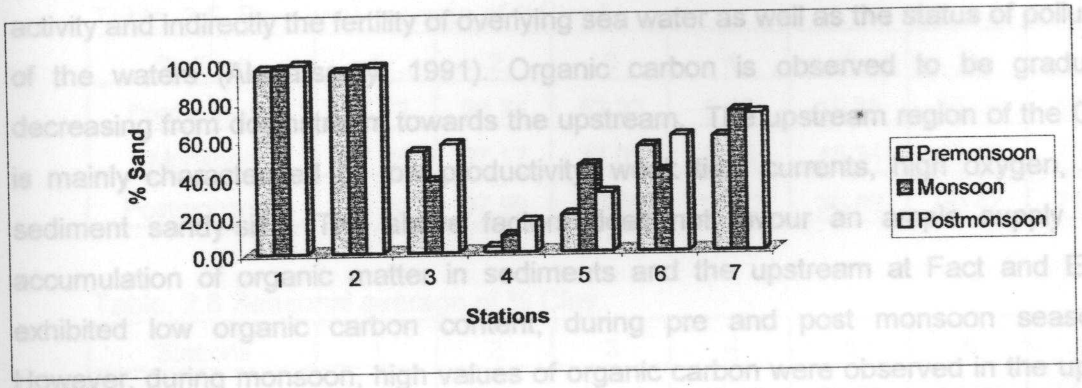


Fig: 2.5 a

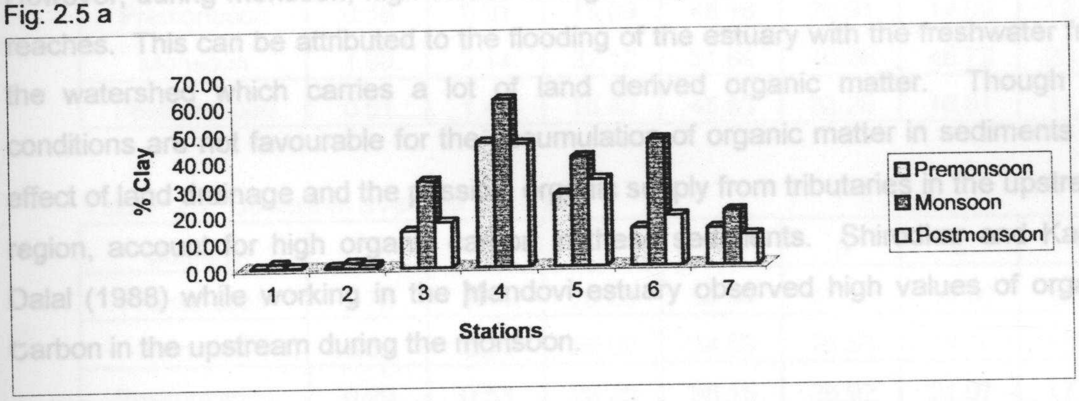
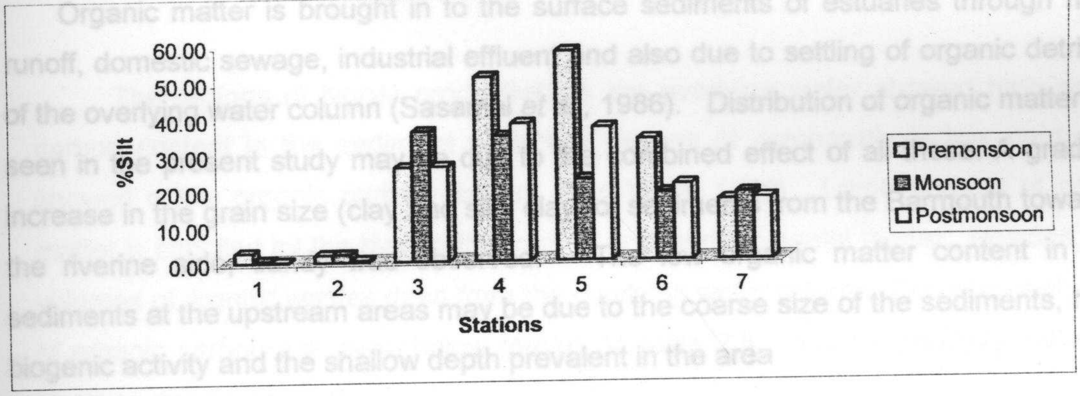


Fig: 2.5 b



Fig; 2.5 c

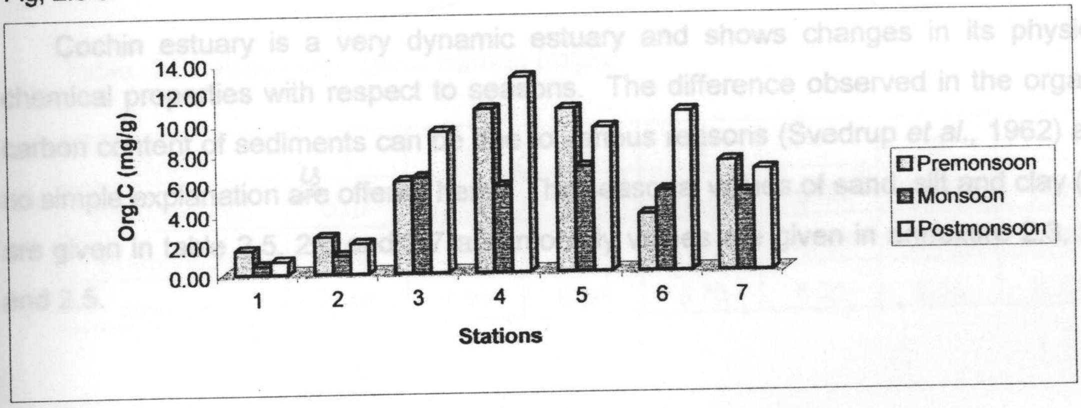


Fig: 2.6

Investigations on the organic matter in sediments indicate the extent of biological activity and indirectly the fertility of overlying sea water as well as the status of pollution of the waters (Alagarsamy, 1991). Organic carbon is observed to be gradually decreasing from downstream towards the upstream. The upstream region of the CES is mainly characterised by low productivity, weak tidal currents, high oxygen, and sediment sandy-silt. The above factors does not favour an ample supply and accumulation of organic matter in sediments and the upstream at Fact and Eloor exhibited low organic carbon content, during pre and post monsoon seasons. However, during monsoon, high values of organic carbon were observed in the upper reaches. This can be attributed to the flooding of the estuary with the freshwater from the watershed which carries a lot of land derived organic matter. Though the conditions are not favourable for the accumulation of organic matter in sediments the effect of land drainage and the possible organic supply from tributaries in the upstream region, account for high organic carbon in these sediments. Shirodkar and Kamat Dalal (1988) while working in the Mandovi estuary observed high values of organic carbon in the upstream during the monsoon.

Organic matter is brought in to the surface sediments of estuaries through river runoff, domestic sewage, industrial effluent and also due to settling of organic detritus of the overlying water column (Sasamal *et al.,* 1986). Distribution of organic matter as seen in the present study may be due to the combined effect of all these. A gradual increase in the grain size (clay and silty clay) of sediments from the Barmouth towards the riverine side, sandy was observed. The low organic matter content in the sediments at the upstream areas may be due to the coarse size of the sediments, high biogenic activity and the shallow depth prevalent in the area

Cochin estuary is a very dynamic estuary and shows changes in its physico-chemical properties with respect to seasons. The difference observed in the organic carbon content of sediments can be due to various reasons (Svedrup *et al.,* 1962) and no simple explanation ~~are~~ is offered here. The seasonal values of sand, silt and clay (%) are given in table 2.5, 2.6 and 2.7 and monthly values are given in annexure 2.3, 2.4 and 2.5.

Table. 2.5 Seasonal average of %Sand

Stations	1	2	3	4	5	6	7
Premonsoon	97.13	95.74	53.22	2.83	19.85	55.18	60.02
Monsoon	97.65	97.17	37.89	9.06	45.34	42.00	73.27
Postmonsoon	99.30	97.99	56.93	16.32	30.89	60.42	71.88

Table. 2.6 Seasonal average of % Clay.

Stations	1	2	3	4	5	6	7
Premonsoon	0.58	0.91	13.69	46.16	26.91	14.09	13.76
Monsoon	1.89	2.14	32.12	61.89	40.56	46.72	20.18
Postmonsoon	0.51	1.49	16.82	45.53	32.20	18.51	11.05

Table. 2.7 Seasonal average of % silt.

Stations	1	2	3	4	5	6	7
Premonsoon	2.75	2.14	26.08	50.94	57.86	33.56	16.61
Monsoon	0.56	2.26	36.02	34.59	22.53	18.70	18.68
Postmonsoon	0.20	0.53	26.25	38.15	36.92	21.07	17.06

The regions of higher productivity in the overlying water showed high organic carbon content in the sediment while the regions of comparatively low productivity showed a low organic carbon content (Paropkari, 1979). Large amount of organic matter is supplied by the river in the form of suspended vegetal matter. Besides, large volumes of organic wastes drain from the overlying water column. The seasonal values of organic carbon are given below (mg/g) in table 2.8 and the monthly values are given on annexure – 2.6.

Table. 2.8 Seasonal organic carbon (mg/g)

Station	1	2	3	4	5	6	7
Postmonsoon	0.87	2.01	9.38	12.94	9.56	10.59	6.69
Premonsoon	1.62	2.46	6.15	10.85	10.81	3.77	7.28
Monsoon	0.59	1.21	6.36	5.73	6.96	5.33	5.19

According to Svedrup *et al.,* (1942), "an abundant supply of organic matter in the column of water, a relatively rapid accumulation of fine grained inorganic matter and low oxygen content of the waters immediately above the bottom sediments would favor high organic matter in the bottom sediments".

Emery (1956) points out that water temperature is an important factor determining the degree of accumulation of organic matter. In addition to the supply from the terrigenous plant materials, the relatively high content of organic matter in sediments of the deeper offshore areas is attributed to the cumulative result factors, viz. (1) high organic production from the abundant planktonic material, (2) availability of low oxygen in the environment, and (3) presence of fine clay sediments.