

**SURFACE ACTIVE SUBSTANCES IN THE COCHIN
ESTUARINE SYSTEM**

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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 the 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 this system to modification. 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 synonymous^{ous} 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 ^{as} 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).

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., 1981 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-^{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 weighed 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 $6(\pm 4) \times 10^{14}$ 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; Sivali^{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).

LC₅₀ 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; Stephun ^{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; Marten ^{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 algacides, 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, 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. Lesion 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; Brenzly *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, 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 Sudan, 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 ^{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 ~~Magnum, (1991)~~ and 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.*, 1978) 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 weak acid, its solubility increases with increasing pH (Ramprasad, 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 mineralisation 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 be attributed to the fact that ~~that~~ the agricultural soils had been treated previously with PCP as a herbicide (Watanabe 1978, 1977). Watanabe (1977) also examined changes in the PCP-degrading bacterial 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, ~~moister~~^{moisture} 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 pK_a (Saarikoski and Viluksela, 1982; Schultz, 1987; Kishino and Kobayashi, 1994, 1995). When acidic phenols are evaluated, pK_a is a significant descriptor of toxicity. The pK_a 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 week, 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 ^{& Wiedert} *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, 1979). 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°29'- 10°10'N and 76°13' – 76°31'E and with an area of 240 km² 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 elloor-edayar region consumes around 1, 75000 m³/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 trophic transfer.

The estuarine waters of Cochin receives $11 \times 10^9 \text{m}^3$ of fresh water annually and the effluents from various industries and sewage discharge from the urban areas amounted to $1.4 \times 10^6 \text{m}^3$ / 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 disciplines 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, characterisation 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

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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.

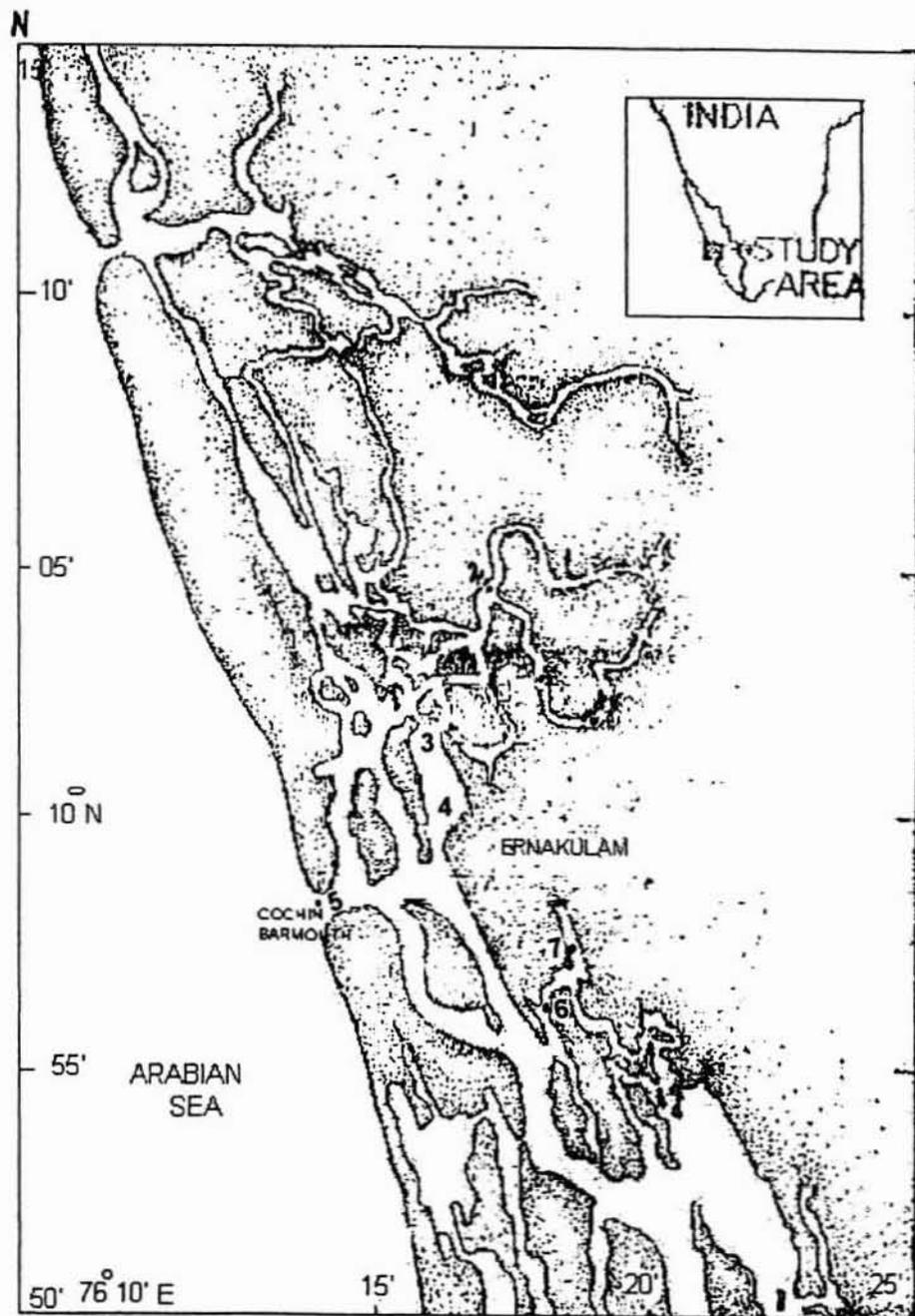


Fig. 2 Map of Cochin Estuary showing location of stations

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 (0.032m³) 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 °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, 19⁷²₇₂). pH of the water sample was measured using an Elico pH meter (model L₁-120). 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, thiocyanates and proteins is reduced to negligible amounts. The detection limit is about 0.002mg/l MBAS. Interference s 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°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 antipyrine, Phenols form condensation reaction with 4 - AAP at pH 7.9 ± 0.1 in the presence of potassium ferricyanide to form a colored antipyrine 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°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°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 μ g 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 of 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 ^{twice} 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 1 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: N₂, flow \cong 5 ml/min (40cm/s), ECD make up 25 ml/min. Injector – 250°C Split injection mode. Oven program: 50°C (hold 2 min), 50 - 250°C at 5°C/min, 250°C (hold 23 minute). Detector: ECD – 375°C.

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 classified 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 1 in 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

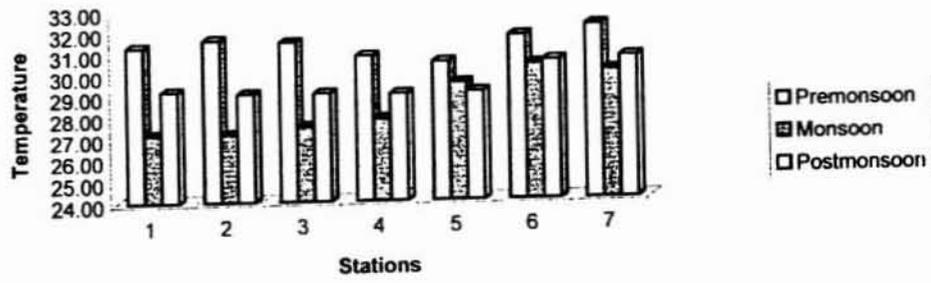


Fig: 2.1 a

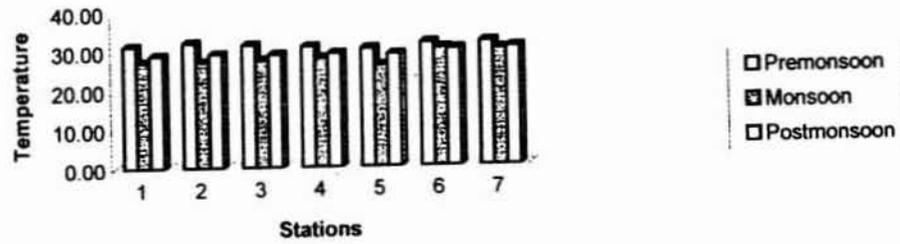


Fig: 2.1 b

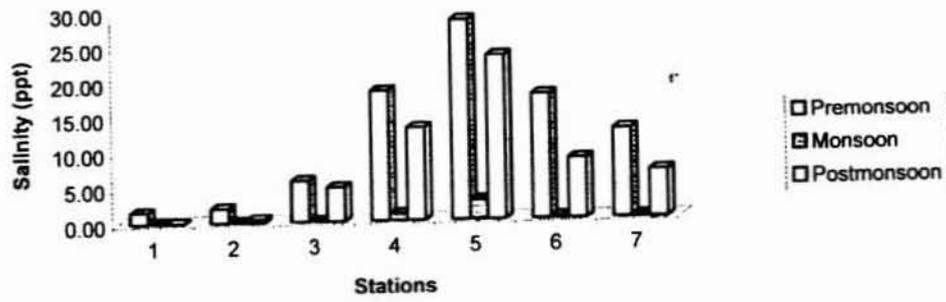


Fig: 2.2 a

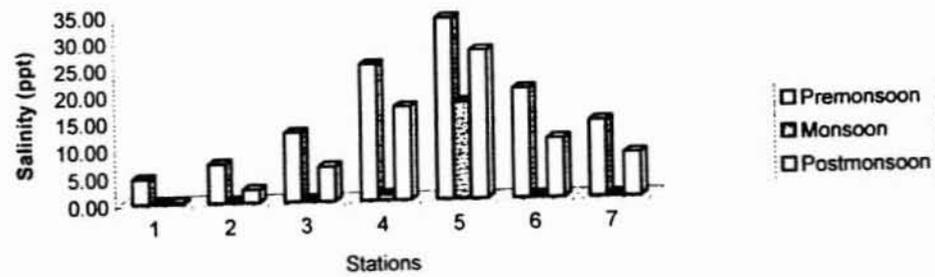


Fig: 2.2 b

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

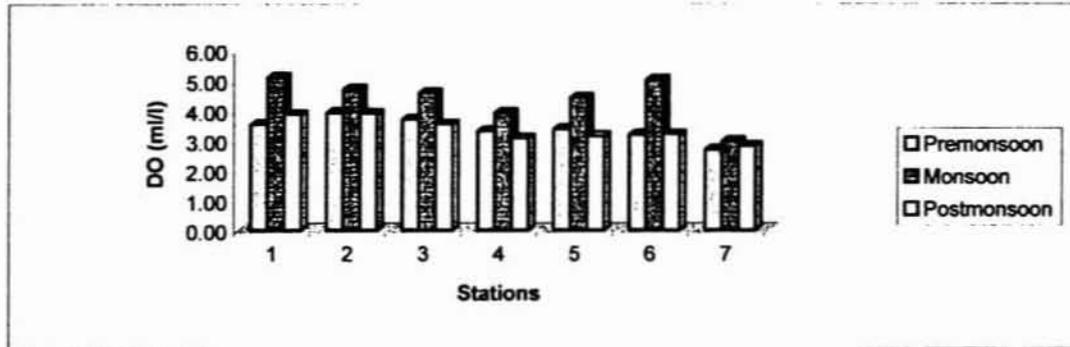


Fig: 2.3 a

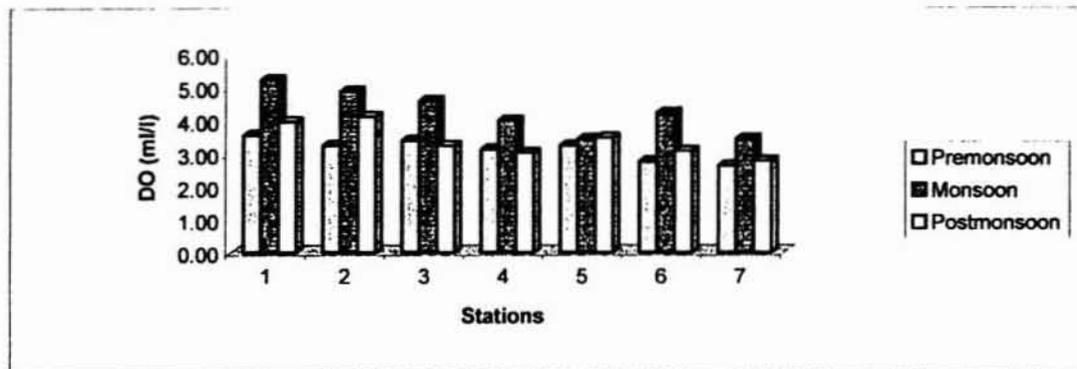


Fig: 2.3 b

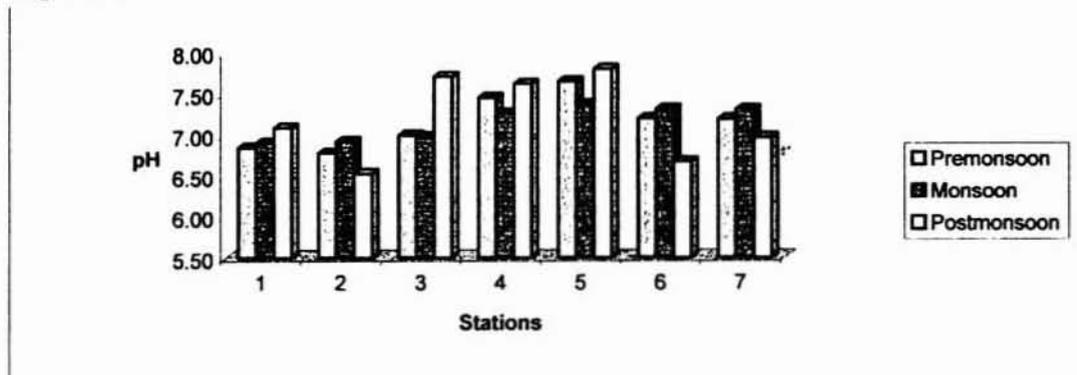


Fig: 2.4 a

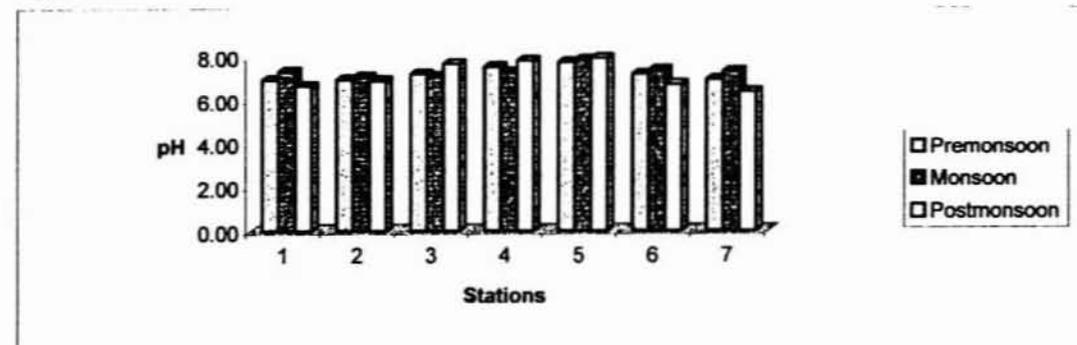


Fig: 2.4 b

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.

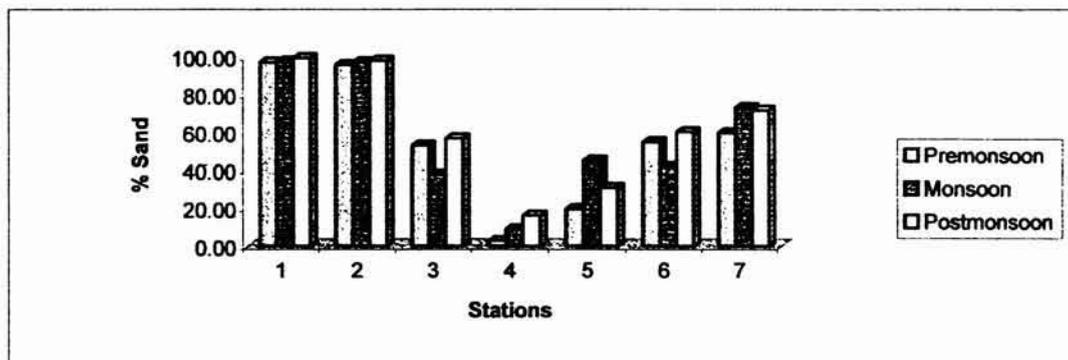


Fig: 2.5 a

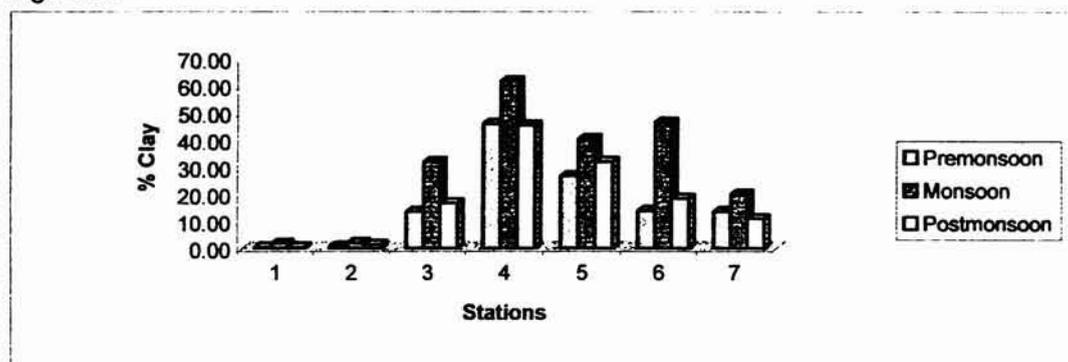


Fig: 2.5 b

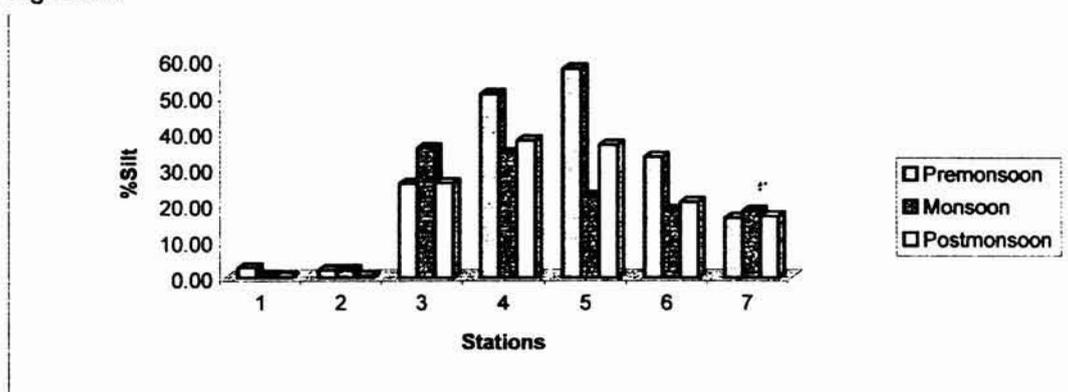


Fig: 2.5 c

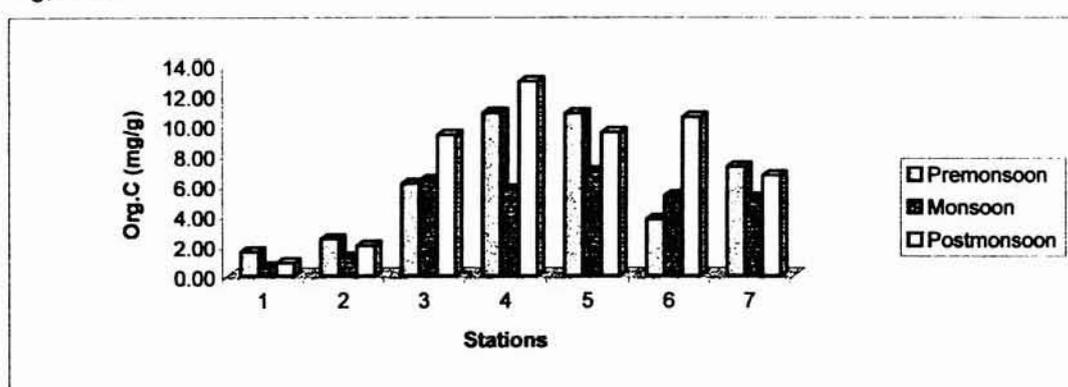


Fig: 2.6

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 ^{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 (Paro'pkari, 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.

Chapter 3

Distribution of Surface Active Substances

Dissolved organic matter (DOM) is a large contributor to the pool of organic matter in fresh and marine water and thus plays an important role in the global carbon cycle (Cauwet, 1978; Mooper and Degem, 1979). In polluted waters the composition of organic matter is quite different (Sontheimer (1976). Surface active substances form a major fraction of the DOC. Considering the industrial applications, human usage and aquatic discharges, the surface active substances present in the aqueous environment in this study can be grouped into two, the anionic surfactants and the phenolics.

3.1 Anionic Surfactant (MBAS)

Anionic surfactants are widely introduced in to the marine environment through out fall discharges or directly from wastewater treatment plants. The presence of surfactant organic matter in marine water is well known. Marine slicks formed both by natural and man made substances are clear proof of the existence of surfactant compounds. The significant changes in the dilatational properties of the sea surface, shown by means of the short gravity wave attenuation, constitute a specific characterisation and spreading and adsorption films (Lombardini *et al.*, 1982; Scott, 1986; Cini *et al.*, 1987). Surfactants are highly sorptive and become associated with sediments in the aquatic environments and sludges in wastewater treatment systems. Sludges often undergo anaerobic digestion and are disposed to soils.

Anionic surfactants in the aquatic environment are methylene blue active substances, which include linear alkylbenzene sulfonate (LAS), branched alkylbenzene sulfonate (ABS), alpha olefine sulfonate (AOS), fatty alcohol sulfate (AS) and fatty alcohol ethoxy sulfate (AES). There is little or no biological degradation of ABS in the aquifer, but LAS and NaLS detergents degrade fairly. Ammonium, ABS, LAS and Coprostanol are well-known pollutants originating from domestic wastes. Coastal and estuarine waters in some densely populated areas receive significant quantities of various derived chemicals, include anionic surfactants. Reports on these surfactants in marine and estuarine waters are relatively scarce (Hon-Nami and Hanya, 1980; Ishiwatari, 1983) compared to the rather numerous studies on the occurrence and the behavior of LAS in the wastewater treatment and in natural waters (Painter and Zabel, 1988; Fell, 1989).

The presence of enhanced LAS concentrations could have a significant effect on marine fauna, especially in the first stages of development (Lewis, 1991). Moreover, it was shown that biodegradation of LAS in the marine part of the estuary was significantly slower than in its freshwater part (Terzic^{et al.}, 1992). Monitoring these pollutants using reliable analytical methods is, therefore, of great importance in preventing deleterious effects in estuarine and coastal environments.

Dispersion of LAS from sewage in to the lower part of the Karka River Estuary (Sibenik Harbor) was found to be highly significant in lowering the concentration, particularly under favorable wind conditions (Zutic and Legovic, 1987). High LAS concentration was found only in the immediate region of municipal waste water outlets (from 420 to 780 µg/l). After a distance of only 50 m from the sewage outlet the concentration dropped to only 7.2 µg/l and 3.2 µg/l, at depths 0.5m and 6 m, respectively. Further decrease in concentration was very slow, 1-2 µg/l, at the distance greater than 100 m. During longer periods of calm weather the wastewater plume can reach further parts of the Harbor. In such situations the concentration of LAS increased significantly in the freshwater layer but not in the saline water layer. The vertical distribution of LAS was characteristic for a highly stratified estuary. The concentrations were negatively correlated with salinity and the maximum was found at the microlayer (24 µg/l). The vertical transport of the pollutants was greatly reduced by the fresh and saline water boundary. Along with the biodegradation, dispersion and dilution also lead to decrease in the bioavailability of these compounds.

The Tamagawa, Sumidagawa, and Arakawa River comprise 24-40 % of the freshwater inflow to the Tokyo bay. In Tamagawa river, the LAS concentration varies from 0.78 to 4.49 mg/g; in Sumidagawa the values varies between 0.12 and 36.6 and in Arakawa the LAS con varies between 0.31 to 14.4 $\mu\text{g/g}$ (Hideshige Takada^{et al.} 1992). A concentration range between 0.8 and 30 $\mu\text{g/l}$ of LAS was found in Tokyo bay water and from below 0.2 to 69 $\mu\text{g/g}$ (dry basis) for sediments.

The sum of concentration of 26 isomers of LAS, expressed as Σ LAS, in the sediments of Tokyo coastal zone range from 0.12 to 45.1 $\mu\text{g/g}$ dry sediment (Hideshige Takada *et al.*, 1992). These are substantially lower than the concentrations found in the river sediments of Tokyo 36.3-567 $\mu\text{g/g}$ (Takada and Ishiwatari, 1987), indicating that considerable amounts of LAS disappear during transport from the upper river to the estuary. The concentration of LAS decreases from >10 $\mu\text{g/g}$ in the upper estuaries to <1 mg/g in the lower estuaries.

Temperature modifies the amount of biodegradation but not adsorption. Consequently, in winter biodegradation is minimum and LAS decrease was attributed to adsorption by the wet land. In the summer, decrease by biodegradation was larger than that of LAS in the inflow, and thus, LAS already adsorbed was also decreased (Kazuho Inaba, 1992).

The study on the variation of MBAS on the Sea water (Martinez^{et al.} 1989) collected from 2 miles offshore from Barcelona (J-1), the natural beach of Barcelona (CNB), a Mediterranean city with more than 2 million people and high urban and industrial activity; coastal water from Sant Feliu de Guixols (SFG) a small village with low pollution. Freshwater came from the Ebro River at its entrance to Amposta (Tarragona), a small village situated 30 km from the rivers mouth. Most of the surface samples analysed in this study contained <0.1 mg/l of MBAS. One of the cases occurred with seawater from CNB were 0.26 mg/l of MBAS was detected. The second case occurred when working with freshwater from the Ebro river, whose MBAS content was 0.34 mg/l. It is assumed that MBAS is a measure of anionic surfactants (natural or manmade), and other chemical products present in surface waters such as humic acids, proteins etc., as well as metabolites originated during the first step of biodegradation. However, intermediate biodegradation compounds of LAS are far less toxic than the same concentration of the intact compound (Brown 1978; Swisher^{et al.} 1964).

The concentration of MBAS found in the samples collected from CNB varies between 0 to 0.26 mg/l with an average value of 0.066 mg/l. In SFG the value varies between 0 and 0.08 and in J-1, MBAS value varies between 0 and 0.11mg/l. The freshwater samples collected from the Ebro river has a concentration range of 0 to 0.34 and the average value for 9 samples will be 0.112 mg/l (Martinez, 1989).

The concentration of anionic surfactant in the Adriatic Sea at location > 1N mile offshore are low and rarely exceeds 10 µg/l. Higher values detected in the upper 5m layer in the north Adriatic during stratification periods are highly correlated with the influence of freshwaters of the river Po (Cosovic *et al.*, 1979; Degobbis *et al.*, 1979). Excessive surfactant contents and concentration of anionic detergents due to pollution by municipal and industrial sewage were detected in the Adriatic Sea only near by the pollution sources. Surfactant activity of seawater (MBAS) from West Istrian coast varies from ND to 0.620 mg/l (Kozarac *et al.*, 1975).

The distribution of MBAS, alkyl benzene sulphonate in a small lake, Jyonuma Lake, in Tatebayashi, Gunma prefecture has a small surface area (about 0.5 km²) and is relatively long and shallow average water depth about 1m. The river flows through Tatabayashi City, which has a human population of about 65,000. MBAS ^{concentration} in the water varies from 0.29 to 1.46 ppm, ABS ^{concentration} varies from ND to 0.6 ppm. In sediment MBAS varies from 107.3 to 377.8 µg/g (dry mud) and ABS varied from 16.9 to 96.3 µg/g (dry mud) (Uchiyama, 1979).

In Lake Suwa, one of the most polluted lakes in Japan situated in the central part, which has a diameter of 5 km and a maximum depth of 7 meters. The amount of ABS flowing in to the lake is estimated to be about 70 tons/year, and a considerable part of this deposited in the bottom of the lake. The content of MBAS in the lake mud was higher in the northern part of the lake, but in the south it was lower. Accordingly, ABS was higher in the north eastern part of the lake, especially in the region near Suwa city, where very high values (20-30 µg/g) were found reflecting the pollution by the inflowing urban waste waters. Thus, the ABS absorbed on the suspended matters in the polluted river waters flowing in to the lake is considered to have deposited immediately after the mixing with the stagnant lake water (Yoshinari Ambe, 1973).

The MBAS concentration of Dong Hu lake water varied from 15 to 82 µg/l during September to November 1987 (Ayfar Yediler ^{et al.}, 1989). The study on the effect of microbial population on the degradation of LAS shows there will be a good correlation between the LAS degradation rates and total bacterial population size was observed in all LAS experiments. Quality assurance procedures were undertaken to check the accuracy of the MBAS method in the study on a sample of distilled water spiked with 20, 40, 60, 80, 100 and 120 µg/l. Seventeen analysts obtained means of 18.9, 39.2, 56.7, 74.2, 84.7, and 95.5 with an overall relative standard deviation of 0.009, 0.01, 0.03, 0.005 and 0.027.

In the surface water of Pacific Ocean surfactant (MBAS) concentration varied from 0 to 33 µg/l (Tkalin, 1987). The concentration of detergents in the upper meter of the northeastern part of Atlantic Ocean varied insignificantly, from 20 to 45 µg/l (Mikhaylov, 1978).

In seawater, surfactant concentration increases due to rough sea condition and inland winds were likely to take place (were the synthetic surfactant concentration were low; Oppo *et al.*, 1999). In Guido Bacci, Leghorn (Tyrrhenian sea, Italy), water samples collected during calm condition MBAS concentration varies from 0.005 to 0.009 mg/dm³ and during rough time the concentration varies from 0.1 to 0.8 mg/dm³.

3.1.1 Results and Discussion

The concentration of MBAS varies from 3.74 to 73.72 µg/l in the northern part of the Cochin estuary and 2.60 to 80.78 µg/l in the southern part (Annexure 3.1 a).

Seasonal values of MBAS showed high values in the surface water (fig: 3.1 a; Table 3.1, 3.2) during monsoon season compared to premonsoon and postmonsoon in the northern part. MBAS showed a decreasing trend from upstream to downstream during postmonsoon and in the southern part an increasing trend was observed in the bottom water during premonsoon and postmonsoon. No significant trend was observed in other seasons.

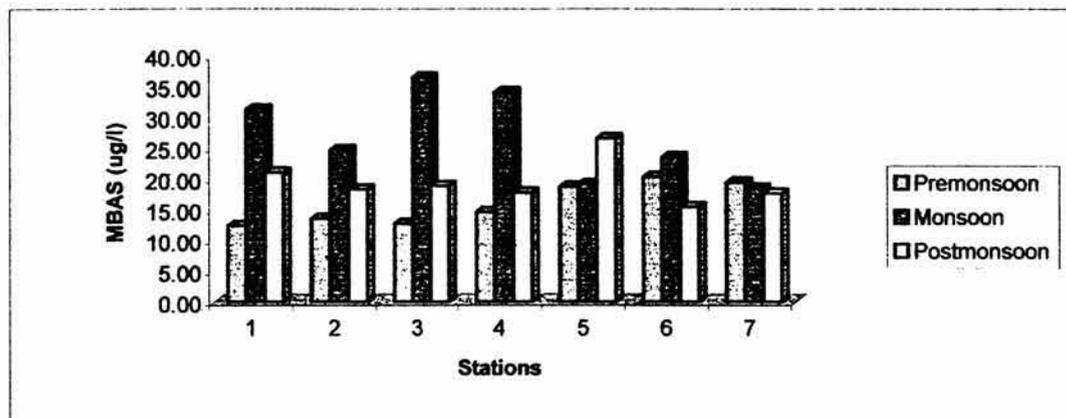


Fig: 3.1 a

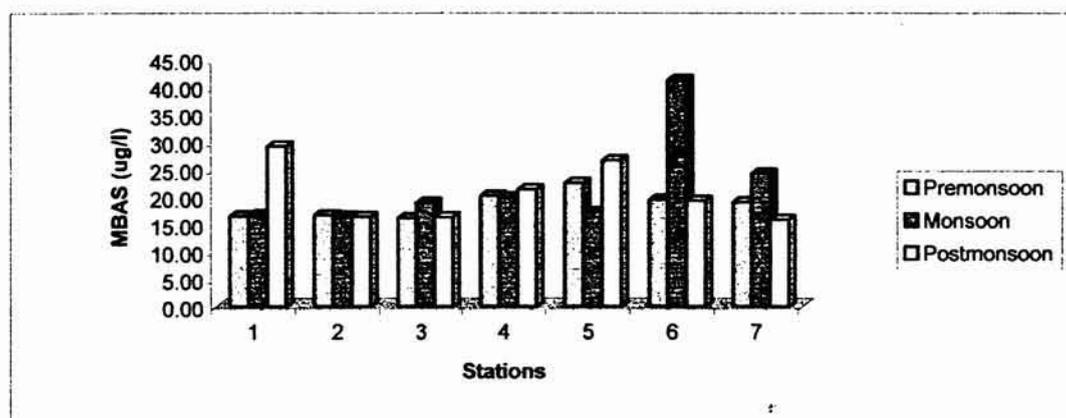


Fig: 3.1 b

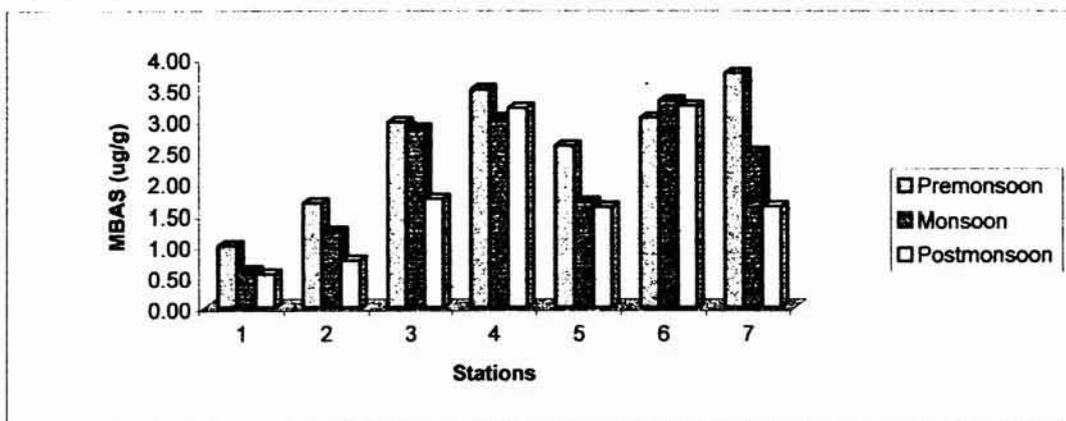


Fig: 3.1c

Table. 3.1 Seasonal average of MBAS in water (ppb).

Station	1	2	3	4	5	6	7
Postmonsoon. S	21.14	18.30	18.86	17.83	26.67	15.47	17.69
B	29.28	16.46	16.37	21.45	26.71	19.36	15.86
Premonsoon. S	12.38	13.62	12.73	14.65	18.84	20.45	19.51
B	16.57	16.75	16.21	20.28	22.59	19.56	19.14
Monsoon. S	31.39	24.79	36.54	34.18	19.22	23.59	18.57
B	16.76	16.49	19.02	19.92	17.33	41.38	24.35

S - surface; B - bottom

Table. 3.2 Seasonal average of MBAS in sediment (ppm).

Station	1	2	3	4	5	6	7
Postmonsoon	0.54	0.75	1.73	3.20	1.60	3.23	1.61
Premonsoon	1.00	1.66	2.97	3.50	2.59	3.04	3.76
Monsoon	0.59	1.23	2.87	3.04	1.69	3.32	2.49

In postmonsoon season, the MBAS showed maximum values in surface water during Nov.'96 (38 $\mu\text{g/l}$ in station. 7) and minimum value during Nov.'95 (7.04 $\mu\text{g/l}$ in station 7). During premonsoon and monsoon seasons the anionic surfactant showed maximum values during May '96 (29.55 $\mu\text{g/l}$ in station. 6) and July '96 (64.31 $\mu\text{g/l}$ in station. 1) and the minimum value was during April '96 (1.95 $\mu\text{g/l}$ in station 1) and June '96 (9.86 $\mu\text{g/l}$ in station.3) respectively.

In the bottom water, MBAS concentration showed maximum values during postmonsoon season during Dec'95 (57.38 $\mu\text{g/l}$ in station.1) and minimum value in Nov'95 (4.23 $\mu\text{g/l}$ in station. 6) (fig 3.1 b). In monsoon and premonsoon seasons the maximum value were observed during Aug. '96 (80.78 $\mu\text{g/l}$ in station. 6) and May'96 (33.83 $\mu\text{g/l}$ in station. 6) and minimum value during Jul.'96 (8.63 $\mu\text{g/l}$ in station.1) and Apr. '96 (4.8 $\mu\text{g/l}$ in station. 3) respectively. Station 1 showed very high values in the bottom water compared to other stations in the northern part during Dec. '95, Feb.96, May '96 and Jun.96, this may be due to the anthropogenic activities.

In the northern part of the estuary the MBAS concentration in the sediment varied from 0.075 $\mu\text{g/g}$ to 4.77 $\mu\text{g/g}$ and in the southern part the value varied from 0.28 $\mu\text{g/g}$ to 6.87 $\mu\text{g/g}$ (Annexure 3.1 b). No relationship between organic carbon, grain size and MBAS in the sediments of Cochin estuarine system was observed.

MBAS in the sediment shows an increasing trend in all seasons from upstream to down stream in the north zone and showed high values in station. 4. (fig: 3.1c). In the south zone only during premonsoon there was a decreasing trend from upstream to downstream was observed, and in other seasons station.7 and Barmouth has low values compared to station.6.

Surface active substances in general and MBAS in particular are highly reactive in the aquatic systems. So building up of a high concentration in the natural water bodies is a rare chance. The earlier study on the distribution patterns of MBAS confirms this reactivity (Zutic and Legovic, 1987). In the CES there are abundant chances for the delivery of a huge amount of surfactants because of the industrial activities and also because of the heavy urbanisation, but no background data is available on the distribution and reactivity of surfactants in this positive estuarine system. The discussion so has to be limited to the biogeochemical characteristics of the MBAS with respect to the general behavior of this system and to a comparison with the distribution pattern observed elsewhere.

The observed concentration ranges of MBAS in different water masses are given in table 3.3. It can be seen from the table, generally the water bodies contain significantly high concentration of MBAS except the unpolluted riverine and oceanic systems. The observed concentration in CES can be seen, to be considerably lower to the values observed elsewhere. The seasonal distribution pattern is a clear indication of the terrestrial input, high values in the monsoon and low values in the premonsoon and postmonsoon. The higher concentration observed between 50-80 $\mu\text{g/l}$, were from the upstream stations, where the industrial discharges always show a key role in defining the chemical character of the system.

Table 3.3. MBAS concentration in water and sediment samples

<u>Environment</u>	<u>Concentration</u>	<u>Reference</u>
Lake Dong Hu.	15 to 82 µg/l.	Ayfer Yediler <i>et al.</i> , 1989.
Po. River	15 to 78 µg/l.	Galassi <i>et al.</i> , 1992
Seawater (Barcelona)	0.0 to 260 µg/l.	Martinez <i>et al.</i> , 1989.
Ebro river	0.0 to 340 µg/l.	Martinez <i>et al.</i> , 1989.
Pacific Ocean (surface water)	0.0 to 33 µg/l.	Tkalin, 1987.
Atlantic Ocean (northeastern part)	20 to 45 µg/l.	Mikhaylov, 1978
Jyonuma Lake (Tatebayashi)	290 to 1460 µg	Uchiyama, 1978.
Alexandra canal, Breakfast South, Cattai, French's, Middle Harbor, Oxford and Cowan creek.	190 to 900 µg/l	Pakalns <i>et al.</i> , 1978
Lane Cove river, Carrol, Ku-ring-gai and Neverfail creek.	30 to 80 µg/l	Pakalns <i>et al.</i> , 1978
Jyonuma Lake sediment	107.3 to 377.8 µg/g	Uchiyama, 1978.
Cochin estuary	3.7403 to 73.7255 µg/l in the northern part of the Cochin estuary and 2.6019 to 80.7843 µg/l in the southern part (present study).	
Sediment	0.075 mg/g to 4.7734 mg/g in the northern part of the estuary and in the southern part the value varied from 0.2818 mg/g to 6.868 mg/g (present study).	

The observed distribution can, therefore, be compared only with unpolluted water bodies. The estuarine and down stream stations showed only very low values, though it will have contributions from the upstream and urban discharges. The major reason for this can be the high reactivity of MBAS, which is evident from the almost steady value at the Barmouth. It is also to be noted that MBAS does not give any correlation with any of the hydrographic parameters. It is clear, so, that the concentration of MBAS have a bearing, along with the mixing process, to pathways other than mixing.

From a station wise analysis of the data, one can see that more than the estuarine reactivity or characteristics it is the station characteristics that determines the concentration of MBAS. Though a decreasing trend towards the downstream is the overall character, the concentration values do have no interrelations or the trend is neither uniform nor have a direct relation to any of the general character of the estuary.

Sedimentary MBAS gave significantly high correlation with sedimentary organic carbon, thorough out the entire study. The seasonwise relationship and correlation coefficient values given in table. 3.4.

Table 3.4 Organic carbon vs MBAS in the sediment

Season		r	n
Postmonsoon	$Y = 0.1447 x + 0.7437$	0.51706#	34
Premonsoon	$Y = 0.1032 x + 1.7841$	0.39004*	28
Monsoon	$Y = 0.148 x + 1.5528$	0.49277*	20
Total	$Y = 0.1151 x + 1.399$	0.41987#	82

Y - organic carbon, x - MBAS in sediment

* - above 95% significance, # - above 99% sinificance.

The sediments of the CES, though the depth of water column is only about 3 m, were reported as having reducing environment (Vasudevan Nayar, 1992). Though one can infer from the increase of sedimentary MBAS concentration from the upstream to downstream that MBAS from the water column transported to the sediments during mixing process, the absence of the correlation between dissolved salinity and MBAS rules out this. No correlation between the sedimentary and dissolved MBAS was also observed. The correlation between the sedimentary organic carbon and sedimentary MBAS, indicate the operation of diagenitic processes that govern the diagenitic processes of organic matter, in the case of MBAS also. A differential but related diagenitic demineralisation was reported earlier also (Vasudevan Nayar, 1992; Beenamma Jacob, 1993). The pattern observed in the southern part of the estuary and the barmouth confirms this agreement. In these stations, the MBAS showed a decreasing trend towards down stream in premonsoon, which can be due to the increased diagenic activity. The shallow nature of the overlying water may be the reason. During monsoon and postmonsoon, these stations behaved similar to stations in the northern part.

In conclusion, the behavior of MBAS and the distribution pattern in water indicate that MBAS is not a potential pollutant in these waters at present. The sedimentary level, though, showed higher concentration, it is removed along with the general diagenic processes of organic matter.

3.2 Phenolic compounds (4-AAP method)

Application of appropriate separation techniques of DOC gave, for phenols of high river flow, the following main components: 36% small molecule biodegradable, 42% humic and fulvic acids, 10% sulphonated lignin's, 7% smaller sulphonated aromatics, and 5% chlorinated organic compounds. During periods of low flow the percentages shifted towards man-made pollutants, the latter three groups increased to 53% (Sontheimer, 1976).

In most natural waters, aquatic fulvic acids are a major fraction (20-80%) of DOC (Thurman, 1985). Aquatic fulvic acids comprise heterogeneous, yellow, biogenic organic acids; their formation is poorly understood. Fulvic acid molecules may be formed by condensation of smaller monomers released by degradation or they may be residual products of degradation of precursor macromolecules.

According to the polyphenol theory of humate formation, natural phenolic compounds are capable of being used as building units for the enzyme mediated synthesis of soil organic matter (SOM) or humus (Stevenson, 1982). Condensation of humate precursors may also results from abiotic reactions catalyzed by mineral oxides or clays (Shindo and Huang, 1984; Wang *et al.*, 1978). Different processes involved in the synthesis of SOM can therefore result in the production of organic matter at different locations, which may be similar but not identical.

The highest permissible concentration of phenol in sea water should not exceed 1 µg/l (Buikema, *et al.*, 1979) while polluted coastal waters, the concentration of phenol was found to be in the range of 2-15 µg/l (Baetman and Vyncke, 1979; Krajnovic, 1988)

In the past few decades anthropogenic activities have resulted in the introduction of several substituted phenols in to the soil environment. These compounds, which include chloro, bromo and alkyl phenols are different from naturally occurring phenolic materials. Some of these synthetic phenols can be incorporated in to humic macromolecules by various oxidative coupling reactions in a manner similar to natural humus formation processes (Bollag *et al.*, 1980; Berry and Boyd, 1985 a).

The samples of final effluent collected from Sydney's three major sewage treatment plants contained the higher concentration of phenolics, which include the five chlorinated phenols. The chlorinated compounds are potentially more toxic and bioavailable than the phenols and cresols (Connell, 1988) and were readily bioaccumulated by mussels and the fish. The concentration of specific phenolic compounds were less than 150 µg/l, and after discharge through the deep water ocean outfalls those phenolics would be diluted to approximately 250:1 at the edge of the dilution zone, resulting in final concentration less than 0.6 mg/l. Again such concentration are unlikely to be acutely toxic, although chronic effects are possible.

The storm water samples contained low concentrations (0 to 1.7 µg/l) of eight of the ten phenolic compounds monitored including pentachlorophenol, with the most abundant compounds being o- and m-cresol and 2,4- dimethylphenol. These values, although low, may be of some concern in relation to both aquatic life and human health because these storm water drains discharge directly onto inter tidal and beach areas that are readily used as recreational areas and where little dilution occurs at low tide.

Concentration of phenolics in wet water storm-water flows were generally higher than after periods of dry weather, with most dry-weather samples containing only trace amounts of individual phenolic compounds (<.5 µg/l)(with the exception of Malabar and Greendale Creek, which had the highest concentration of pentachlorophenol). This is probable a result of flushing of roadways or possibly overflowing of the sewage system during rain, and the differences between the storm-water compositions of different drains could be accounted for by different land-use zones in each catchment.

In Ulhas estuary water samples with salinity range 5.3 to 35.8 ppt was analysed for phenols using 4-AAP. Concentration of phenolic compounds in this estuary varies from 0.00 to 23.5 µg/l (Kadam, 1996) and the highest value observed in the extreme upstream station. The value decreases with increase in salinity downstream. However, marginally high values were observed near the mouth of the estuary. The phenol concentration in surface waters during ^{flood} flood were 1.7 to 21.5 µg/l ranges, which decreases to 1.7 - 9.8 µg/l during ebb. Comparatively low values in bottom water and consistently high concentrations at upstream stations were the observations. The average concentration values increased from 0 to 16.4 µg/l towards upstream stations.

Krajnovic^{et al.} (1988) observed that the concentration of phenol during the experiments was decreasing and after a few days it dropped down to 50% of the initial values. This was attributed to the rapid proliferation of some phenolic bacteria, which have been demonstrated by inoculation of water samples from basins contain phenol, in to Bushnel- Hass culture media enriched with phenol only. From the basins containing 7.5 mg/l phenol the number of developing bacterial colonies was about 20 times higher than the control phenol free basins and they appear to be the main type of microorganisms population. It was suggested that moderate concentration of phenol in the marine environment do not represent a serious problem of pollution. It was also suggested that as in freshwaters (Trama, 1955; Kristoffersson, 1973) group of hetrotrophic bacteria prevent their excessive accumulation in the marine environment.

Sediments are major sinks for many phenols, and, in general, increasing substitution leads to an increase in their persistence in sediments. Phenol, because of its biodegradability is seldom detected in sediments. The same may be generally said about a number of other compounds such as the cresols, phenyl phenol, and the nonylphenol. By contrast some of these alkylphenols occur at remarkably higher concentrations, particularly near waste discharge site. Jungclaus^{et al.}, (1978) reported that two isomers of dibutylphenol reached 100-150 mg/kg in the sediments of Pawtuxet river, were as the corresponding maximum values for tributylphenol and dibutylmethyl phenol were 25 and 60 mg/kg, respectively.

Relatively little information is available on nitrophenols, methylphenols, and alkylphenols in water. One of reports (Jungclaus, 1978) indicated that the concentration of 11 alkyl phenols in the Pawtuxet river (USA) ranged from <1 to 6 µg/l. A similar range in values was reported for 4 -alkyl phenols in the Delaware River receiving both municipal and industrial wastes (Sheldon and Hites, 1978). Although nitrophenols were not found in either river, such compounds, especially trinitro-phenol, may be detected in rivers with input from munitions factory (USEPA, 1980).

Some phenolic compounds which occur in soil as degradation products of lignin's, humus and other polymeric materials are known to be toxic to plants (Wang & Chung., 1967; McCalla & Hasking., 1964.). The phenolics formed as the intermediates in the microbial degradation are essential for the cycling of nutrients in the environment (Subba Rao, 1971; Knoesel, 1959). The detection of different phenolics in mangrove soils of Goa (Agacaim and Banastarim) could help in understanding the productivity of these regions (Karanth *et al.*, 1975).

Sediments contain a large amount of plant polymers like cellulose, amylose, pectin and lignin especially in mangrove. Lignin is resistant to bacterial attack, is decomposed mainly by white rot fungi to phenolic subunits (Burges, 1967). The latter are converted to polymeric forms and humus, which also serves as food material for fungi (Burges, 1967; Doetsch and Cook, 1973). Thus phenolic compounds also formed during the degradation of organic matter derived from plants (Stout et al., 1976) . Molloy, 1976). Effluents^{are} also one of the factors for increasing the phenol concentration in the ecosystem.

Par and Mindola estuary receive substantial quantities of phenolic compounds through the wastewater resulting in their occurrence in the receiving water in measurable quantities especially during low tides. The input of phenolics in to the estuary was 180 and 573 kg/day respectively. The low tide concentration of 32 µg/l at the mouth of par estuary increases to 1050 µg/l in the inner estuary. Although kolak estuary received only 22 kg/day of phenolics, the level in the receiving water are markedly high due to weak flushing (Zingde^{et al.}, 1987).

In Kolak river the value of phenolics vary between 6-392 µg/l (Zingde, 1980). The phenolic content increased substantially at the down steam. The sharp increase in the phenolic content was considered to arise from GIDC industrial discharge that adds about 20 kg/day of phenolic compounds to the river wáter.

In Delaware Estuary, 4-AAP complexed phenolic compounds varied between 1-142 µg/l in water samples (Hunt ~~et al.~~, 1976) collected from 73 sites. In the upper estuary the phenolic concentration varies between 1-32 µg/l, in the lower estuary the values varies between 1-29 µg/l and in the shore samples the concentration is comparable with other stations which it varies between 1-142 µg/l. In mud samples collected from 58 sites, the phenolic concentration varies between 10 to 917 µg/g. Delaware Estuary receives many industrial and several petroleum refinery effluents, and is reflected in the phenol content.

The occurrence of total phenols was reported down stream from refinery outfalls in the region of Montreal (Polisois ~~et al.~~, 1975). Phenol concentration decreases with down stream distance from the source. Mass balance calculations at

the many transverse sections indicated that this decrease in concentration was not attributed to dilution only. Microbially mediated degradation was a contributing factor.

Lignin, a phenolic polymer unique in vascular plants (Sarkanen & Ludwick., 1971), detected and quantified by the presence of individual phenols comprising the vanillyl, syringyl and cinnamyl families (Hedges & Man., 1979; Hedges & Ertel., 1982). Lignin contains about 15% free phenolic groups and is present in all of the dissolved humic and fulvic acids from the amazon river system (John R. Ertel *et al.*, 1986). Lignin phenols are released from these humic substances with the same efficiency as from vascular plants. Vanillyl phenols 30% and 90 % for syringyl phenols and estimated that up to 8% of carbon in humic acids and 3% of the carbon in fulvic acids are contained in chemically recognisable lignin structural units.

The photochemical reactivity of dissolved lignin and photobleaching of dissolved organic matter were examined in river and ocean water by Stephen Opsahl & Benner (1998). Approximately 75% of the total dissolved lignin in Mississippi River were lost during 28 d of incubation in sunlight, mostly due to photooxidation. The remaining fraction of dissolved lignin was much susceptible to photooxidation. About 90 % of the dissolved lignin in river water was present as high molecular weight (>1000 Dalton) DOM. However, after exposure to sunlight, about 80% of the remaining lignin was present as low molecular weight (<1000 Dalton) DOM. An absolute increase in concentration of LMW lignin provides direct evidence for the photo transformation of macromolecular DOM in to smaller molecules. The composition of riverine dissolved lignin also changed dramatically during photooxidation. The abundance of syringyl relative to vanillyl phenols decreased twofold, while concentration of vanillic acid relative to vanillin , increased four folds. The dissolved lignin in HMW DOM from the equatorial Pacific Ocean was highly resistant to photooxidation. This finding suggests that photochemical reactions play a prominent role in determining the composition and reactivity of terrigenous DOM in the Ocean (Stephen Opsahl & Benner (1998).

3.2.1 Results and Discussion

In the Cochin estuary, no high concentration of phenolic compounds was observed in the study. The seasonal values are given in the Table 3.5, 3.6. In the northern part the concentration varied from 0.389 to 50 $\mu\text{g/l}$ where as in the southern

part values ranged from ND (not detected) to 66.53 $\mu\text{g/l}$ (Annexure3.2a). Minimum seasonal variation is observed in the Barmouth region, the values been between 3.13 and 34.39. In the northern part, the highest value for phenolic compounds was shown by station 1 (50 $\mu\text{g/l}$) bottom water during July 1996. In the southern part bottom water of station 7 (66.53 $\mu\text{g/l}$) exhibited the maximum value during Oct.1996.

Table. 3.5 Seasonal average of phenol in water (ppb).

Station	1	2	3	4	5	6	7
Postmonsoon. S	12.48	14.84	14.59	11.12	13.43	15.77	17.51
B	17.52	18.73	16.26	10.90	12.45	15.62	24.83
Premonsoon. S	12.09	11.94	9.35	12.44	13.01	10.43	9.85
B	12.43	17.95	9.14	9.06	12.24	12.17	10.26
Monsoon. S	31.30	24.95	28.00	18.46	23.39	13.75	14.78
B	40.84	24.95	28.00	19.48	9.51	18.81	18.60

S - surface; B - bottom

Table. 3.6 Seasonal average of phenol in sediment (ppm).

Station	1	2	3	4	5	6	7
Postmonsoon	10.50	2.19	5.80	3.25	16.17	5.51	11.64
Premonsoon	1.78	5.53	2.97	11.19	3.90	1.78	6.32
Monsoon	0.10	0.39	2.26	27.46	7.89	0.20	4.87

The seasonal values of phenolic compounds in the surface waters of Cochin estuary showed higher values in the northern part during monsoon and in the southern part during postmonsoon. In the monsoon season, the average value of phenolic compounds in the surface waters of Cochin estuary along the Periyar River shows an increasing trend towards the upstream. In the southern part of the estuary also showed a similar trend as that of the north zone, where phenolic concentration shows high values in the upstream station (station 7). Highest value for phenolic compounds during the monsoon months in the northern part of the estuary was during June 96 (46.17 $\mu\text{g/l}$ in station. 1) and in the southern part was in August 96 (24.06 $\mu\text{g/l}$).

The distribution of phenols during premonsoon indicates a similar trend to that of monsoon in the northern part of the estuary except in station 4 (fig. 3.2 a). But in southern part there is a decreasing trend towards upstream. The maximum concentration of phenolic compounds in the northern part during premonsoon months was observed on May 96 (35.97 $\mu\text{g/l}$ in station.2) and minimum in April 96 (0.39 $\mu\text{g/l}$ in

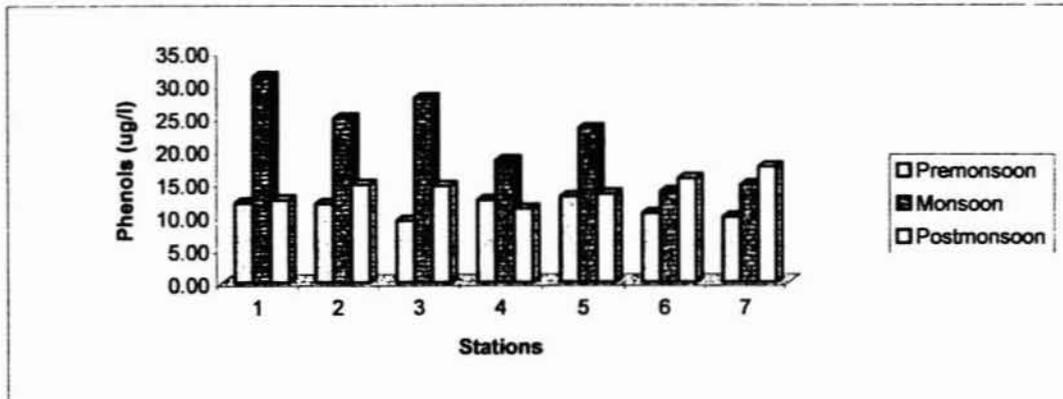


Fig: 3.2 a

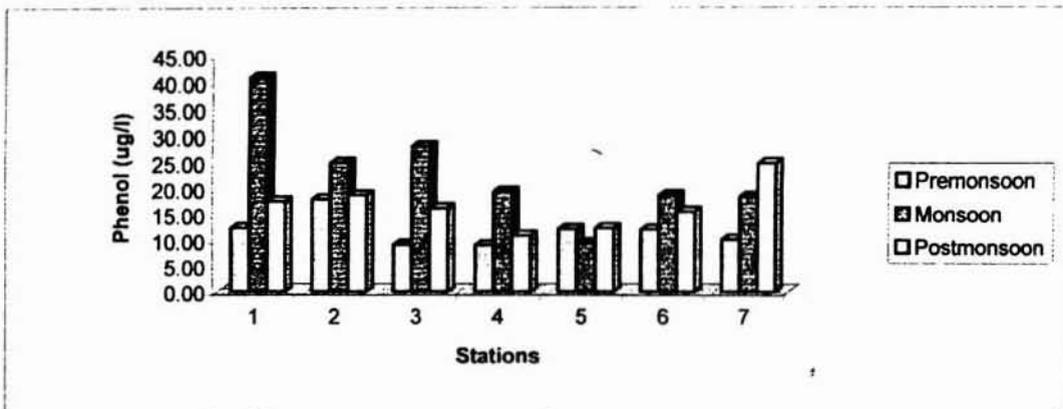


Fig: 3.2 b

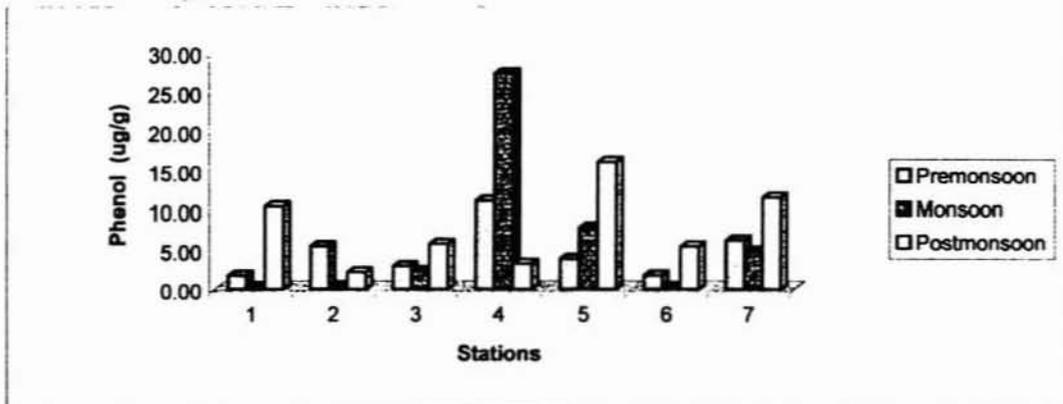


Fig: 3.2 c

station.1). The maximum value in the south zone was during May '96 (25.16 $\mu\text{g/l}$ in station. 7) and minimum value in February '96 (1.68 $\mu\text{g/l}$ in station.7).

In post monsoon season, the average concentration of phenolic compounds in station 5 is close to that of premonsoon values and no specific trend was observed in northern part. In the southern part, there was an increasing trend towards upstream.

In the bottom water (fig: 3.2 b), phenolic concentration showed an increasing trend towards upstream, except in station.2. In southern part also there was an increasing trend during postmonsoon towards upstream. During premonsoon the southern part of the estuary indicated a decreasing trend towards upstream. Station.6 showed slightly higher phenolic value than station 7 during monsoon season. In postmonsoon months, very high values of phenolic concentration were observed during October 96 in all the stations. In premonsoon, May 96 show maximum values in stations except Barmouth. In monsoon season, all stations except Barmouth showed higher values in all months.

Phenolic compounds in the sediments of the Cochin estuary showed wide fluctuations (Annexure 3.2 b), in the Barmouth and station.4 showing high concentration compared to other stations. In these stations, the phenolic concentration varied between ND level to 61.57 $\mu\text{g/g}$ and in southern part of the estuary, the value varied between ND to 35.04 $\mu\text{g/g}$. In the other stations of the northern part the concentration was in the range of ND level to 46.17 $\mu\text{g/g}$.

Phenolic compounds in the sediment during monsoon showed an increasing trend from station 1 to station 4 (fig 3.2 c) and in other seasons there is no specific trend and in the southern area station.7 showed high value in all seasons compared to station.6. The concentration of phenols in the sediment was always very low in station 1, except in November 96 (46.17 $\mu\text{g/g}$).

In the Cochin estuarine system, there are several potential sources of phenols along the banks of Periyar and Muvattupuzha rivers. The oil refinery, Hindustan Organic Chemicals and HIL discharge effluents containing phenols to the Muvattupuzha River. The sewage system is also used by many industries to dispose of their trade waste. Both the sides of the rivers are having high agricultural activities

and there is a heavy input of vegetative matter and remains of agriculture to the river system.

The distribution pattern of the phenols in all the three seasons is indicative of considerable contribution from the land. The upstream stations can be seen to have considerably high concentration compared to the saline region, this is more evident from the sedimentary values where an increase in concentration is observed towards the down stream. This can be attributed to the deposition of phenolic compounds during the mixing processes. Kadam^{Chargale} (1996) has reported a decrease in the phenol concentration in the Ulhas estuary with an increase in salinity. The comparatively low values observed in the bottom water and consistently high values in the upstream stations were observations of Kadam. This is a clear indication of anthropogenic input. In the present study such a distinct vertical distribution pattern is not observed mainly because of the low depth (~2.5m) which does not allow a differential to operate. The observed values are more or less high than that observed in the coastal waters of Thal, but lower^{than} to the values reported^{for} to Kolak River. The Par and Mindola estuary also reported to have considerably high concentration of phenols. The high industrial activity and the discharge of waste are considered as the reason for these high values. Such high concentration were reported from other estuaries also which receive high industrial discharge, the Delaware, Lake Traunsee, River Traun and Sanfransiso Bay (Table 3.7).

Table 3.7 Phenol concentration in water and sediment samples

<u>Environment</u>	<u>Concentration</u>	<u>Reference</u>
Delaware Estuary and coastal water:	1-142 µg/l in.	Hunt., 1976
Delaware Estuary sediment:	10 to 917 µg/g	Hunt., 1976
Ulhas estuarine water:	0.00 to 23.5 µg/l	Kadam. & Bagle., 1996.
Polluted coastal water:	2 to 15 µg/l	Krajnovic-Ozretic, and Ozretic, 1988)
Coastal water of Thal (Alibag):	below 10 µg/l	Zingde <i>et al.</i> , 1987.
Par and Mindola estuary water:	32 to 1050µg/l	Zingde <i>et al.</i> , 1987.
Kolak river water:	6 to 392 µg/l	Zingde <i>et al.</i> , 1980
Lake St Clair:	below 10 µg/l	EPA, 1973
Lake Erie:	5 to 30 µg/l	EPA, 1973
NorthWest Coast of India:	0 to 18.7 µg/l.	Kadam <i>et al.</i> , 1992
Lower San Joaquin River and Suisun Bay:	2.2 to 30 µg/l,	James <i>et al.</i> , 1962.
Lake Traunsee and River Traun:	8 to 45 µg/l.	Franz Bucher, 1993.
Mangrove sediments (Mandovi-Zuari)	0.26 to 1.01 mg/kg.	Helga R Gomas, 1982

The seasonal characteristics also indicate the dominance of terrestrial input to the phenolic content of the water as well as the sediments. Especially the monsoon values are clear indicative of such processes. The monsoon periods observed to have the lowest concentration in the bottom water, which is indicative of a low contribution from the seaside. The decreased flow in both rivers during the post and the premonsoon periods may be the reason for lowering the phenol content from that of the monsoon.

A few random exemptions, to the general trend, was one of the major observation, the localised effects may be the contributing factor. The average observed high value in station 4 Compared to station 5 can be due to the retting operations near the station 4 which releases a high load of phenolic compounds to the water. Another station to be specifically mentioned is station 2, which exhibited a higher concentration than station 1 during the premonsoon period. The low flow rate and the heavy industrial discharge may be the reason. A large number of industries including Fertiliser manufacturing drain just above station 2.

Except in the case of premonsoon, phenol gave significant correlation with salinity. The relation obtained is given in table 3.8. In sediment phenol gave correlation with organic carbon during premonsoon (table 3.9) and in other seasons there was no significant correlation.

Table.3.8 Correlation parameters: Salinity vs Phenol in water.

Season		r	n
Postmonsoon	$Y = -0.3942 x + 18.429$	0.35426#	68
Premonsoon	$Y = -0.743 x + 12.661$	0.08231	55
Monsoon	$Y = -0.5362 x + 23.489$	0.294412\$	40
Total	$Y = -0.392 x + 19.194$	0.37464#	164

Y - Salinity, x - Dissolved Phenol in water

Table 3.9 Correlation parameters: Organic C vs Phenol in sediment

Season		r	n
Postmonsoon	$Y = -0.5005 x + 11.915$	0.21508	34
Premonsoon	$Y = 0.4775 x + 1.8553$	0.31277\$	28
Monsoon	$Y = 0.6823 x + 3.1082$	0.19279	20
Total	$Y = 0.0131 x + 6.3909$	0.00558	82

Y - Salinity, x - Dissolved Phenol, *- above 95% significance,

- above 99% significance, \$ - above 90% significance.

This indicates that mixing processes have significant effect on the distribution and reactivity of phenol. A significant correlation was observed between sedimentary phenol and sedimentary organic carbon during the premonsoon only. There can be two reasons for this, (1) the major pathways of degradation of phenols is not the general diagenic process. Phenols are considerably reactive in aquatic systems (Krajnovic-Ozretic, 1988) and so the sedimentary concentration of phenols are not reflections of the normal diagenic activity. (2) The reducing conditions prevailing in the sedimentary environment relatively restricts further diagenic processes. Considering the general reactivity of phenols, the first is the most probable in the CES.

In short, phenol has not become a potential pollutant in CES, even though there is significant contribution from land, mainly through industrial effluents. The positive character of the estuary and the reactivity of the phenols may be the contributing factors to this situation. A regular monitoring of the phenol content to keep the system in a sustainable condition is essential.

Chapter 4

Chlorophenolic compounds in the water and sediments

The release of industrially derived halogenated organic compounds into the aquatic environment is of great concern, mainly because of their toxicity, resistance to degradation, and tendency to bioaccumulate and form part of the food web. All these compounds are toxic to aquatic species, but to varying degrees depending on the number and the position of the chlorine substituents on the benzene ring (Olli-Pekka Penttinen, 1995). The wood pulp industries, which use different chlorine bleaching processes, are one of the main sources of organic chlorinated compounds. Chlorophenolic compounds have been reported to ^{be} are the major constituents produced from lignin residues (Rogers & Keith., 1976). Some of them are toxic and can be accumulated in living organisms (Tian-Min Xie *et al.*, 1986). Knowledge of chemical characteristics that affects environmental partitioning is required to evaluate environmental hazard (Widdows and Donkin, 1991; Depledge and Fossi, 1994).

4.1 Chlorophenols in the aquatic environment

Structurally, chlorophenols fit to the requirements of receptor-producing respiratory uncoupling. However, uncoupling oxidative phosphorylation is the mode of toxic action for chlorophenols with two or more chlorine substituents, while non-specific polar narcosis is the proposed mechanism in the case of mono substituted phenols

(Exon, 1984). However this division is not generally accepted. Schultz (1987) and Bryant and Schultz (1994) classified only the tetra chlorophenols and PCP as uncoupling agents, and the mode of toxic action of lower substituted chlorophenols were described as polar narcotics. In vitro studies have shown that even mono and dichlorophenols have instantaneous uncoupling properties (Ravanel *et al.*, 1985, 1989; Tissut *et al.*, 1987), although PCP is about 200 fold more potent uncoupler than mono substituted chlorophenols.

When PCP was added to an acclimated soil in concentrations of 10, 20, 40 and 80 mg/kg of soil by dry weight, a decrease in mineralisation was observed with increase in PCP concentration (Ramaprasad, 1994). The amount of PCP in solutions depends on several physical and chemical characteristics of soil such as pH, moisture content, and bulk density (Justin Hurst *et al.*, 1997).

The toxicity of chlorophenols can be considered as due to the three specific chemical characteristics (Terada, 1990); (1) an acid dissociable group (hydroxyl substituents), (2) a strong electron withdrawing moiety (halogen substituents), and (3) a bulky hydrophobic group (benzene ring). The hydroxyl group decreases hydrophobicity but increases reactivity (Bryant and Schultz, 1994). Replacement of the acid- dissociable group by a non-acid dissociable moiety results in complete loss of uncoupling activity (Terada, 1990). The addition of a chloro group increases both hydrophobicity, which dictates exposure, and the acidic strength (reactivity) of phenol. The more acidic the chlorophenol is, the more uncoupling the character of the chlorophenol (Saarikoski and Viluksela, 1982). Thus, the potency of chlorinated phenols in uncoupling oxidative phosphorylation depends on the degree of chlorine substitution (Shannon *et al.*, 1991; Ravanel *et al.*, 1989).

PCP is a general metabolic poison used extensively as a biocide in many industrial applications and as such is a contaminant in many water bodies (Rao, 1978; Jones, 1981). A primary action of PCP is the uncoupling of oxidative phosphorylation (Weinbach, 1957; Weinbach and Garbus, 1965) along with other effects on energy metabolism (Bostrom and Johansson, 1972). The net effect is to increase the rate of energy metabolism in compensation for the reduced efficiency in ATP production. One important consequence of this is a reduced rate of growth, (Krengel *et al.*, 1966; Webb and Brett, 1973; Hodson and Blunt, 1981; Holcobe *et al.*, 1982; Sloof and Canton, 1983; Mathers *et al.*, 1985).

The majority of the organochlorinated compounds are high molecular weight chlorolignins (>1000). These are likely to be biologically inactive and have a small contribution to the toxicity, mutagenicity and BOD. They are stable against biodegradation, thus they cannot be removed by conventional primary and secondary treatment. However, long term, slow biodegradation of high molecular weight chlorolignins may cause environmental problems. Low molecular weight chlorinated neutral compounds are major contributors to mutagenicity and bioaccumulation due to their hydrophobicity and ability to penetrate cell membranes (Carlberg and Nashøaug, 1986; Heimbürger *et al.*, 1988a, b; Sun *et al.*, 1989).

Wegman & Hofstee., (1979) studied the chlorophenols in the surface waters of the Netherlands during 1976-1977. In river Rhine the concentration of 2,4-, 2,5- and 2,6-dichlorophenol, 2,4,5- and 2,4,6- trichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol had a frequency of occurrence of over 30%. However, in this period only the median values of the concentration of 2,6-dichlorophenol (0.15 and 0.1 µg/l), 2,4,6-trichlorophenol (0.19 and 0.18 µg/l), 2,3,4,6-tetrachlorophenol (0.14 and 0.08 µg/l) and pentachlorophenol (0.73 and 1.1 µg/l) were found above the detection limit. In the Dutch part of the river Rhine the concentration of chlorophenols did not increase down stream. The concentration of PCP was maximum (11 µg/l) during the spring of 1977. In the river Meuse at Eijsden only the median values of the concentration of 2,3,4,6- tetrachlorophenol (0.06 and 0.05 µg/l) and PCP (0.38 and 0.79 µg/l) were above the detection limit. The concentration of chlorophenols found in a polderditch at Valkenberg was higher than those found in the river Meuse (Piet and De Grunt, 1975). The values reported were monochlorophenols 3-20 µg/l, dichlorophenols 0.03-1.5 µg/l and trichlorophenols 0.07 - 0.1 µg/l.

In lake Ketelmeer, 2,5- dichlorophenol, 2,3,5 and 2,4,5- trichlorophenol, 2,3,4,5- and 2,3,4,6-tetrachlorophenol and PCP had frequency of occurrence of 100%

in sediment samples collected during 1979-1980 from 35 stations (Wegman ~~et al.~~^f, Van Den Broek 1983). 2- and 4-monochlorophenol and 2,3,6-trichlorophenol were never found above the detection limit. However, the detection limits for monochlorophenols were much higher than those for other chlorophenols. Median values of the concentration in sediment samples of above 5 mg/kg were found for 2,5-, 3,4-, and 3,5-dichlorophenol, 2,4,5-trichlorophenol and PCP. The ratio of PCP in sediment to water was 20. Generally, the concentration in sediment was much higher than in water. The sediment samples from the harbor and the Spui River was dumped in the North Sea and were hardly contaminated with chlorophenols. The contamination of the Haringvliet River was comparable to that of Lake Ketelmeer. The highest concentrations of chlorophenols were found in the sediment samples from the Nieuwe Maas River at Rotterdam and Vlaardingen, a highly industrialised area (Wegman ~~et al.~~^e, Van Den Broek 1983).

Bromophenols may be formed during chlorination of phenol in the presence bromide ions. The formation of 2,4,6-tribromophenol was reported under these conditions (Janet A. Sweetman, ~~et al.~~^{& Simmons}, 1980). A brominated phenol was observed also in the process of chlorinating humic acid when chlorination was done from a system containing bromide ion.

During 1979, a chemical spill occurred in Missouri as a result of train derailment (U.S. Environmental Protection Agency, 1980). The concentration of 2-chlorophenol at the site reached a maximum of 1 mg/l on the day of the wreck, decreasing to, 0.0015 mg/l within two months. Bevenue *et al.*, (1972) reported PCP residues of 0.002 to 0.27 µg/l in the snow of Maunakea Summit. This resulted in the PCP levels of 0.01 µg/l in Lake Waiau, fed almost exclusively by the summit snows. Arsenault (1976) found that PCP occurred at relatively high levels (max 0.3 mg/l) in the air of wood-preservation plants.

Some of the highest values of PCP in water (306 - 895 µg/l) have been reported for the Hayashida River (Japan), which receives uncontrolled input of leather tannery wastes (Yasuhara *et al.*, 1981). Elevated concentrations (10-100 µg/l) have occurred in the Pawtuxet River (USA) owing to discharge from a chemical plant (Jungclaus *et al.*, 1978), whereas residues of 1-6 µg/l were reported for the Delaware and Mississippi Rivers (Sheldon and Hites, 1978).

Chlorinated phenols are widely distributed in surface waters and occur at high variable concentration, depending on waste source. Peit and De Grunt (1975) reported that total monochlorophenol level in rivers and coastal waters of the Netherlands ranged from 3-20 $\mu\text{g/l}$ compared with 0.01 - 1.5 and 0.003 - 0.1 $\mu\text{g/l}$ for dichlorophenols and trichlorophenols, respectively. Marked weekly and monthly variations in these levels were observed which was largely related to rain water and water flow (Wegman & Hottée 1979). Jones (1981), having reviewed much of the Canadian literature, reported that the release of effluents from a pulp and paper mill resulted in average DCP and TCP levels of 4 and 13 $\mu\text{g/l}$, respectively, in the coastal waters of Lake Superior. In addition, water collected from stream mouths and inshore areas of lake Ontario contained PCP ranging from 0.005 to 1.4 mg/l with transient levels of up to 23 $\mu\text{g/l}$, being recorded after periods of heavy rainfall.

Water and sediment samples from Lake Bonney (Van Leeuwen *et al.*, 1993) showed the presence of chlorophenolic compounds. In water samples, the major chlorophenols detected were 2,4,6-trichlorophenol, tetrachlorocatechol and chlorinated guaiacols. In sediment samples, chlorinated guaiacols and chlorinated catechols occupy the major fractions.

In Naylor's Run Creek the concentration of PCP ranges from about 0.1 to 10 ppm (Fontaine *et al.*, 1976). Near the stream source, the levels were highest, while the down stream levels (away from the factory area) were much lower. Since PCP, most likely, does not decompose to any significant extent in its flow of several miles the lower concentrations must be either due to adsorption or dilution, or both.

Fish may contain a wide range of phenols in their tissues. Some of the more commonly detected compounds include chlorinated phenols, their methylated derivatives and alkylphenols. Paasivirta *et al.*, (1980) measured the concentration of 12 polyhalogenated phenols in fish from lake Pajanne (Finland), which has a number of pulp mills situated on its shore. Only six compounds were regularly detected, the most common of which were 2,4,6-TCP and 4,5,6-trichloroguaiacol, and tetrachloroguaiacol. Similarly, discharge of pulp mill wastes in to Atlantic coastal waters (Canada) resulted in the adulteration of fish tissues with highly chlorinated phenols, whereas fish inhabiting the Fraser river (Canada) were contaminated with chlorophenols from wood preservation industries. The methylated derivatives of PCP (pentachloroanisole) has been found in fish from the Detroit River (USA) and fish from

15 of the 26 rivers sampled near the Great Lakes (Kuehl, 1981). Lower chlorinated anisoles and pentachloroanisole have also been found in fish from the Arkansas River and in fish exposed to municipal wastes (Veith *et al.*, 1979).

Wolfgang Ernst & Weber, (1978) studied the distribution of PCP in the Weser river, estuary and German Bight (coastal area) from November 1976 to December 1977. They observed that PCP concentration in the water samples of Weser River and estuarine water varied from 49 to 496 ng/l. In the German Bight, PCP level dropped near to the detection limit with increasing distance from the coastline, the value varied between <2 to 26ng/l. The highest value (26 ng/l) was due to the input from river Elbe and in the remaining stations the PCP concentration was below 10 ng/l. Tidal variations of the PCP- levels in Weser estuary clearly correlated to tidal fluxes resulting in highest levels at low tide, thus indicating the input of river-borne PCP.

In addition to PCP, six lower chlorinated phenols were identified and quantified. The sum of the chlorinated phenols in estuarine waters averaged 20% of PCP, 2,3,5,6- and 2,3,4,6- tetrachlorophenol and 2,4,6 trichlorophenol predominated. River input of chlorophenols can be derived from decreasing concentrations in the rivers way to the open sea. No change was showed in the comparing patterns of chlorophenol levels in water from different areas of the estuary (Weser, 1978).

Weber (1978) reported that PCP residues in the sediments of Weser estuary averaged 13 µg/kg dry weight compared with 0.3 to 1.5 µg/kg for dichloro-, trichloro-, and tetrachlorophenol. The coastal waters of British Columbia (Canada), where the effluents from a wood preservative plant was discharged had an average PCP concentration of 65 µg/kg, tetrachlorophenol 96 µg/kg and trichlorophenol 26 µg/kg (Jones, 1981).

In Tama River that covers 60% of the total Tokyo area a concentration of 1 - 9 x 10² ng/l were observed. In Sumida, which is, a tidal river in the central part of Tokyo had a concentration of 1-9 X 10³ ng/l (Matsumoto *et al.*, 1977)

In Danube River average chlorophenols concentration ranged from 0.017 to 1.151 µg/l. The highest concentration measured for 2,4-dichlorophenol and the lowest for the isomers of tetrachlorophenol (Veningerova *et al.*, 1998).

4.2 Results and Discussion

The chlorinated organic compounds in the aquatic environments are of great concern because of their persistence and toxicity. Chlorophenols, a class of compounds having considerably high industrial applications, form a significant fraction of the chlorinated organic compounds which pose considerable threat to restricted and semi enclosed water bodies. The detailed investigations on chlorophenols have identified about 19 of them, with varying number of chlorine and varying concentrations (Buikema *et al.*, 1979; Olli-Pekka Penttinen, 1995). A number of them are the result of industrial and urban discharges and the rest produced within the system. In this study, due to unavailability of standards in the required purity, formal identification and assessment was done only for three of the species. Seven more prominent fractions were quantified with respect to o-chlorophenol and so the values reported here are only relative in the case of these seven fractions (Representative gas chromatograms are given in Annexure 4.1 to 4.3). In general fraction 6 are the most abundant in the CES and fraction 7 the least abundant. Trends given denote decrease or increase, as the case may, towards downstream (station 1 to station 4 in the north and station 7 to station 5 in the south).

In the Cochin estuary o-chlorophenol showed low values in the surface water compared to bottom water in the northern part of the estuary and higher values in the surface water in the southern zone. In the southern part of the CES o-chlorophenol showed an increasing trend during postmonsoon in the bottom water and there was no significant trend for o-chlorophenol in the Cochin estuary (fig 4.1 a, b, c). Seasonal o-chlorophenol showed high values during monsoon season in the surface and bottom water, except in station 6 surface water during postmonsoon season. In the northern part of the estuary o-chlorophenol in the water samples varied from 2.03 to 43.32 ng/l and in the southern part the value varied from 3.5 to 376.75 ng/l (Table. 4.1 a). In the sediment samples o-chlorophenol showed a decreasing trend during monsoon season in the northern part of the study area and the station.5 showed the maximum value during monsoon (33.82 ng/l). In the northern part of the estuary o-chlorophenol varied from 8.93 to 28.36 ng/g and in the southern part the value varied between 7.1 to 33.82 ng/l (Table. 4.1b).

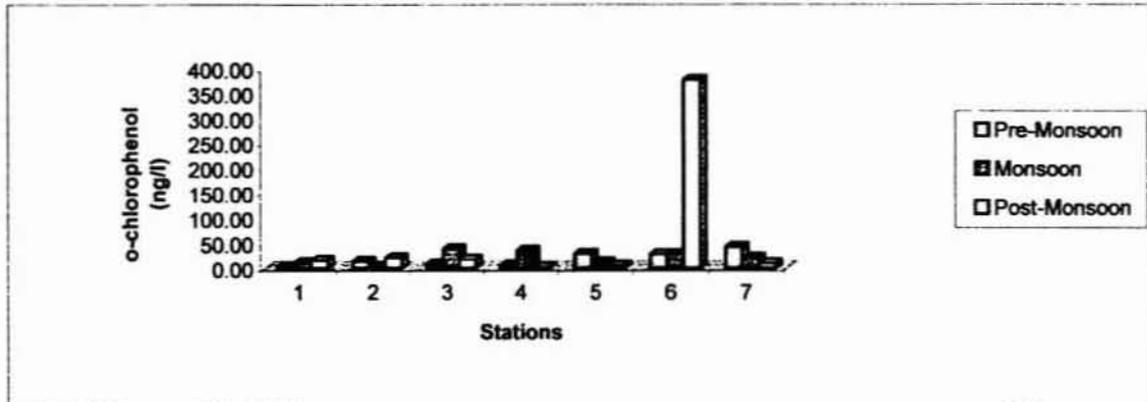


Fig. 4.1 a

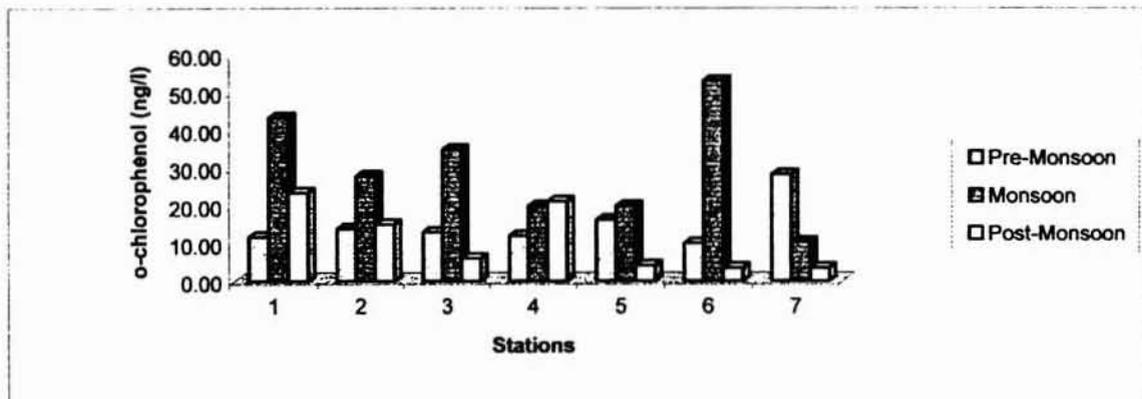


Fig. 4.1 b

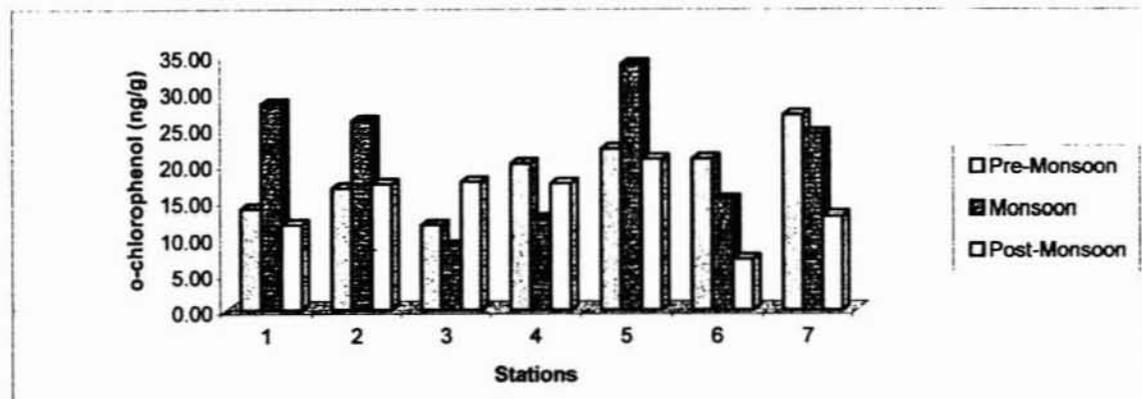


Fig. 4.1 c

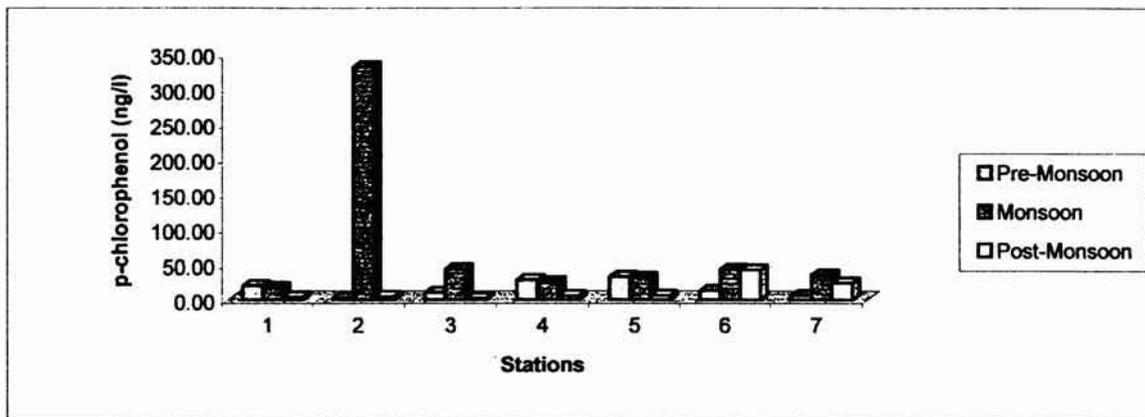


Fig: 4.2 a

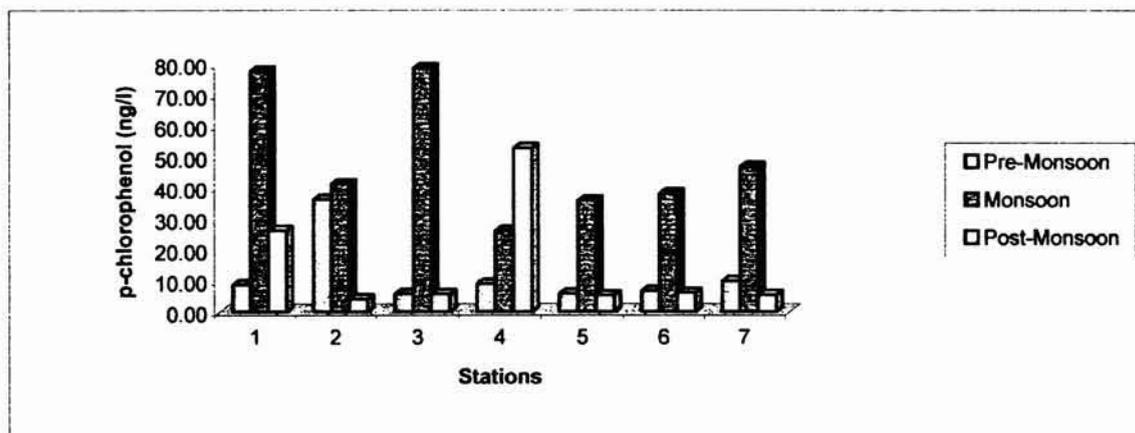


Fig: 4.2 b

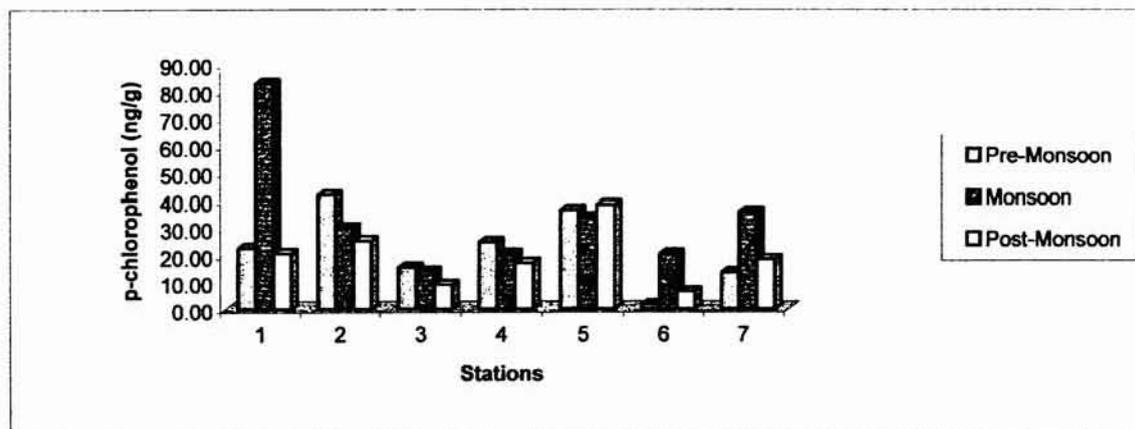


Fig: 4.2 c

Table 4.1.a. o-chlorophenol in water(ng/l)

Station	1	2	3	4	5	6	7
Premonsoon. S	2.91	13.13	8.14	5.47	28.74	27.11	41.76
B	11.74	13.84	12.96	12.00	16.23	9.94	28.28
Monsoon. S	10.73	3.39	37.62	34.50	11.89	27.39	20.44
B	43.32	27.83	34.90	19.92	19.91	53.15	10.37
Postmonsoon. S	15.16	20.31	17.18	2.03	5.10	376.75	9.41
B	23.39	15.06	5.95	21.15	4.09	3.50	3.46

S - surface; B - bottom

Table 4.1.b. o-chlorophenol in sediment (ng/g)

Station	1	2	3	4	5	6	7
Premonsoon	13.95	16.76	11.85	20.17	22.18	20.83	26.88
Monsoon	28.36	26.03	8.93	12.52	33.82	15.18	24.27
Postmonsoon	11.89	17.32	17.67	17.42	20.74	7.10	12.99

p-chlorophenol showed a similar trend as that of o-chlorophenol in the water samples, p-chlorophenol (fig. 4.2 a, b) showed higher values in the surface and bottom water during monsoon season except in station 4 bottom, where the concentration was high during postmonsoon. In the southern part, the values showed a decreasing trend in the bottom water during premonsoon and monsoon seasons and an increasing trend in the surface water during premonsoon. In the northern part of the estuary p-chlorophenol in the water samples varied from 2.07 to 332 ng/l and in the southern part the value varied from 5.32 to 47.03 ng/l (Table 4.2 a). In the sediment p-chlorophenol showed a decreasing trend during monsoon in the northern part and in other seasons there was no significant trend in the north and southern part (fig.4.2 c). In the northern part of the estuary p-chlorophenol in the sediment varied from 9.05 to 83.05 ng/g and in the southern part the value varied between 1.73 to 38.52 ng/l (Table 4.2 b).

Table 4.2.a. p-chlorophenol in water (ng/l)

Station	1	2	3	4	5	6	7
Premonsoon. S	19.91	2.83	10.40	28.45	32.93	13.07	5.82
B	8.86	36.40	5.89	9.17	5.97	6.81	10.00
Monsoon. S	17.35	332.00	44.06	25.37	31.59	43.34	35.38
B	77.95	41.50	78.87	26.34	36.06	38.37	47.03
Postmonsoon. S	3.92	4.31	2.07	5.48	5.86	42.54	24.26
B	26.30	4.13	5.81	53.07	5.32	6.18	5.52

S - surface; B - bottom

Table 4.2.b. p-chlorophenol in sediment (ng/g)

Station	1	2	3	4	5	6	7
Premonsoon	22.81	42.10	15.60	24.97	36.71	1.73	13.68
Monsoon	83.05	30.27	14.13	20.61	34.00	20.54	36.06
Postmonsoon	20.75	25.44	9.05	17.22	38.52	6.52	18.56

m-chlorophenol in the surface water showed only a decreasing in the southern part of CES during premonsoon and in other seasons there was no significant trend in the study area (fig 4.3 a, b, c). In water samples m-chlorophenol showed higher values during monsoon season in the surface and bottom water, but in sediment samples it showed low values during monsoon except in station.1. Generally m-chlorophenol showed higher values in the bottom water than surface water. In the northern part of the estuary m-chlorophenol in the water samples varied from 2.71 to 163.36ng/l and in the southern part the value varied from 4.91 to 285.88 ng/l (Table 4.3 a). In the northern part of the estuary m-chlorophenol in the sediment varied from 6.53 to 87.99 ng/g and in the southern part the value varied between 18.42 to 84.32 ng/l (Table 4.3 b).

Table. 4.3.a. m-chlorophenol in water (ng/l)

Station	1	2	3	4	5	6	7
Premonsoon. S	9.70	21.14	44.31	11.54	4.91	7.56	9.17
B	32.66	2.71	4.38	39.25	11.90	20.81	14.61
Monsoon. S	11.07	163.36	114.17	154.76	132.55	59.57	112.34
B	111.87	70.96	140.29	117.13	285.88	40.63	125.94
Postmonsoon. S	38.13	7.48	12.27	23.09	26.84	105.77	39.01
B	5.41	16.08	106.40	6.14	7.78	48.82	5.53

S - surface; B - bottom

Table. 4.3.b. m-chlorophenol in sediment (ng/g)

Station	1	2	3	4	5	6	7
Premonsoon	12.69	42.48	6.53	46.50	55.53	84.32	48.97
Monsoon	87.99	38.62	15.12	32.74	45.16	51.68	39.05
Postmonsoon	8.81	12.58	48.51	39.42	18.42	60.17	30.37

The concentration values of o-, p- and m-chlorophenols in CES are more or less close to each other both in water and sediment. Though m-chlorophenol did not give any specific trend, the concentration of all monochlorophenols showed higher concentration in monsoon season. Considering this observation along with the general high reactivity of monochlorophenols, the observed concentration of monochlorophenols can be considered as of anthropogenic origin. Concentrations of

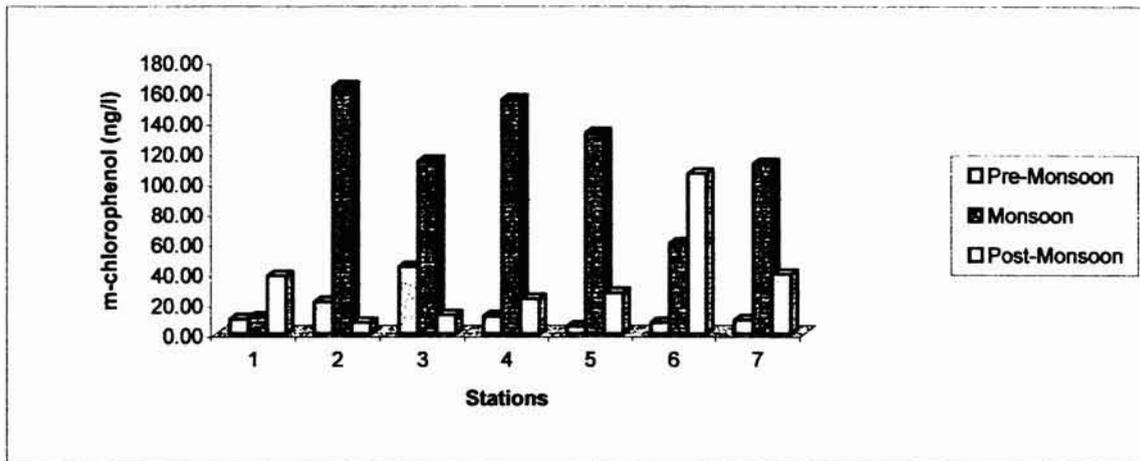


Fig: 4.3 a

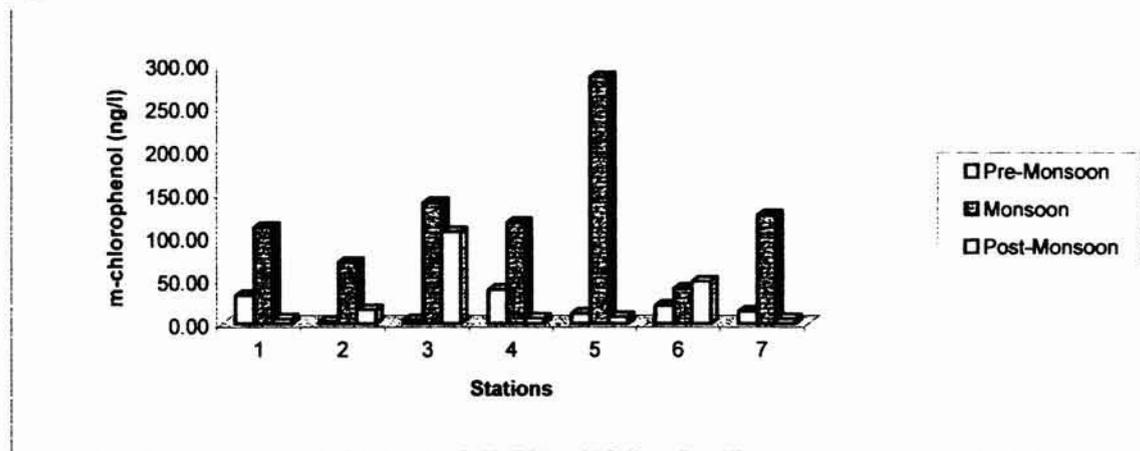


Fig: 4.3 b

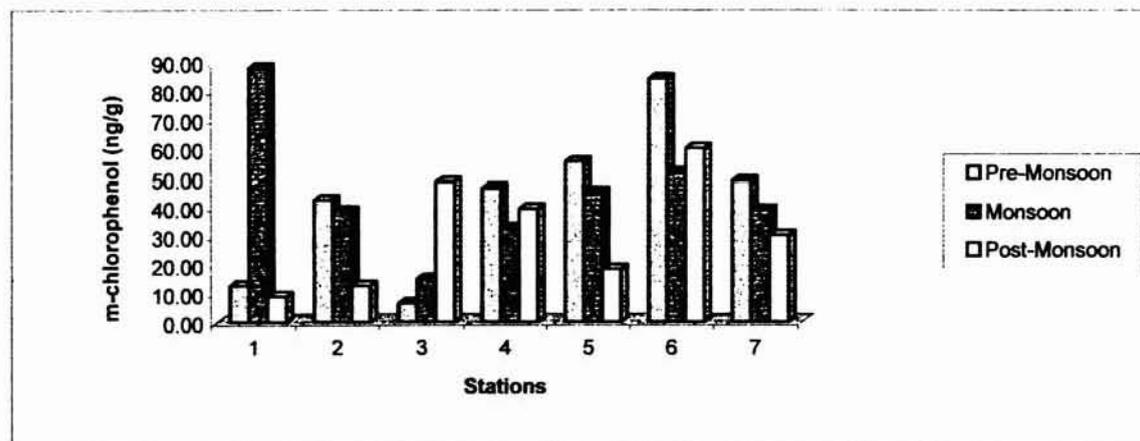


Fig: 4.3 c

monochlorophenols in most of the sediments are near to not detected level (Wegman *et al.*, 1983). In this study, these compounds showed significant concentration in sediments. This may be due to the low depth and considerably high discharge through fresh water. The concentration in water confirms this possibility. The decreasing trends in the concentration of these compounds from upstream to downstream in the sediments also support this view.

Fraction 1 showed a decreasing trend in the northern part of the estuary during monsoon in the bottom water. The surface water of the southern part also showed the similar trend during monsoon and in other seasons the surface and bottom water gave no significant trend (fig 4.4 a, b). In the northern zone fraction 1 concentration varied between 2.26 to 60.87 ng/l and in the southern zone the value varied between 3.5 to 117.48 ng/l (Table 4.4 a). The sediment exhibited an increasing trend during monsoon and postmonsoon in the northern part and in the southern part during monsoon (fig 4.4 c). In the northern part fraction 1 concentration varied from 32.81 to 57.84 ng/g and in the southern zone the value varied between 3.64 to 47.49 ng/g (Table 4.4 b).

Table 4.4.a. Fraction.1 in water (ng/l).

Station	1	2	3	4	5	6	7
Premonsoon. S	39.77	37.39	39.15	36.40	45.77	5.62	31.02
B	42.31	39.48	9.72	34.74	6.01	4.12	6.38
Monsoon. S	28.33	47.67	42.06	33.81	32.14	36.93	49.09
B	60.87	44.06	40.24	39.40	39.62	40.17	47.03
Postmonsoon. S	5.70	32.06	5.27	37.87	39.48	42.54	3.50
B	3.87	2.26	45.98	53.07	41.27	117.48	37.47

S - surface; B - bottom

Table. 4.4.b. Fraction. 1 in sediment (ng/g)

Station	1	2	3	4	5	6	7
Premonsoon	47.71	54.48	47.69	32.81	3.64	27.56	45.03
Monsoon	46.82	48.85	49.97	51.54	46.78	45.28	26.71
Postmonsoon	35.32	39.25	49.55	57.84	47.49	38.99	39.39

Fraction 2 showed an increasing trend in the southern part during the premonsoon and a decreasing trend in postmonsoon season in the bottom water (fig 4.5 a, b). The sediment and surface water had no significant trend in the study area (fig 4.5 c). The fraction.2 varied between 16.19 to 95.76 and 23.73 to 74.79 ng/l for the northern and southern zones respectively (Table 4.5 a). In sediment samples

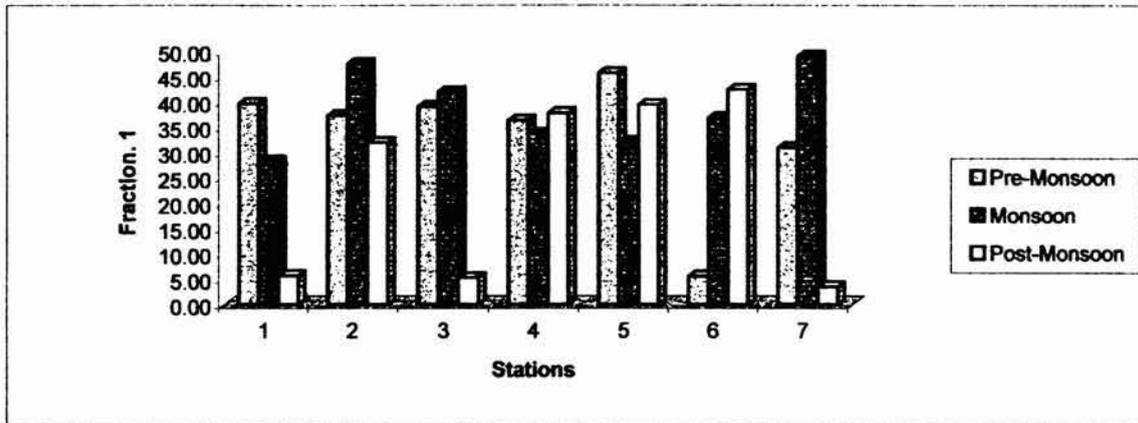


Fig: 4.4 a

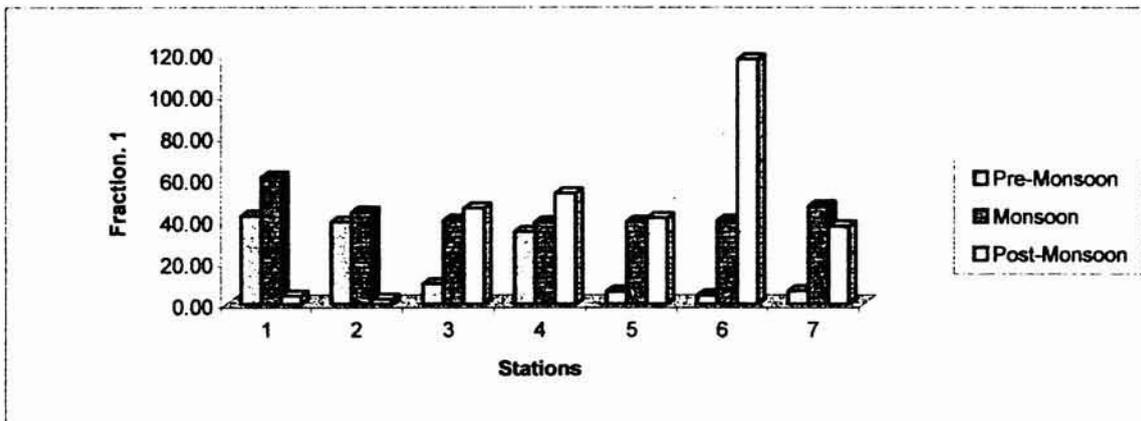


Fig: 4.4 b

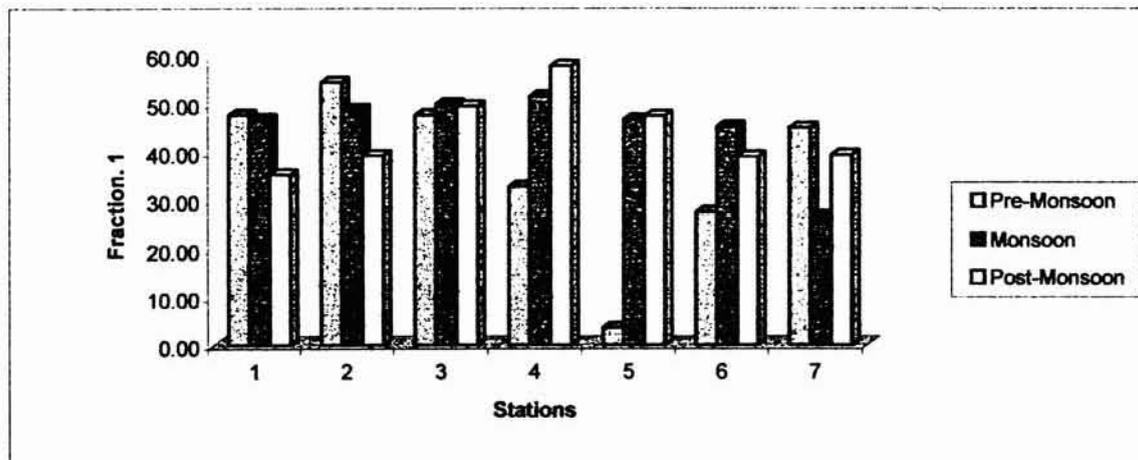


Fig: 4.4 c

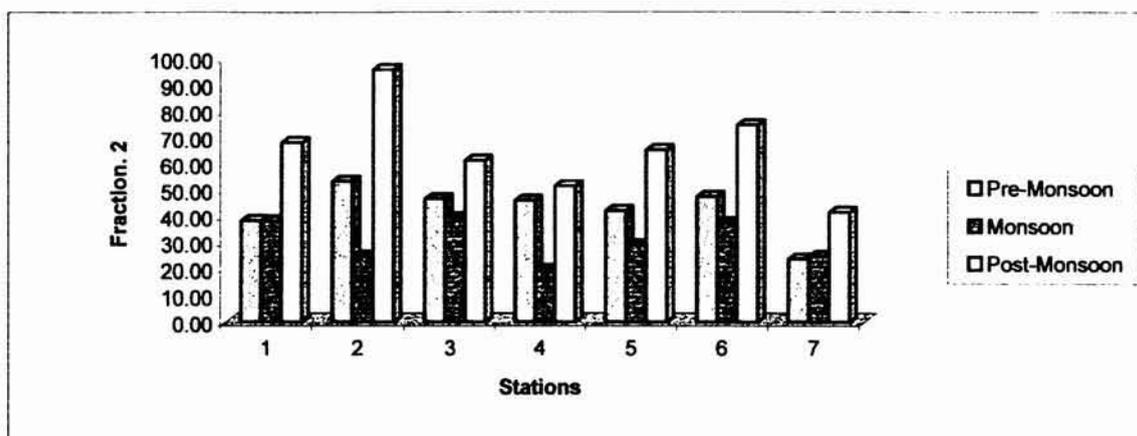


Fig: 4.5 a

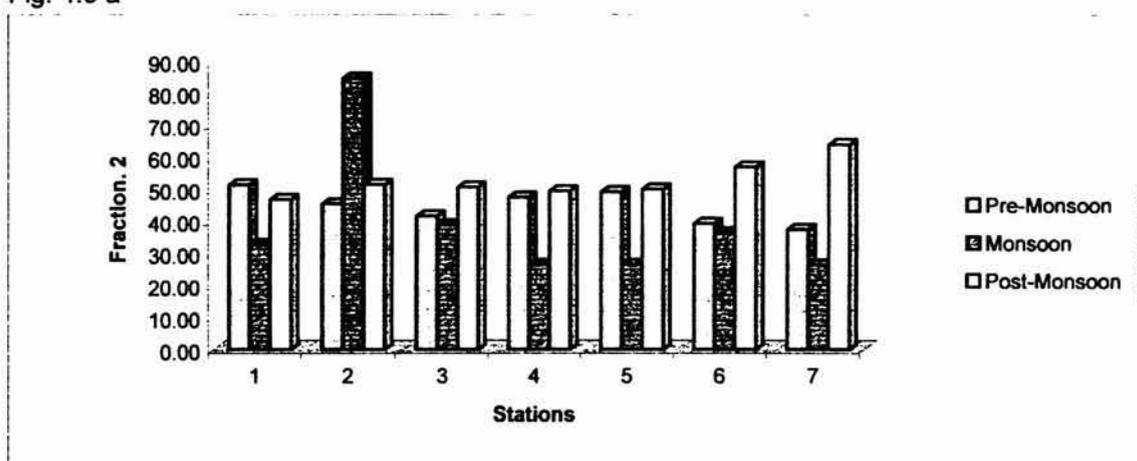


Fig: 4.5 b

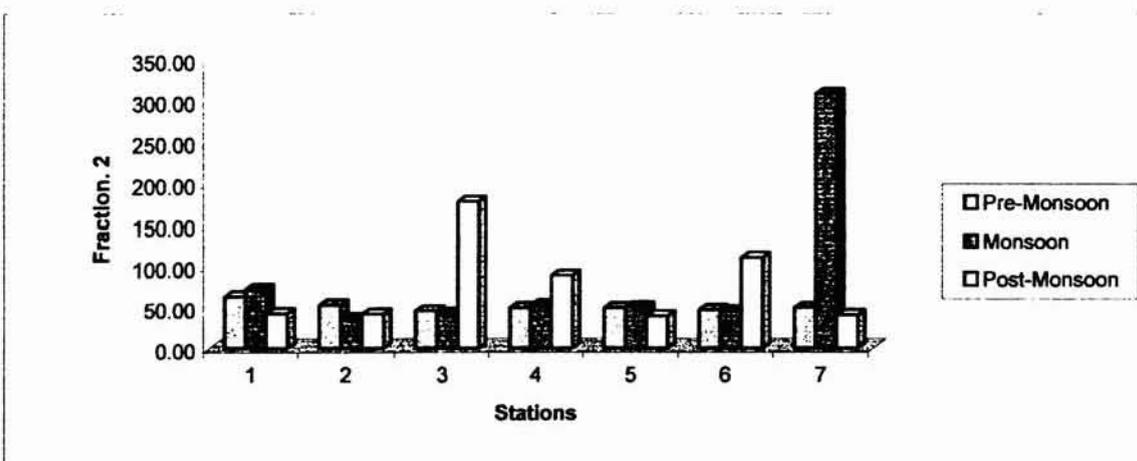


Fig: 4.5 c

fraction 2 varied between 36.64 to 178.14 ng/g in the northern part of the estuary and 39.51 to 308.95 ng/g in the southern part (Table 4.5 b).

Table 4.5.a. Fraction 2 in water (ng/l).

Station	1	2	3	4	5	6	7
Premonsoon. S	38.31	53.41	46.67	46.09	42.15	47.60	23.73
B	51.38	45.47	41.65	47.59	49.22	39.33	37.51
Monsoon. S	38.20	24.77	39.46	19.65	29.13	37.46	24.74
B	32.72	84.82	38.83	26.37	26.53	36.31	26.41
Postmonsoon. S	68.05	95.76	61.30	51.55	65.34	74.79	41.59
B	46.80	51.51	50.75	49.39	50.08	56.97	63.98

S - surface; B - bottom

Table 4.5.b. Fraction 2 in sediment (ng/g)

Station	1	2	3	4	5	6	7
Premonsoon	63.47	53.04	45.85	49.52	49.47	47.15	49.73
Monsoon	72.71	36.64	42.40	52.90	50.60	45.46	308.95
Postmonsoon	42.40	41.95	178.14	89.24	39.51	110.89	40.91

Fraction 3 showed an increasing trend in the surface water of northern part during monsoon and postmonsoon. The bottom water also showed a similar trend during premonsoon of southern part (fig 4.6 a, b). The sedimentary concentration indicated high values in station 1 during monsoon and there was no significant station wise trend (fig 4.6 c). In the northern zone the value of fraction 3 varied between 3.71 to 172.74 ng/l and 1.27 to 130.07 ng/l in the southern part (Table 4.6 a). In sediment the value varied between 42.73 to 133.47 ng/g in the northern part and 36.69 to 73.35 ng/g in the southern part (Table 4.6 b).

Table 4.6.a. Fraction 3 in water (ng/l).

Station	1	2	3	4	5	6	7
Premonsoon. S	83.24	22.02	50.29	41.12	50.42	38.98	41.91
B	40.44	16.19	56.11	37.65	65.49	24.87	1.27
Monsoon. S	17.66	51.84	172.74	30.97	13.20	46.67	28.97
B	20.99	47.05	44.28	29.93	42.50	58.47	43.54
Postmonsoon. S	4.51	3.71	11.09	46.32	41.19	130.07	72.29
B	27.89	22.51	48.28	41.48	52.19	68.52	2.35

S - surface; B - bottom

Table. 4.6.b. Fraction 3 in sediment (ng/g)

Station	1	2	3	4	5	6	7
Premonsoon	101.72	71.42	76.98	83.07	68.80	73.35	66.25
Monsoon	133.47	42.73	45.26	52.69	68.47	36.69	50.86
Postmonsoon	56.85	50.78	69.62	44.46	68.09	44.83	58.29

Fraction 4 showed an increasing trend in the surface water during premonsoon in the southern part and a decreasing trend during postmonsoon in the surface of northern part of CES (fig 4.7 a, b). The surface water concentration of fraction 4 generally showed high values during premonsoon compared to bottom water and in monsoon season the bottom water showed higher values. In water samples fraction 4 varied between 17.36 to 417.78 ng/l in the northern zone and 21.19 to 1018.31 ng/l in the southern part (Table 4.7 a). In the sediment samples the value varied between 2.93 to 69.08 ng/g in the northern part and 7.49 to 59.91 ng/g in the southern part of the estuary (Table 4.7 b). The sedimentary concentration also showed a decreasing trend during premonsoon and monsoon of the southern part and monsoon in the northern part of the estuary (fig 4.7 c). But in postmonsoon season, the southern part of the estuary showed an increasing trend.

Table 4.7.a. Fraction 4 in water (ng/l).

Station	1	2	3	4	5	6	7
Premonsoon. S	225.70	166.38	185.76	277.83	280.13	113.24	59.04
B	41.50	178.74	134.40	194.13	162.83	86.28	101.49
Monsoon. S	82.07	166.56	78.74	38.71	21.19	51.97	57.41
B	165.37	153.99	175.20	17.36	30.82	148.16	77.11
Postmonsoon. S	132.44	130.16	77.48	92.61	87.44	1018.31	317.17
B	182.05	101.31	408.42	417.78	72.38	172.99	113.01

S - surface; B - bottom

Table. 4.7.b. Fraction. 4 in sediment (ng/g)

Station	1	2	3	4	5	6	7
Premonsoon	21.83	51.08	27.77	11.16	20.04	28.91	49.53
Monsoon	39.97	12.76	11.60	2.93	7.49	20.51	45.54
Postmonsoon	80.69	69.08	40.64	68.24	59.91	48.02	36.89

Fraction 5 generally showed high values in the surface and bottom water during premonsoon season in the northern part of the estuary except in station 1 surface, where high values were observed during monsoon. In the surface water

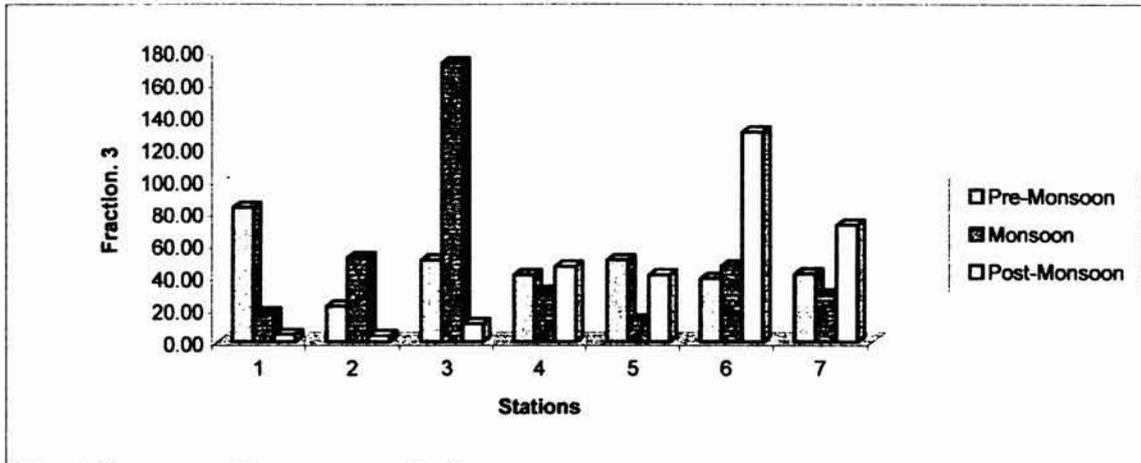


Fig: 4.6 a

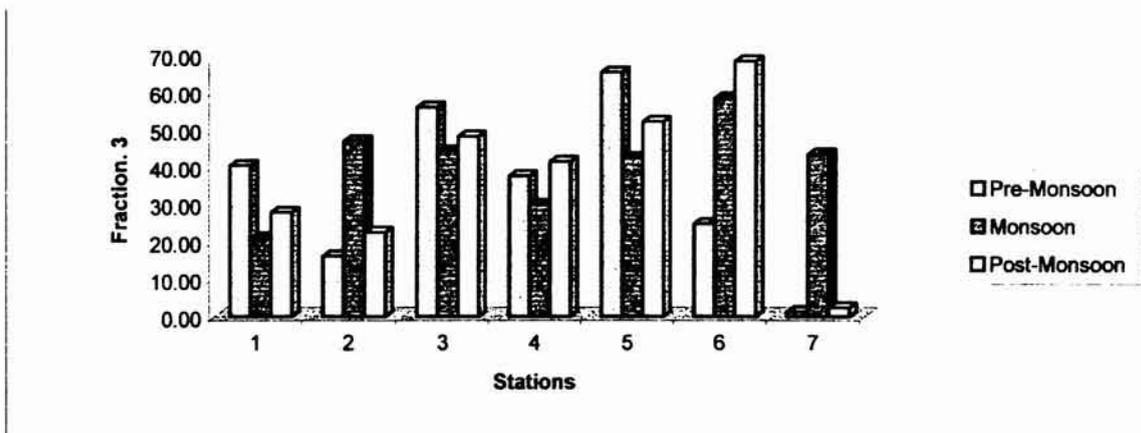


Fig: 4.6 b

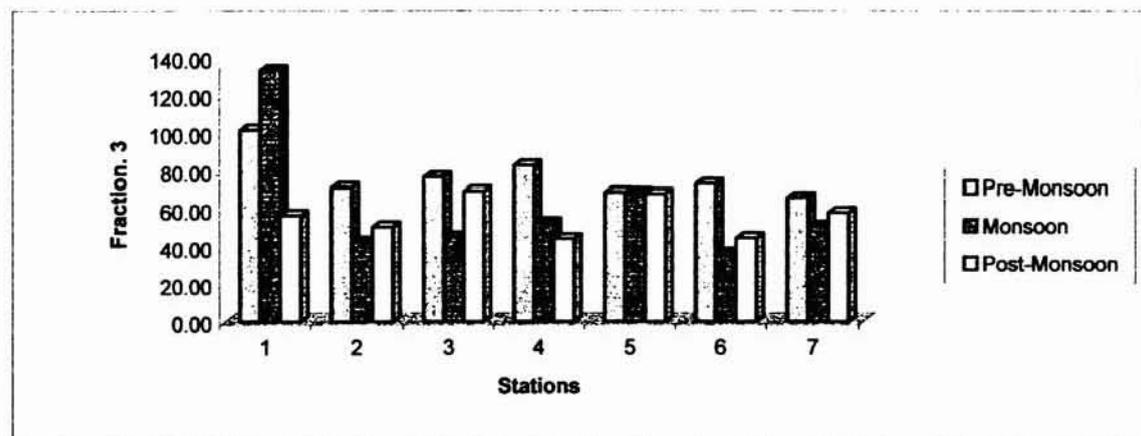


Fig: 4.6 c

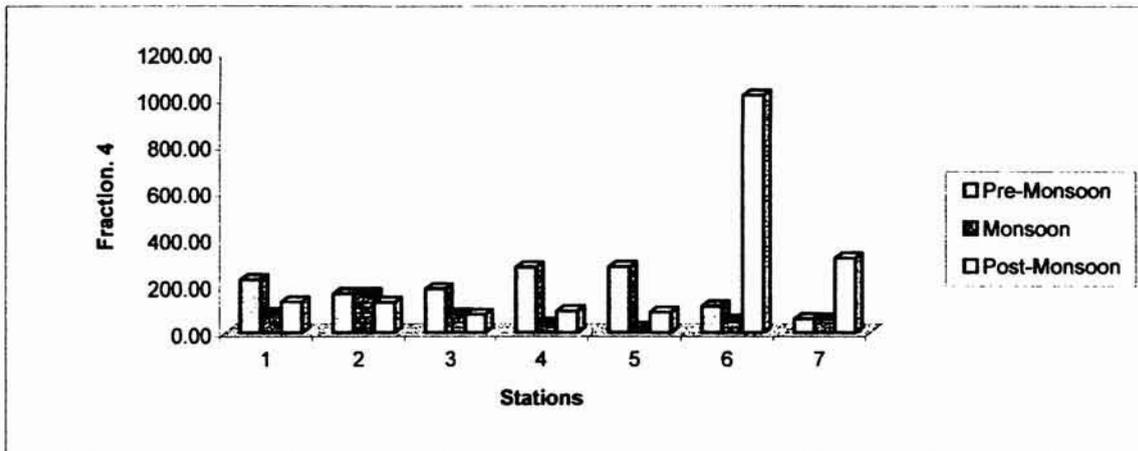


Fig: 4.7 a

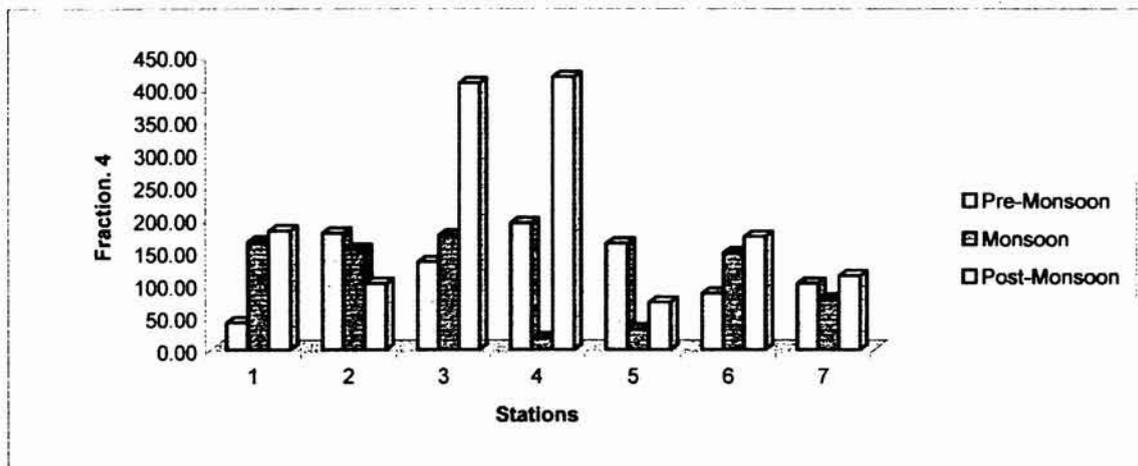


Fig: 4.7 b

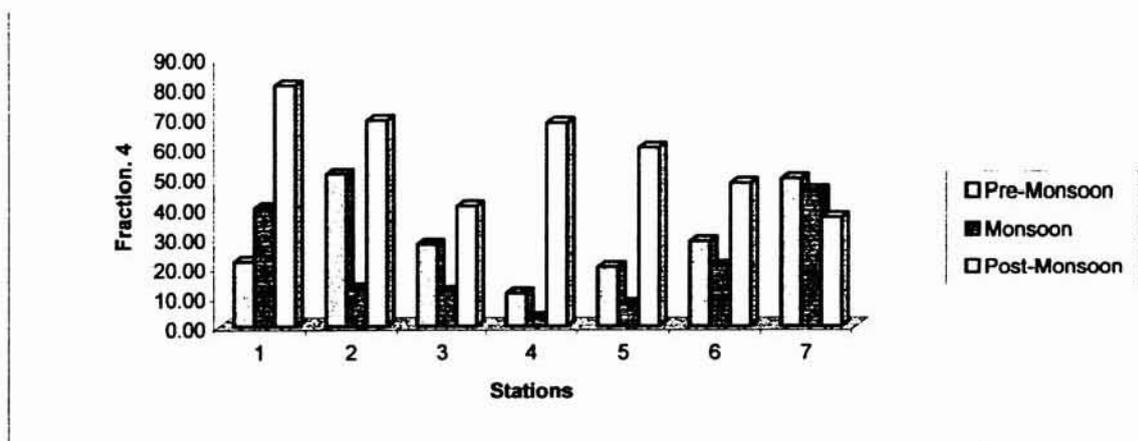


Fig: 4.7 c

during premonsoon and postmonsoon in the north and postmonsoon in the south showed an increasing trend. In the premonsoon bottom water indicated an increasing trend in the northern part towards downstream and in postmonsoon a decreasing trend was showed in the southern part (fig 4.8 a, b) the sediment in the north showed a decreasing trend during premonsoon and an increasing trend in postmonsoon. An increasing trend was observed in the southern part during premonsoon and a decreasing trend in premonsoon (fig 4.8 c). The concentration of fraction.5 varied between 7 to 380.32 ng/l in the northern part and 3.63 to 384.55ng/l in the southern part of the estuary (Table 4.8 a). In the northern part fraction.5 concentration in the sediment varied between 3.24 to 173.04 ng/g and 2.58 to 90.44 ng/g in the southern part (Table 4.8 b).

Table 4.8.a. Fraction 5 in water (ng/l).

Station	1	2	3	4	5	6	7
Premonsoon. S	36.73	308.04	379.52	295.69	291.36	384.55	4.58
B	184.86	340.72	380.32	211.05	274.13	5.12	265.46
Monsoon. S	256.59	122.33	119.20	82.51	103.78	163.58	125.22
B	87.59	54.97	58.88	117.85	10.85	3.63	182.47
Postmonsoon. S	7.00	146.46	214.22	18.85	355.20	339.23	187.78
B	99.56	252.14	59.77	270.49	183.53	236.07	268.79

S - surface; B - bottom

Table. 4.8.b. Fraction 5 in sediment (ng/g)

Station	1	2	3	4	5	6	7
Premonsoon	36.41	12.38	10.99	3.24	3.06	73.15	90.44
Monsoon	47.56	6.21	8.39	23.68	16.64	10.82	2.58
Postmonsoon	44.60	51.62	99.66	173.04	8.20	5.06	14.98

Fraction 6 generally showed higher values in the bottom water than surface in the northern part of the estuary and in the southern part surface water had higher values except in station. 5. The surface water showed an increasing trend in premonsoon and a decreasing trend in monsoon and the bottom water showed a decreasing trend in all seasons except in station. 4.in the northern part of the estuary (fig. 4.9 a, b). There was no significant trend available in the southern part of the estuary. The concentration of fraction.6 in the northern part of the estuary varied between 1.41 to 451.91 ng/l and 2.38 to 442.44 ng/l in the southern part (table 4.9 a). In the northern part of the estuary the sedimentary concentration showed minimum during monsoon and maximum in postmonsoon season. In the sediment, the

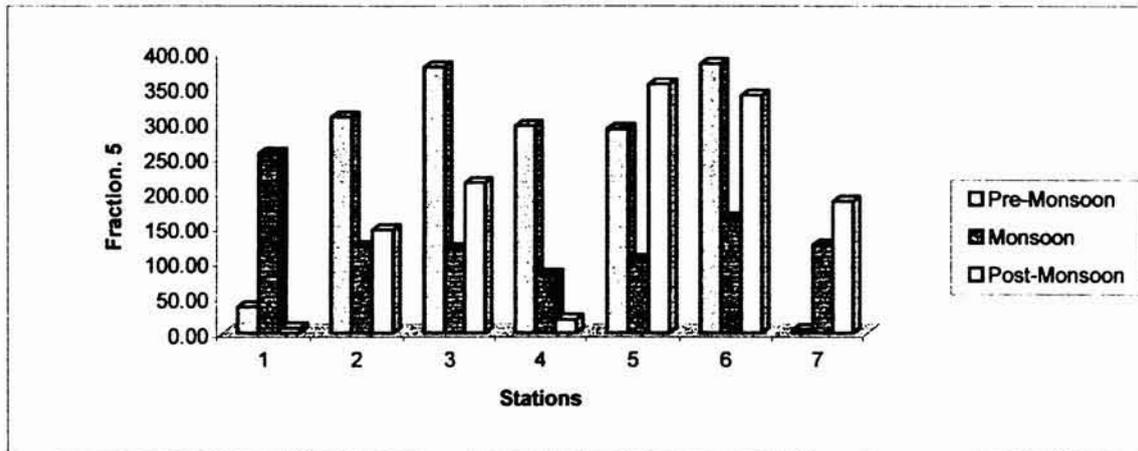


Fig: 4.8 a

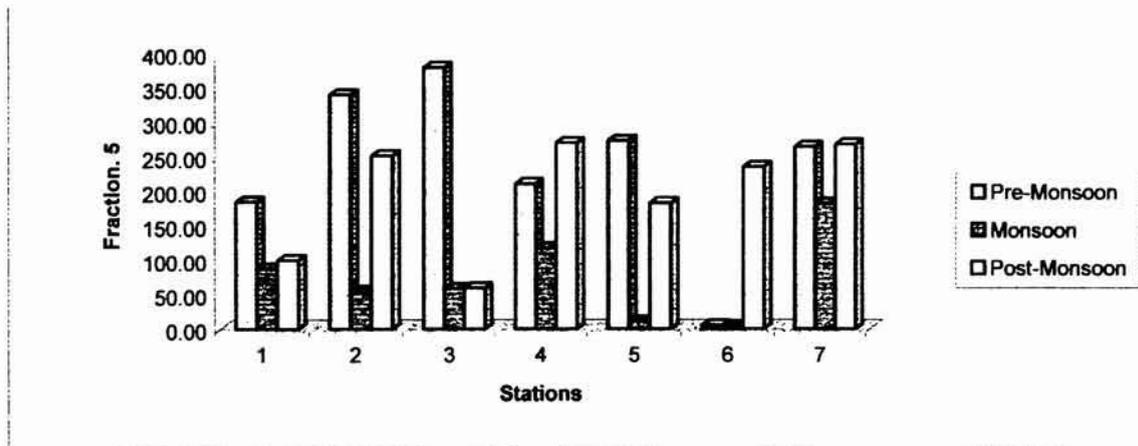


Fig: 4.8 b

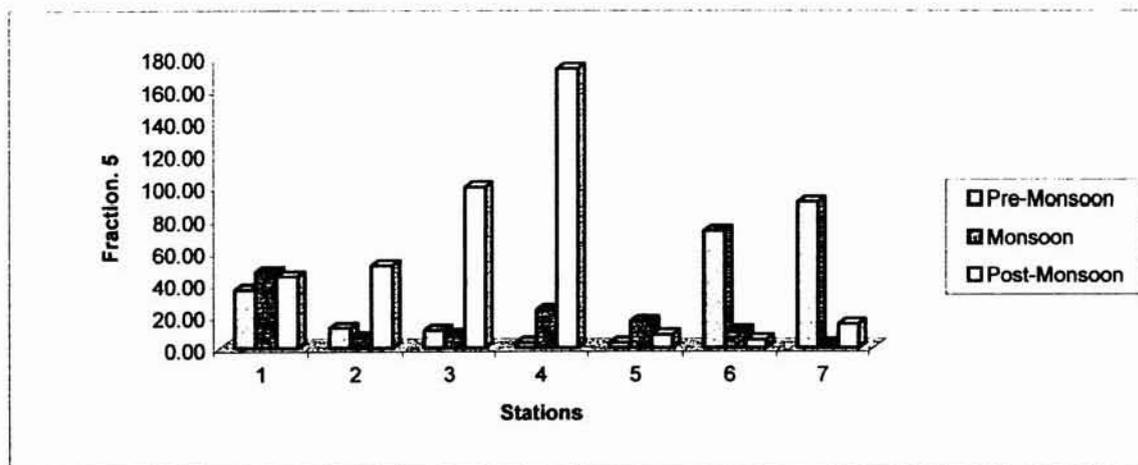


Fig: 4.8 c

premonsoon values showed a decreasing trend in the northern and southern part of the CES and an increasing trend in the southern part during postmonsoon season (fig 4.9 c). The concentration of fraction.6 varied between 3.72 to 198.58 ng/g in the northern part and 6.38 to 189.45 ng/g in the southern part (Table 4.9 b).

Table 4.9.a. Fraction 6 in water (ng/l).

Station	1	2	3	4	5	6	7
Premonsoon. S	64.12	375.19	450.15	218.50	283.49	331.15	297.85
B	451.91	431.46	284.88	304.71	442.44	2.36	277.62
Monsoon. S	293.28	162.07	1.41	196.67	102.64	204.02	152.12
B	251.37	162.73	91.43	185.97	242.15	7.75	87.42
Postmonsoon. S	199.67	287.03	154.10	279.78	216.29	61.07	327.74
B	261.69	225.96	174.32	357.94	335.50	167.05	268.51

S - surface; B - bottom

Table 4.9.b. Fraction 6 in sediment (ng/g)

Station	1	2	3	4	5	6	7
Premonsoon	92.23	64.84	46.90	95.45	77.98	118.10	150.30
Monsoon	47.56	3.72	49.76	31.42	98.12	33.47	88.11
Postmonsoon	97.42	58.57	89.01	198.58	189.45	9.73	6.38

Fraction 7 in the water samples showed low values during monsoon and in the sediment during postmonsoon. A decreasing trend was observed during postmonsoon and monsoon surface water in the southern part where as an increasing trend in the north during postmonsoon in the bottom (fig 4.10 a, b). In sediment samples southern part of the estuary showed an increasing trend during monsoon and a decreasing trend during monsoon and postmonsoon in the north (fig 4.10 c). In the northern part of the estuary the concentration of fraction 7 varied between 1.71 to 451.91 ng/l and 2.07 to 442.44 ng/l in the southern part (Table 4.10 a). In the sediment samples the value varied between 1.37 to 55.8 ng/g in the northern part and 1.39 to 35.67 ng/g in the southern part (Table 4.10 b).

Table 4.10.a. Fraction 7 in water (ng/l).

Station	1	2	3	4	5	6	7
Premonsoon. S	2.70	43.87	39.15	44.70	71.81	4.09	50.88
B	36.73	45.85	28.91	31.80	66.25	1.40	1.86
Monsoon. S	3.22	5.11	5.73	1.64	2.07	4.95	11.82
B	26.51	2.71	3.74	2.51	61.64	2.57	12.53
Postmonsoon. S	25.32	3.19	1.71	87.89	86.83	111.79	187.78
B	4.79	18.53	202.51	64.59	56.63	77.85	52.40

S - surface; B - bottom

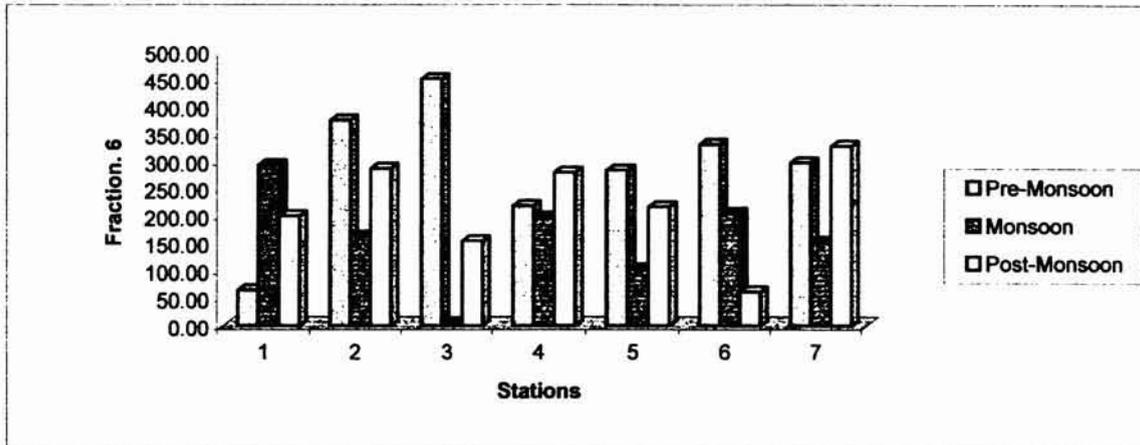


Fig: 4.9 a

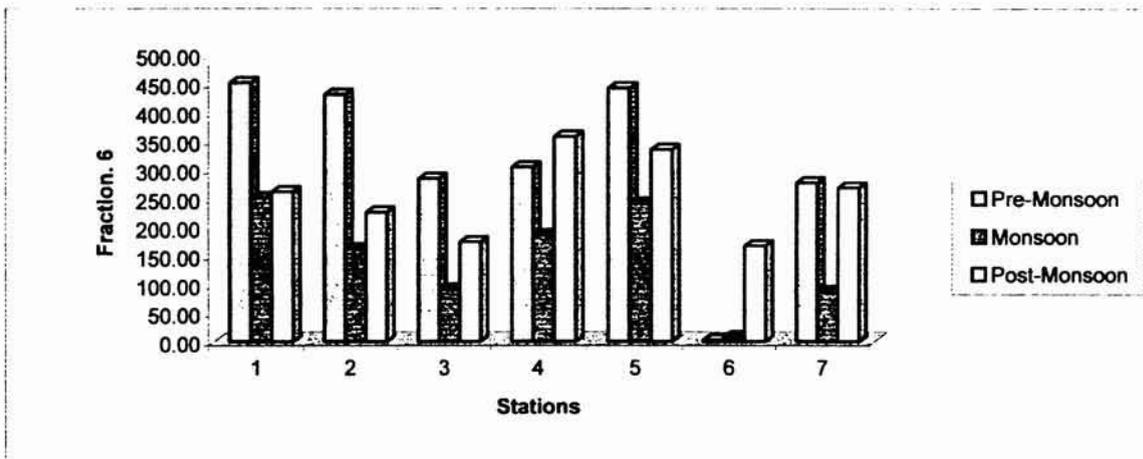


Fig: 4.9 b

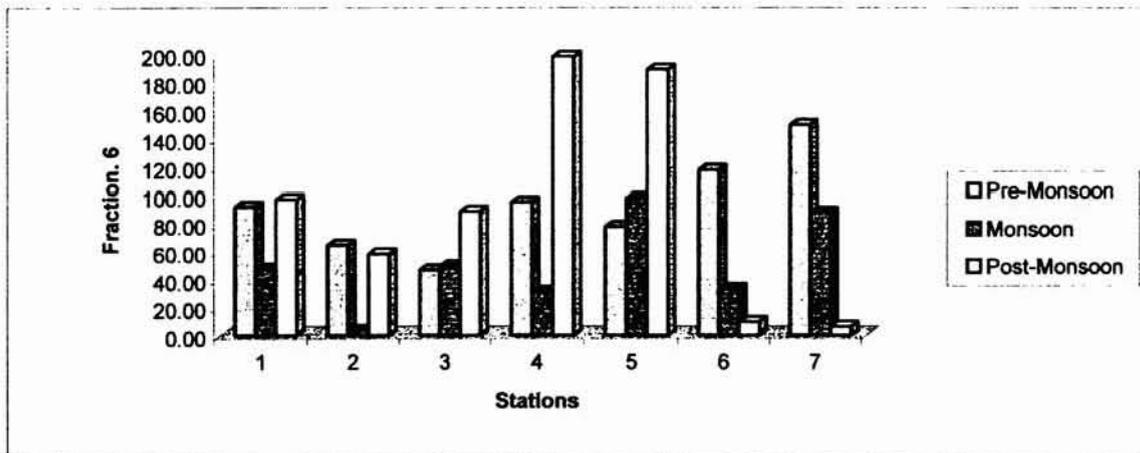


Fig: 4.9 c

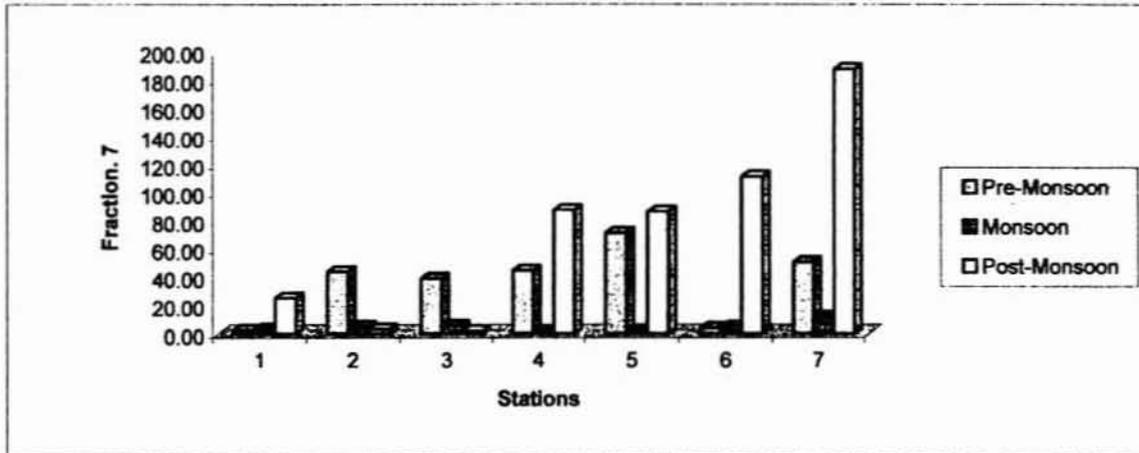


Fig: 4.10 a

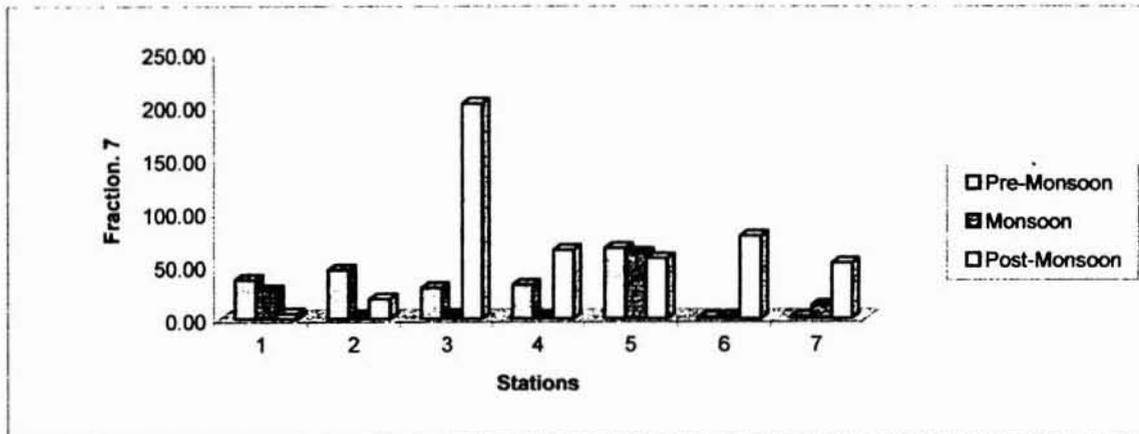


Fig: 4.10 b

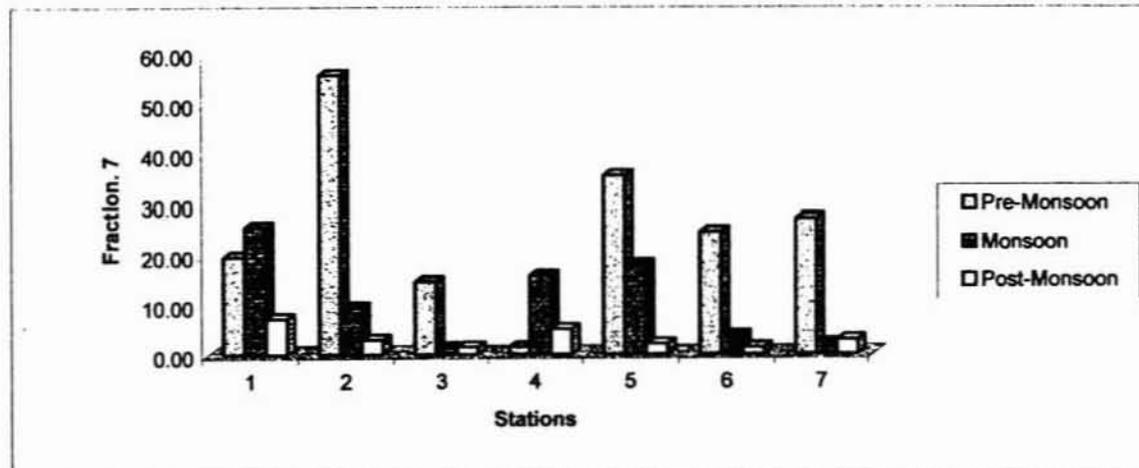


Fig: 4.10 c

Table. 4.10.b. Fraction. 7 in sediment (ng/g)

Station	1	2	3	4	5	6	7
Premonsoon	19.67	55.80	14.73	1.54	35.67	24.51	27.13
Monsoon	25.58	9.47	1.37	15.94	18.05	3.85	2.18
Postmonsoon	7.23	2.96	1.54	5.11	2.11	1.39	2.95

As the identity of the different fractions ^{is} are not clear, no specific explanations for their distribution and seasonal character can be offered, except the following general observations.

(1). The relative concentration values observed indicate a differential distribution pattern with a preferential higher level of some of these fractions. For e.g. in water fraction 6 is having a higher concentration than the rest.

(2). In seasonal distribution the following trend was observed in water.

- (a). In monsoon, fraction 5 (293.28ng/l in station 1) having the highest concentration in the northern part and fraction 6 (242.15 ng/l in station 5) in the south.
- (b). In premonsoon, fraction 6 (442.44 ng/l in station 5) having the highest concentration in the northern part and fraction 6 (451.91ng/l in station.1) in the south.
- (c). In postmonsoon, fraction 6 (287.03 ng/l in station 2) having the highest concentration in the northern part and fraction 4 (1018.31 ng/l in station 6) in the south.

(3). In sediment the seasonal trends are,

- (a). In monsoon, fraction 3 (133.47 ng/g in station.1) having the highest concentration in the northern part and fraction 2 (308.95 ng/g in station 7) in the south.
- (b). In premonsoon, fraction 3 (101.72 ng/g in station 1) having the highest concentration in the northern part and fraction 6 (150.3 ng/g in station 7) in the south.
- (c). In postmonsoon, fraction 6 (198.58 ng/g in station 4) having the highest concentration in the northern part and fraction 6 (189.45ng/g in station 5) in the south.

(4). No common trend can be assigned to the fractions, individual variations in distribution pattern prevails. At the same time, the general observation was that distribution of any fraction in the sediment exhibited either a trend opposite to that

observed in water or no trend was shown. This can be attributed to the close relationship between the concentration of chlorophenols in water and sediment. The low reactivity of chlorophenols along with the common origin can be the major reason.

In conclusion, it can be seen from the results that though significant concentrations of different chlorophenols are present in the CES, their concentration values are more or less in the ng/l level. This low concentration indicates that none of the chlorophenols have reached the level of pollutant, which can modify the ecosystem. At the same time few of the spots either reaches or covers the pollution line, i.e. 500ng/l (Joane G. Jennings *et al.*, 1996) and many are near to it. The distribution patterns clearly indicate the addition of the compound from the anthropogenic sources. These, so, warrants a detailed management study of the CES with respect to these compounds.

Chapter 5

Modeling of chemical parameters in the CES

5.1 Introduction

The present structure and behavior patterns of estuaries are a result of the various biogeo and physicochemical processes. The level of complexity of the system depends on the number of interacting or superimposed processes and increases generally with time. The knowledge on the dynamics of evolution and the present state of affairs is essential for the development of a working model. Models should not only explain the experimental data but should predict future probability. This is an attempt to predict the overall reactivity of the Cochin Estuarine System in terms of the behaviour of boron.

The estuarine systems are having a special significance in the hydrosphere because of its role as a link between land and sea. The impact of human activities is at its maximum in the estuarine waters. The agricultural drains, industrial effluents sewage and sullage etc deliver considerably to this system modifying the chemical characteristics. Compared to the rivers and oceans, the estuarine waters are the most vulnerable points in terms of pollution. A special significance is attributed in the hydrosphere to the estuarine systems because of the multitude and complexity of the processes; the system can not be defined by interpreting any of the individual properties. The various independent but interdependent processes include geochemical processes such as sedimentation, resuspension, precipitation and

dissolution, chemical transformation such as complexation, exchange, species modification etc, and biochemical process such as uptake, depuration, death and decay. The seawater undergoes various chemical and physical modifications during its mixing with fresh water from the land. The dilution of seawater, which is the major phenomena during mixing, is associated with a re speciation of the elements present in these waters also. The speciation and residence time of any species in an estuary is dependent on fresh water discharge, density gradients, atmospheric input, tidal and water current pattern. No comprehensive model is available which can be applied to an estuarine system in its totality.

The various approaches adopted for the interpretation of estuarine system can be grouped in to two and primarily utilises only the physical parameters. In the first group the averaging of tidal flow (Tee, 1976; Sinha *et al.*, 1995, ^{Sinha *et al.*, 1998}, Prandle, 1978) and in the second group time averaged equations of motions (Nihoul and Rondonay, 1987) were used. A few theoretical models using the baroclinic effects are also available (Smith and Chang, 1987; Jin and Raney, 1991). The model developed in this study, though considers both tidal contribution and time averaged flow, and basically is different from these two. In the first phase, because of the regular and continuous pattern of the physical and chemical processes, the system is considered to be at a steady state and so the initial state will not have much significance in defining the system. Secondly chemical reactivity of the estuary is assumed to regulate the species concentration of any element in the system than the physical processes. Thirdly, in positive estuarine system like CES, where regulate^y flow of fresh water and tidal intrusion of sea water are present, the mixing time and the flushing time can be considered as better representative of the physical processes rather than the tidal flow.

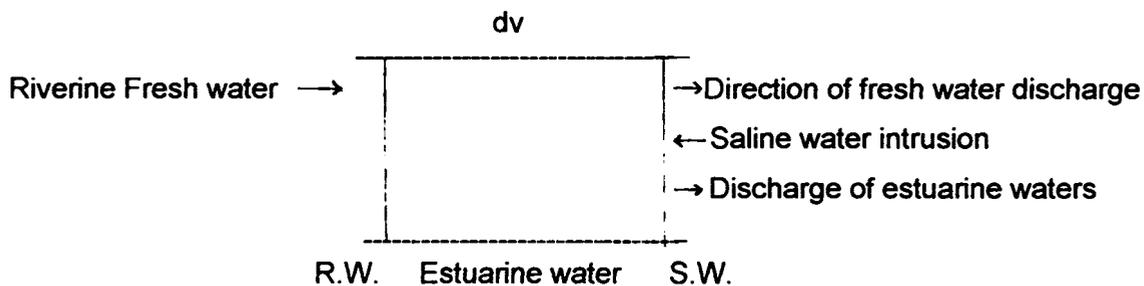
5.2 The System

1. As mentioned in earlier chapters, the CES is a tropical positive estuarine system with two distinct arms through the rivers Periyar at the North and Muvattupuzha at the South. These rivers which flows through the adjoining land masses of agriculture, are the major contributors of fresh water to the system and so contains considerable vegetative matter.
2. The Barmouth, ca 450m wide, is the only permanent opening to the sea.
3. The average depth of the estuary is around 3m and the maximum tidal height is about 1m. The tidal processes thus have profound influence in this system.

4. During monsoon months, the river and estuary get flooded with fresh water and will show only fresh water characteristics.
5. During postmonsoon and premonsoon the riverine flow is considerably slow and the estuarine system up to the river mouths will give saline characteristics.
6. Though the system is highly positive with a flushing time of 7 days and the depths are very low, significant vertical salinity gradient is observed in the entire estuarine region.
7. Though the average depth is very low, the high organic content in the sediments results in an anoxic condition in the sediments.

5.3 The Model

The estuarine system with its riverine discharge and saline water intrusion can be considered in a broader sense a flow reactor.



The reactor starts from the river mouth where salinity is zero or near to zero and ends at the Barmouth where salinity is equivalent to the salinity of seawater. Through the reactor the reactant 1, the fresh water, flows at a flow rate of V m/s. The reactant 2, the seawater, enters the reactor at a velocity that can be indicated by the time average of high tide and leaves the reactor by the time average of low tide.

If U liter/ S is considered as the rate of flow of the chemical entity to the reactor and C the concentration of the entity, then during a time interval dt the amount of the species that is transferred to the reactor will be $UC dt$. If the order of the reaction in the rate transformation

$$V = -dc/dt = k C^n.$$

If dv is the volume of the reactor of reaction that will take place in a time interval dt , the rate $v = -dc/dt = kc^n dv$.

After a period of time the component leaves the compartment at the rate of $U (C + dc)dt$. Because of the regular cycling feature, the reactor is assumed to be in a steady state: or the rate of addition and the rate of removal are equal.

The steady state contains contributions from

- (1) the amount of species that enters the reactor, i.e., $U C dt$.
- (2) the amount of species that leaves the compartment i.e., $U (C+dc) dt$.
- (3) the amount of species that undergoes reaction i.e., $k C^n dv dt$.

At the steady state $UC dt = U (C+dc) dt + kC^n dv dt$.

Rearranging $-U dc dt = kC^n dv dt$
or $dc/C^n = -k dv/U$

In adapting this kinetic scheme, the following assumptions are made:

1. Compared to seawater, the fresh water is having only negligible amount of ions to contribute the salinity of the estuarine water. So the fresh water flows, with its composition and unidirectional pattern and is considered as a base line.
2. Because of the semidiurnal character of the tides and rapid interactions of the chemical entities, the biochemical removal of any entity is considered to be not affecting the chemical environment of the system.
3. The sedimentary incorporation and exchange is regarded as the major phenomena in the regulation of availability of a particular species of the element in the estuarine waters. Considering the concentration changes associated with the mixing processes and possible magnitude of the unidentifiable interdependent multitude of the various transformations, the overall order of the reaction is considered to be one.
4. The tidal distribution of salinity is more or less regularised by the riverine flow and can be considered as in a steady state. The horizontal salinity gradient is a function of the ratio of flow rate to tide height.
5. The major ions, which constitute the salinity because of its conservative character generally, will exhibit a normalised distribution pattern with the addition of fresh water.
6. In a natural estuarine system, though the river flow can be measured precisely, the salinity intrusion, or the seawater influx, can not be measured. At the same time, the dilution patterns can be taken as an index of the rate of flow of seawater to the

estuary or from the estuary. As mixing will lead to a general dilution pattern, the volume element can be replaced by the salinity element.

7. Boron is a major element, which is conservative in seawater, but susceptible to biogeochemical modifications. So a comparison of the dilution patterns of boron with salinity can give an idea on the biogeochemical reactivity of the system.

The equation with this modification takes the form

$dC/C = -K ds/T$ where ds is the salinity element and T time averaged tidal height during the addition of seawater. T can be considered as a function of the physical processes operating in the system and K the geochemical reactivity. The ratio K/T can be considered as an index of the total estuarine reactivity that varies with changes on the physical characteristics processes and is ~~a~~ constant at a particular period.

This on integration

$$\log C = - (K/T) S + \text{constant} = - K_e S + \text{Constant}$$

A plot of $\log C$ versus S will give the slope K_e , the reactivity of the estuary. The reactivity is depend on the substrate as well as the estuarine character. The distribution data of boron is applied to the model for estimating the reactivity of the CES.

5.4 Boron

Boron is one of the most important elements, which is significantly involved in the marine biogeochemical cycle. Boron, a metalloid, occurs in more than 100 minerals, the most common being tourmalins, a complex silicate mineral present in igneous rocks and sedimentary rocks. Boron in this form is largely inert and is released in to the environment at an extremely slow rate through natural weathering processes. The building block for the borates is BO_3 triangles linked together with Na or Ca ions. Natural weathering releases approximately 360×10^3 metric tons of elemental boron worldwide every year (Westall ^{Stumm} ~~et al.~~, 1980). Although the amount of boron mobilised annually from anthropogenic sources has not been accurately determined, it is widely assumed that the most important source to surface waters are sewage, sewage sludge, and user industries such as detergent manufactures.

About 76 % of the total boron are present as boric acid, $B(OH)_3$, about 13% as borate, $B(OH)_4^-$ and nearly 11% is complexed with cations (Na, Mg, Ca, Co, Ni, Pb etc.)

(Robert R. Bryne, (Jr) *et al.*, 1974). Polysaccharides and high molecular weight polyhydroxy compounds complex with boric acid to form macromolecular structure (Deuel & Nuekom., 1949).

Boron is one of the major elements that have long been regarded as characterising the seawater and marine sediments. Soon after the fundamental work by Goldschmidt and Peters (1932) on the geochemistry of boron, an attempt was made to classify using the boron content whether a sediment had been deposited in marine or lacustrine environment (saline or fresh water environment). Boron was used as a geochemical indicator of salinity and temperature of the depositional medium and there will be relation between the boron content in the water and boron content in the deposited (Harder, 1970).

The concept of constantancy of major ions becomes a misnomer when one considers an estuarine environment. The rapid response of the estuarine environment to the time dependent physico-chemical parameters such as land runoff, precipitation and evaporation, brings about changes in the behavior of most of the elements of these waters (Shirodkar & Anand., 1985; Rajagopal *et al.*, 1981; Liss & Pointon., 1973; Narvelkar., 1980;). Exchange of solid solution components under varying chlorinity conditions in estuaries often result in nonconservative behavior of several major ions which normally bear a constant ratio with chlorinity in oceanic waters. The behavior of boron in estuaries has been studied detailed by several workers and the results indicated that some estuaries it was conservative (Liddicoat *et al.*, 1983) while in many estuaries boron showed removal and addition processes (Shirodkar & Anand., 1985; Zingde *et al.*, 1987. Rajagopal *et al.*, 1981; Liss & Pointon., 1973}

Although, boron is an essential micro nutrient, low levels of boron in phytoplankton indicate that the uptake of boron may not be the primary factor responsible for lower boron levels at the surface. The global average of boron and chlorinity in river water is 0.013 mg/l and 0.01 respectively (Livingston, 1963). This gives a B/Cl of 1.3. The ratio observed for surface water however is not indicative of any increase due to riverine influence.

The interesting features that can be seen from the depth profiles are two maxima for the boron and the B/Cl between 50 and 200m, and 300 and 500 m. Chlorinity also shows a maxima in these regions. The first maxima are at about the thermal

discontinuity layer and appear to be the result of accumulation of colloidal and particulate matter. This may also be influenced by the Gulf water. The second maximum centered around 400m which lies in the region of maximum apparent oxygen utilisation (AOU) (Naqvi, 1978) and is possible due to combined effect of the higher boron in the oxygen minimum zone and the high boron level associated with the Red sea water flowing at its characteristic density level.

A fairly good correlation coefficient of -0.73 observed between the suspended solids and PAR (percentage addition or removal) in Purna estuary suggests the importance of suspended load in controlling the levels of dissolved boron. A more or less inverse relationship between PAR of boron and suspended solids is observed in Ambika estuary. Good correlation between PAR of boron and chlorinity in Purna and Auranga estuaries and similar pattern of boron removal at low chlorinities suggests that the ionic strength also play an important role in the behavior of boron in these estuaries. High and low B/Cl ratios with the highest ratio of 0.269 and the lowest 0.202 observed in the coastal waters of eastern Arabian sea (Shirodkar ^{& Singbal} ~~et al.~~, 1992) indicate addition as well as removal of boron along the coast. The percentage addition and removal of boron calculated by taking in to consideration the world average B/Cl ratio for sea water (Uppstrom, 1974) 0.232, gave an addition from 0.43 to 16% and removal from 0.43 to 11.6% in the coastal waters.

Boron content showed a high correlation with chlorinity in the Central West Coast of India (Shirodkar ^{et al.}, 1982) at various depth stations, high average variations of B/Cl was reported at oxygen minima. In general lower values of boron in the upper layers of shallow stations show that boron is utilised by phytoplankton and also it may be due to evaporation loss (Sevenko, 1977). In the south-western Indian Ocean region of the southern ocean (Sugandhini Naik *et al.*, 1986). The average concentration of boron was 4.62 ± 0.44 mg/kg and the B/Cl ratio is 0.242 ± 0.023 . The relation $B \text{ (mg/kg)} = 0.227 \times Cl \pm 0.050$ with the observed mean chlorinity in this case as 19.124 gives boron concentration as 4.39 mg/kg and the corresponding B/Cl as 0.230. The ratio, as calculated, is somewhat as higher than that obtained from low chlorinity Baltic Sea water by Dyrssen and Uppstrom (1974), which was 0.230. Culkin (1965) has reported that the average concentration of boron to the 4.5 mg/kg at a salinity of 35‰.

It is well known that marine clay sediments are strongly enriched in boron (100 ppm), as they, together with altered oceanic crust, are the earth's most significant boron reservoirs (Goldschmidt, 1954; Thomson et al., 1970; Harder, 1974).

The water temperature, too, has an effect on the boron content (Harder, 1959b, 1961b). Sometimes the organic compounds influence the boron content of clays. Eager (1962), Curtis (1964) and Harder, (1970) have shown an inverse relationship between boron content and organic carbon. It appears that the presence of organic matter and relatively low contents of total boron in these sediments (perhaps not in all) are related (Eager, 1962).

In an aquatic system, sediments store by removing it from the overlying water through the physical process of adsorption and chemical complexation. Boron from the overlying water is removed by the differential adsorption on to suspended solids during the estuarine mixing of sea and river waters (Levinson and Luddwick, 1976; Liss and Pointon, 1973). Biological removal of boron by phytoplankton have also been observed which adds boron back to the sediments on the death and decay of phytoplankton (Subba Rao, 1981; Shirodkar *et al.*, 1982).

Acid treatment was carried out for two calcareous sediments, to examine the influence of biogenic carbonates on the bulk content and isotopic composition of boron in these sediments. The sediments contain 58% and 36% of HCl soluble component (carbonate), and the residues corresponding to pelagic clay and diatom ooze respectively. Boron content of pelagic clays determined in this study (Tsuyoshi Ishikawa & Nakamura., 1993.) vary from 96 to 132 ppm, which is essentially consistent with the range of 80-157 ppm given in Spivack *et al.*, 1987 and 120 ppm for average argillaceous sediments (Harder, 1974).

5.5 Boron in CES - Results of the present study

Dissolved boron in the surface water of Cochin estuary varied between ND level to 3.07 mg/l (Annexure.5a). Boron in the northern zone of the estuary varied from ND level to 2.36 mg/l and in the southern zone 0.16 to 3.07 mg/l, the maximum value was showed in the Barmouth. Boron in the bottom water has slightly higher concentration than surface water. In the bottom water dissolved boron varies from ND level to 5.91

mg/l in the north zone and the maximum value was showed in station.1. In the south zone, dissolved boron concentration varied from 0.31 to 3.58mg/l.

Dissolved boron generally showed an increasing trend in surface waters during the three seasons from upstream to downstream except in station 1 during premonsoon and monsoon (fig: 5.1 a & Table 5.1). Station 1 showed high values during premonsoon and monsoon season compared to station.2, this may be due to the input from anthropogenic sources.

Table 5.1. Seasonal average of dissolved boron in water (ppm).

Station	1	2	3	4	5	6	7
Postmonsoon. S	0.38	0.69	0.95	1.79	1.92	1.23	0.49
B	2.16	0.75	1.05	2.11	2.80	1.14	1.32
Premonsoon. S	0.29	0.15	0.38	1.09	1.81	0.87	0.67
B	0.39	0.48	0.94	1.61	2.22	1.14	0.79
Monsoon. S	0.70	0.27	0.29	0.69	0.38	0.98	0.52
B	0.59	0.15	0.32	0.33	2.27	0.88	0.79

S - surface; B -bottom

The bottom water also showed a similar trend as that of surface water monsoon (fig: 5.1 b) in all stations except station 1 and station 7 during postmonsoon. In postmonsoon and monsoon, station 1 have higher values than station.2 and also in the southern zone station 7 showed higher values than station 5 in postmonsoon season. Generally boron in the surface and bottom waters of Cochin estuary increases with salinity, clearly indicating the introduction of boron in to the CES through saline water.

Water-soluble boron in the estuarine sediments of Cochin varied from 4.5 to 61.18 ppm in the northern zone and in the southern zone, the value varied from 2.43 to 103.42 ppm (Annexure 5 b). Water-soluble boron in the sediment showed maximum values in station 2 during premonsoon monsoon (fig: 5.1 c & Table 5.2). There was no significant seasonal trend for water-soluble boron in the Cochin estuarine sediment.

Table 5.2. Seasonal average of water soluble boron in sediment (ppm).

Station	1	2	3	4	5	6	7
Postmonsoon	13.11	14.59	12.16	23.01	16.02	12.94	16.74
Premonsoon	13.94	56.91	17.26	22.05	20.18	22.97	15.25
Monsoon	26.45	11.56	19.28	16.75	14.08	53.26	30.46

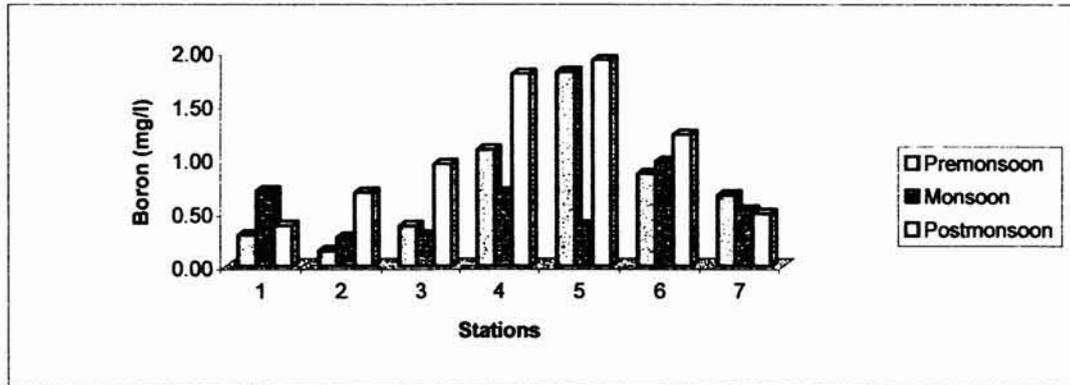


Fig: 5.1 a

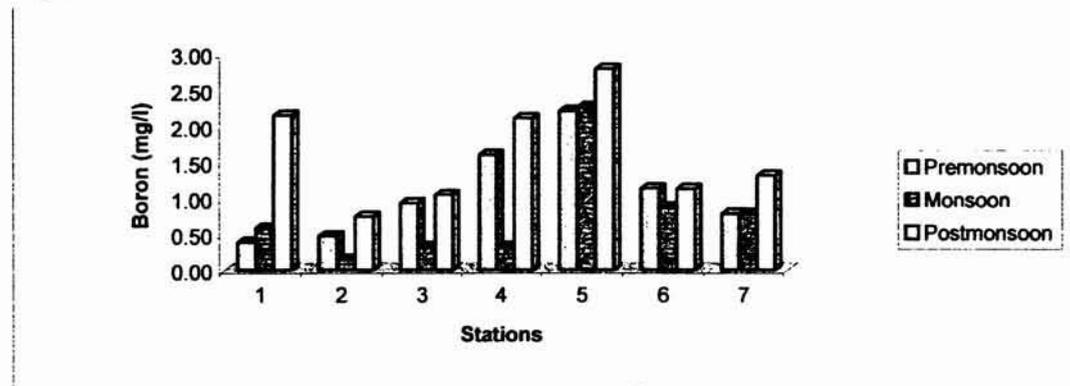


Fig: 5.1 b

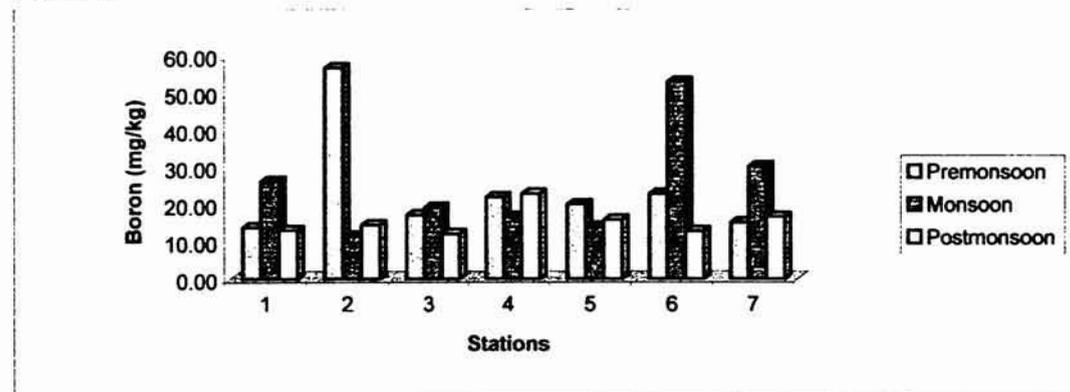


Fig: 5.1 c

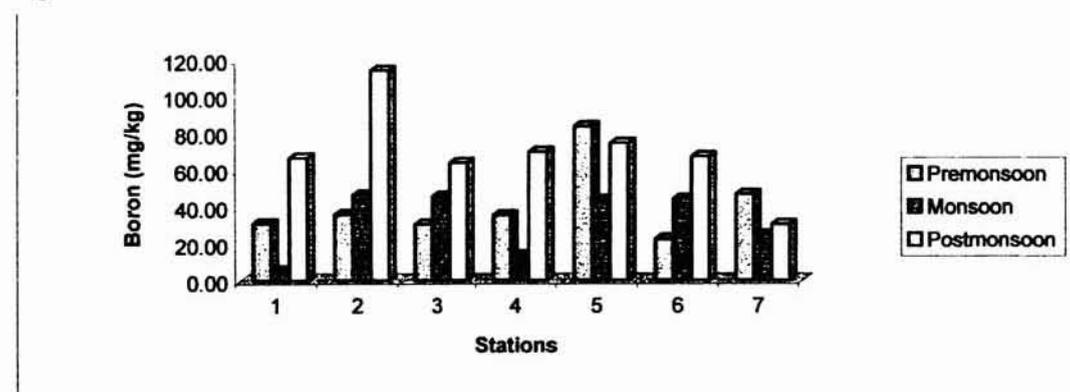


Fig: 5.1 d

Acid-soluble boron in the sediment varied from 5.42 to 191.54 ppm in the northern zone and in the southern zone the value varied from 7.26 to 220.5 ppm (Annexure 5 c). Acid-soluble boron showed an increasing trend from upstream to downstream in southern part of the estuary and in other seasons there was no significant trend in the south and northern part of the CES (fig: 5.1 c & Table 5.3), and have higher values in Barmouth during pre postmonsoon seasons. In monsoon and post monsoon season, station 2 showed maximum values.

Table 5.3. Seasonal average of acid soluble boron in sediment (ppm).

Station	1	2	3	4	5	6	7
Postmonsoon	66.63	114.27	63.95	69.97	74.73	67.36	30.55
Premonsoon	31.19	35.90	30.53	35.42	83.90	22.57	46.72
Monsoon	5.44	46.35	45.69	13.72	43.65	44.21	24.53

5.6 Application of Model to boron in CES.

Boron is a typical element, which can be used as a tool to estimate the reactivity of any estuary because of its stable concentration and conservative character in seawater. More over the biological uptake of boron is comparably less than its geochemical transformation to sediment. In the present study, to check the correctness of the above assumption the distribution of boron both in the water and sediment is determined by simultaneous sampling and analysis. The data gave a high correlation between the dissolved boron and salinity (Table 5.4 a), acid soluble boron (Table 5.4 b) and total boron (Table 5.4 c). It is also to be noted that in the seasonal distribution premonsoon gave good correlation.

It is also can be inferred from these significant correlation's that the geochemical transformation of boron is almost at its steady state.

Boron have an added advantage that the number of species of boron in water is limited to the boric acid and borate so that simple techniques can be used to estimate the concentration very precisely and accurately. Moreover the designing of a model can be completed with a few parameters making the processes comparably less complex.

Table 5.4 a. Dissolved Boron vs Salinity

Season		r	n
Postmonsoon	$Y = 0.0339 x + 1.1038$	0.28778*	68
Premonsoon	$Y = 0.059 x + 0.0845$	0.85407#	56
Monsoon	$Y = 0.0617 x + 0.5395$	0.53025#	40
Total	$Y = 0.0403 x + 0.07$	0.43944#	164

Y - dissolved boron, x - salinity

Table 5.4 b. Dissolved boron vs Acid-soluble boron in sediment

Season		r	n
Postmonsoon	$Y = 6.7063 x + 58.978$	0.1417	34
Premonsoon	$Y = 18.352 x + 21.063$	0.41405*	28
Monsoon	$Y = 7.8144 x + 29.928$	0.20526	20
Total	$Y = 12.906 x + 35.984$	0.284117#	82

Y - dissolved boron, x - acid soluble boron in sediment

Table 5.4 c. Dissolved boron vs Total boron in sediment

Season		r	n
Postmonsoon	$Y = 2.1454 x + 15.141$	0.25242	34
Premonsoon	$Y = 19.206 x + 37.392$	0.40132*	28
Monsoon	$Y = 7.9327 x + 54.919$	0.13786	20
Total	$Y = -5.147 x + 44.037$	0.17042	79

Y - dissolved boron, x - total boron in sediment

* - above 95% significance

- above 99% significance

As the borate to boric acid ratio is part of an equilibrium coefficient, a definite relation between the total boron concentration and any one of the individual species will be present. In short, the reactivity, estimation methodology, the specious diversity and the concentration levels generally observed makes boron the most suitable element for modeling the reactivity of estuaries.

In this study, the observed concentration of boron is substituted to the flow reactor model. In the model C is replaced by the observed boron concentration and salinity (S) of that particular water mass. As the estuarine conditions during the three seasons, monsoon, premonsoon and postmonsoon are significantly different, the reactivity K is calculated independently for the three seasons. Also, the northern arm and the southern arm of the CES shows considerable variations in almost all of the estuarine properties, making it essential to apply the model separately to the two arms.

The relationship obtained and the correlation coefficient from regression analysis is given in table. 5. 5.

The analysis of the results obtained by substitution of data in the model indicate that

- 1) Except for monsoon season, the $\log C_{(\text{Boron})}$ exhibits highly significant correlation with salinity. This confirms the assumptions made during the development of the model. The dilution and flushing characteristics of the Barmouth of CES (coastal inlet) have been studied by many workers (Joseph and Kurup, 1989; Ajith Joseph, 1996). The major observations in these studies were that during the monsoon season, the Cochin inlet is subjected to considerable dilution. The monsoon season is characteristic for its (1) high flooding of the estuary with fresh water, (2) very low seawater intrusion and (3) very low flushing time. The geochemical reactivity as a result of the above reasons the estuary, during monsoon season will generally be very low and the observed concentration of any species of any element will have bearing only to the riverine discharge. The distribution studies of various chemical species done by earlier workers also confirm this (Lakshmanan *et al.*, 1982; Anirudhan, 1988; Babukkutty, 1991; Shibu, 1992; Vasudevan Nayar, 1992).
- 2) The order of reactivity from the K values are Monsoon > Postmonsoon > Premonsoon. As the flushing time is minimum during the monsoon season and as the fresh water inflow is considerably large blocking the seawater intrusion, the monsoon season will show the maximum K value. The absence of a significant

Table 5.5. Model parameters and correlation coefficient.

Log B vs Salinity

North		K	r	n
Postmonsoon	Log C = 0.181025 S - 1.021343	0.18103	0.354821*	34
Premonsoon	Log C = 0.058261S - 0.883477	0.05826	0.75147#	29
Monsoon	Log C = -7.46826 S - 5.846901	-7.46826	0.100168	22
Total	Log C = 0.129865 S - 1.026544	0.12987	0.435539#	89
South				
Postmonsoon	Log C = 0.052425 S - 0.710616	0.05243	0.699223#	30
Premonsoon	Log C = 0.054386 S - 1.134497	0.05439	0.820862#	23
Monsoon	Log C = -0.116861 S - 0.492112	-0.11686	0.044112	15
Total	Log C = 0.053914 S - 0.766983	0.05391	0.627226#	69

C - Boron, S - Salinity

Log MBAS vs Salinity

North		K	r	n
Postmonsoon	Log C = -7.733952 S + 46.22119	-7.73395	0.00263	38
Premonsoon	Log C = 0.079815 S + 0.356413	0.07982	0.449409*	31
Monsoon	Log C = -5.521811 S + 2.029834	-5.52188	0.329979	22
Total	Log C = 0.493925 S - 1.508051	0.49393	0.067384	93
South				
Postmonsoon	Log C = 0.044282 S + 0.632511	0.04428	0.463332*	30
Premonsoon	Log C = 0.177233 S - 2.363043	0.17723	0.15552	23
Monsoon	Log C = 37.45318 S -42.6779	37.4532	0.225078	15
Total	Log C = 0.136258 S - 0.56832	0.13626	0.139423	69

C - MBAS, S - Salinity

Log phenol vs Salinity

North		K	r	n
Postmonsoon	Log C = -0.12006 S + 1.760073	-0.12201	0.328424#	40
Premonsoon	Log C = 0.268722 S - 1.905521	0.26872	0.241558	31
Monsoon	Log C = -10.2145 S + 2.720123	-10.2145	0.081104	22
Total	Log C = -0.326904 + 8.8666	-0.3269	0.191943	96
South				
Postmonsoon	Log C = -0.06367 S + 1.861709	-0.06367	0.47172#	25
Premonsoon	Log C = 0.137355 S - 1.870639	0.13736	0.233575	22
Monsoon	Log C = 0.008179 S + 11.811	0.00818	0.245472	17
Total	Log C = -0.79321 S + 2.057349	-0.79321	0.30748#	64

C- Phenol, S - Salinity

* - above 95% significance, # - above 99% significance

correlation but indicates that the geochemical transformations are not the reason for these high K values. This can only be attributed to the irregular chemical character of the floodwater of monsoon.

- 3) In the postmonsoon, though have a reasonably low flushing time; the estuary gets sufficient time to reach the steady state. The reaction between the reactivity and the flushing time is more evident when we compare the postmonsoon with premonsoon. Though the concept of geochemical reactivity was not attributed to the seasonal variations in the distribution of various chemical species, such a relation between the postmonsoon and premonsoon was observed earlier also (Lakshmanan *et al.*, 1982; Anirudhan, 1988; Babukkutty, 1991; Shibu, 1992).
- 4) During the monsoon season, both the northern and southern regions exhibit more or less the same reactivity with respect to boron. The trend graphs give the same slope for both the regions. The prevailing of fresh water conditions, low salinity and fast flushing may be the reasons.
- 5) The reactivity coefficient K is greater in the northern region than the southern. The lower flow rate of river water and shallow nature of the water column may be the major contributors.

5.7 Application of the model to MBAS and Phenol.

The proposed model is applied to MBAS and phenol and the relation and correlation coefficients are given in Table. 5.5. In the case of phenol a significant correlation between $\log C_{(\text{Phenol})}$ and salinity was observed only for the postmonsoon season and the total period as a whole. The monsoon, as in the case of boron, showed the highest reactivity that can be attributed to the increased flushing (the decreased flushing time) and also to the insignificant addition of the seawater. The premonsoon, because of the higher flushing time, stagnant character of the water body and the high organic content shows only low geochemical reactivity as evidenced by a low value for K. The high retention time because of the low flushing during the premonsoon can lead to reactions other than geochemical such as photochemical reactions. The absence of any significant correlation between Log C and salinity during the premonsoon may be due to such side reactions. Also the insitu biochemical additions of phenols can contribute to the phenol concentration. Evidences for the photochemical transformations of phenols in aquatic systems are available in the literature (Polisois *et al.*, 1975; Stephen Opsal & Benner., 1998).

The absence of significant correlation between $\log C_{(MBAS)}$ with salinity indicates that MBAS is totally out of the model. The reason can be (1) the major source of MBAS in the aquatic system is anthropogenic so that the concentration of MBAS will have bearing only to the fresh water rather than the seawater. The basic structure of the geochemical reactivity model is the modification of chemical species brought to the estuarine waters from the seawater. The flow reactor considers the fresh water contribution to the concentration of chemical species as negligible or at a steady state. (2) MBAS belongs to a group of chemicals that are highly reactive, bioactive and biodegradable. The geochemical reactivity concept cannot be so applicable here; instead a model which can accommodate the above factors also to developed to explain the reactivity of MBAS. This requires more data on the reaction side of MBAS, which was beyond the scope of the present work. Work in this direction has already been initiated in this laboratory.

SUMMARY

Estuaries are unique environments that play an important role in the transfer of products of continental weathering to the ocean. Because of the major physico-chemical conditions existing in fresh and saline water, the distribution and chemical characteristics of constituents in dissolved and particulate forms get modified during the mixing processes in estuaries. Hence, assessment of the quality of water in an estuary is of great significance in the maintenance of a sustained ecosystem.

A wide spectrum of organic and inorganic compounds enters the estuary through different sources such as air, river and direct or indirect anthropogenic discharges etc. Since the subsequent behavior and fate of the substances depend on a variety of factors - physical, biological and chemical - the prediction of their behavior and fate is very difficult. Many pollutants adsorb on to suspended particulate material and get locked in the sediments on settling of these materials. Sedimentation of a pollutant may lead to serious long-term problems in an area, as resuspension of sediments and exchange with overlying water are regular ^{processes} processes in estuarine dynamics.

Surface active agents are substances which cause lowering of the surface tension of liquids, particularly water. They can 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, microlayer enrichment and other surface effects. They are able to control the transfer of gases between the air-water interface

Surfactants (surface active agents and detergents) are very widely used as industrial and household cleaning agents, dispersants and emulsifiers. The number of these compounds is very large and it is continually increasing, although only relatively few types are in extensive use. Synthetic detergents have caused much concern due to their tendency, even in small amounts, to cause foam in rivers and at sewage plants. Harmful effects of detergents in natural waters may result from their general impact on the biogeochemical cycle of other pollutants and biogenic elements.

Natural surfactants ^{form} from a major part of the (estimated about 50-70%) marine humic substances. The fulvic acid fraction, one of the most important soluble component involved in the marine aerosol process, show the characteristics of wet

surfactants. Coastal and estuarine waters in some densely populated areas receive significant quantities of various derived chemicals, which include anionic surfactants. These environments seem to be particularly sensitive to pollution with synthetic surfactants.

The CES is highly influenced by various anthropogenic activities like discharge of agricultural, industrial and urban wastes, operation of shipyard, oil and other transporting activities, fishing, dredging etc. A by-product of the dredging process is the resuspension of the bottom sediment, which contains stored toxic and other compounds. In the present study, the distribution and seasonal variation of anionic surfactants (MBAS), total phenols, chlorophenols and boron in the water and sediments of the CES has been studied

Seasonal values of MBAS showed high values in the surface water during monsoon compared to premonsoon and postmonsoon. In the surface water, MBAS showed a decreasing trend from upstream to downstream in the north zone during postmonsoon and in the bottom water an increasing trend towards downstream in premonsoon and postmonsoon in the southern part of the estuary. No significant trend was observed in the other seasons.

MBAS in the sediment showed an increasing trend towards downstream in the north zone. In the south zone a decreasing trend was observed during premonsoon. MBAS in the sediments of CES showed significantly high correlation with sedimentary organic carbon.

The seasonal values of phenolic compounds in the surface waters of Cochin estuary showed higher values in the northern part during monsoon and in the southern part during postmonsoon. In all the seasons, the average value of phenolic compounds in the surface waters of Cochin estuary along the Periyar River showed an increasing trend towards the upstream. This can be attributed to the input of phenolic compounds in to the estuary from anthropogenic or natural sources. The southern part of the estuary also showed a similar trend as that of the north zone, where phenolic concentration showed high values in the upstream station (Station no.7). Highest value for phenolic compounds during the monsoon months in the northern part of the estuary was in June 96 and in the southern part was in August 96. In the bottom water also, phenolic concentration showed an increasing trend towards upstream.

Postmonsoon in the northern part and premonsoon in the southern part showed to be exceptions to this. In postmonsoon months, very high values of phenolic concentration were observed during October 96 in all the stations. In premonsoon, May 96 showed maximum values in stations except barmouth. In monsoon season, all stations showed higher values except barmouth in all months. Localised high values were observed for phenols because of anthropogenic activities such as retting of coir, industrial discharge etc.

Phenolic compounds in the sediment during monsoon showed an increasing trend towards the downstream and in other seasons there was no specific trend and in the southern area station 7 showed maximum value in all seasons compared to station 6. The concentration of phenols in the sediment was always very low in station 1, except in November 96.

Chlorophenolic compounds are toxic to aquatic species, but to varying degrees depending on the number and the position of the chlorine substituents on the benzene ring. The chlorinated phenols consist of a group of 19 different isomers which include mono, di, tri, tetra and one pentachlorophenol. All these compounds are toxic to aquatic species, but in varying degrees with PCP being the most toxic. They are brought in to the environment, intentionally or unintentionally, through anthropogenic activities. The release of industrially derived halogenated organic compounds in to the aquatic environment is of great concern, mainly because of their toxicity, resistance to degradation, and tendency to bioaccumulate. Chlorophenolic compounds have been found to be the major constituents produced from lignin residues. Some of them are toxic and can get accumulated in living organisms.

The identification of the different chlorophenols in CES could be done with o, p and m chlorophenols because of the non availability of pure standards. The rest of the species observed in the G.C. is represented as fraction 1, 2 etc. The trends given denote decrease or increase, as the case may ^{be}, towards downstream.

In the Cochin estuary o-chlorophenol and p-chlorophenol showed low values in the surface water compared to bottom water in the northern part of the estuary and higher values in the surface water in the southern part. There was no significant trend for o-chlorophenol in the estuarine water. Seasonal average of o-chlorophenol showed high values during monsoon seasons in the surface and bottom water. In the

sediment samples o-chlorophenol showed a decreasing trend during monsoon season and an increasing trend in the postmonsoon and premonsoon season in the northern part. No significant trend was observed in the southern part. In the sediment, p-chlorophenol showed a decreasing trend during monsoon in the northern part and in other seasons there was no significant trend in the north and southern part.

m-chlorophenol showed only a decreasing trend in the surface water during premonsoon and in other seasons the water and sediment samples had no significant trend in the study area. In water samples m-chlorophenol showed higher values during monsoon season in the surface and bottom water, but in sediment samples it showed low values during monsoon except in station.1. Generally m-chlorophenol showed higher values in the bottom water than surface water.

Fraction 1 showed a decreasing trend in bottom water in the northern part of the estuary during monsoon. The surface water of the south zone also showed a similar trend during monsoon and in other seasons the surface and bottom water had no significant trend. The sediment showed an increasing trend during monsoon in the northern and southern part of the study area.

Fraction.2 showed an increasing trend in the southern part during the premonsoon and a decreasing trend in postmonsoon seasons in the bottom water. The surface water and sediment samples had no significant trend in the two zones was observed.

Fraction.3 showed an increasing trend in the surface water of northern part during monsoon and postmonsoon. The bottom water also showed a similar trend during premonsoon of southern part. The sediment concentration showed no significant station wise trend. High values were observed in station.1 during monsoon.

Except for the increase in concentration during premonsoon of the southern part and a decrease during postmonsoon in the surface water of the northern part, no general trend was shown by fraction 4. The surface water concentration generally showed high values during premonsoon compared to bottom water where as in monsoon season the bottom water showed higher values. The sediment also showed a decreasing trend during premonsoon and monsoon in the southern part and monsoon in the northern part of the estuary. But in postmonsoon season, the southern part showed an increasing trend.

Fraction 5 showed high values in the surface and bottom water during premonsoon season in the northern part of the estuary except in station 1. Surface water of the northern part during premonsoon and postmonsoon showed an increasing trend. The southern part also showed an increasing trend during postmonsoon season. In the bottom water premonsoon showed an increasing trend in the north and in postmonsoon an increasing trend was showed in the southern part. The sediment in the north showed a decreasing trend during premonsoon and an increasing trend in postmonsoon. An increasing trend was observed in the south part during monsoon and a decreasing trend in premonsoon.

Fraction 6 showed generally higher values in the bottom water than surface in the northern part of the estuary where as in the southern part, surface water gave higher values except station. 5. The surface water has showed an increasing trend in premonsoon and a decreasing trend in monsoon in the northern part. A decreasing trend was the observed in the bottom waters of the northern part in all seasons except station 4. In the northern part the sediment showed minimum during monsoon and maximum in postmonsoon season. In the sediment, the premonsoon values showed a decreasing trend in the northern and southern part of the CES and an increasing trend in southern part during postmonsoon.

Fraction 7 in the surface water showed low values during monsoon and in the sediment during postmonsoon. A decreasing trend was observed during postmonsoon and monsoon surface water in the southern part where as an increasing trend in the north during postmonsoon in the bottom water. Sediment samples showed an increasing trend in the southern part of the estuary during monsoon and in the north a decreasing trend during monsoon and postmonsoon.

A Kinetic flow reactor model is proposed to explain the overall reactivity of the estuary. The distribution data of boron was used to test the model. It was observed from the model that the order of reactivity was found to be Monsoon > Postmonsoon > Premonsoon. The absence of significant correlation between the model parameters in the monsoon season and the observed reactivity during monsoon was attributed to the irregular characteristics of the floodwater. The northern part was found to be more reactive than the southern part, may be due to the lower flow rate of river water and the shallow nature of the water column in the southern part. The model was found to explain the distribution pattern of phenol but MBAS was totally out of the model.

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