POLYCYCLIC AROMATIC HYDROCARBONS AND TOXIC TRACE METALS IN SEAWATER AND SEDIMENTS FROM THE WEST COAST OF INDIA AND THEIR BIOACCUMULATION IN SOME SELECTED SPECIES OF FISHES

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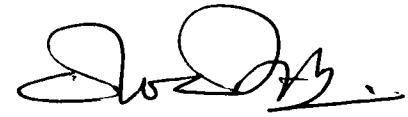
CERTIFICATE

This is to certify that this thesis is an authentic record of the research work carried by Mrs. Latha Unnikrishnan, under my supervision and guidance in the Central Institute of Fisheries Technology, Cochin in partial fulfillment of the requirements for the degree of Doctor of Philosophy and that no part of this work thereof has been submitted for any other degree.



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Chapter 1

INTRODUCTION

GENERAL INTRODUCTION

The large Arabian Sea marine ecosystem includes the western Arabian Sea, bordering Somalia, Yemen and Oman, the Central Arabian Sea bordering Iran and the eastern Arabian Sea bordering India and Pakistan. Each sub region has its own special features in terms of current patterns, physical characteristics, physico chemical qualities, dominant fish species, biodiversity, etc. Depending on monsoon winds, local topography, the width and depth of the continental shelf, and drainage of coastal areas, there are three coastal ecosystems, each charecterised by its own productivity and species distribution (Dwidedi and Choubey, 1998). The continental shelf is widest off the north west coast of India. This region often gets tropical cyclonic storms. The Arabian Sea is a monsoonal area. For half of the year from July to December the winds in this region are from the south-west, inducing a great deal of evaporation from the warm waters of Arabian sea, and heavy rain fall along the coast of India. The wind blow towards India and cause upwelling of low oxygen waters. There is a concentration of fish in near shore areas at this time. In the other half of the year, the winds blow in the opposite direction, and not as strongly as during the southwest monsoon. There is clear difference in salinity in water masses of different origin. Off India's south-west coast, mud banks help to increase productivity whereas the north-west coast is influenced by wind-induced upwelling.

1.1 Fishery resources in Arabian Sea

With a long coastline extending along the mainland and the rich areas surrounding the Andaman and Nicobar Islands and Lakshadweep Archipelago and a fairly wide continental shelf and slope, India has rich and varied marine fishery resources. It consists of different species of fishes, crustaceans and molluscs. The total length of India's coastline is about 8129 km. The west coast of India has a sea front of about 2400 km in length extending from Cape Comerine in the south to Rann of Kutch in the north. The fishing grounds on the continental shelf of west coast up to 200 m depths may be roughly estimated to be 168350 km^2 (Balakrishnan, 1985). The seas that surround the Indian coasts are parts of the Indian Ocean, which has an area of 74917000 km^2 (Balakrishnan, 1985) lying between longitudes 20° E and 115° E. The continental shelf of India is more prominent on the west coast than on the east coast. A large scale turbulence involving upwelling and wind phenomenon occur on the south-west coast of India which contributes to the Arabian sea, becoming one of the most productive fishing grounds in the world. About 3/4th of the Indian sea food production is from the west coast. India's south-west coast ecosystem is dominated by small pelagic fishes, such as oil sardines (*Sardinella longiceps*), mackerels (*Rastrelliger kanagurta*) and tunas. Most of this catch comes from a narrow 10-15 km coastal belt, and accounts for 23.6% of India's marine fish catch. The dominant fish species off India's central – west coast ecosystem are Scianids (*Pseudoscianata diacanthus*), carangids (*Caranx* spp) and anchovies. The dominant species of

India's north-west coast are prawn, Scianids and Carangidae. Small tuna migrate this area to breed.

Current fishing methods have resulted in the over-exploitation of coastal resources such as sardines, prawns, pomfrets and mackerel. However, most of the fish stock breed in deeper off shore waters so there is an opportunity to rebuild stocks. The over-exploitation is mostly due to the large fishing vessels that fish illegally near the coast. Population pressure in India will continue to put pressure on coastal resources. India has over 1 billion people to feed. Seventy percent of them eat fish. India would require 13 million tones of fish to meet the minimum requirements. Yet the present production is 3.9 million t. So there is an urgent need for a long-term plan for conservation and management of the marine ecosystem. Indian coasts have a large variety of sensitive eco-systems. Sand dunes, coral reefs, mangroves, and sea grass beds and wetlands are some that deserve special mention. These ecosystems are the spawning grounds and nurseries for a number of commercially important fishes, gastropods and crustaceans. A critical feature of these ecosystems is the variety of bioactive molecules that they host. Recent monitoring of organisms from the tidal and inter-tidal zone has revealed large numbers of molecules with obvious implication for human health and some have industrial applications also. This could be the most commercially important aspect of the Coastal Zone. Molecules that show bioactivity from one ecosystem may not show the same activity, or level of activity, when mined from a different locale or different season. This feature alone should be reason enough for the protection of all such ecosystems, and

not only representative isolated units in protected areas / parks.

1.2 Marine Pollution

Exploitation of marine environment for food, minerals, chemicals, etc, recreational activities and waste disposal led to constant pollution of the aquatic environment by anthropogenic inputs. The word pollution generally refers to virtually any substance or energy released into the environment by human activities, which are detrimental to mankind or ecosystem. Increased industrialisation for economic development necessitates a greater awareness of the dangers of consequent environmental pollution. Presence of organic and inorganic pollutants in surface waters continues to be one of the most important environmental issues of the world. Global economy is expected to reach 13 trillion dollars by 2050, more than five times what it is today. Improved and increased utilization of the available resources will invariably lead to increased production of wastes. On account of this, more area is required for waste disposal. The enormous volume of sea naturally appears to offer virtually an unlimited capacity for mineralizing organic refuse. Many coastal towns take advantage of this and release their domestic sewage and industrial effluents into the sea. Deposition of harmful industrial byproducts and contaminants into the surface waters poses serious problems to the environment. Despite the size of the ocean and their thorough intermixing, water circulation is mostly slow and dispersion of materials in sea is sometimes a very gradual process. Consequently, where, large amounts of wastes are discharged into shallow waters, pollutant concentration may reach high proportions. In addition to the waste disposal by man, accidental

discharge and natural or accidental calamities also add to the pollution dynamics in the marine environment.

Pollutants can be classified into highly persistent pollutants, moderately persistent pollutants and transient pollutants. The different pollutants that enter the marine environment include heavy metals, hydrocarbons, radioactive wastes, petroleum hydrocarbons, agricultural run-off containing harmful pesticides and domestic and industrial effluents.

Any exposure of the food fishes to the toxic contaminants in the environment will lead to their subsequent bioaccumulation in them. This in turn is transferred to human beings through food chains. This situation necessitates regular monitoring of pollution in the marine environment.

1.3 Pollution of the Indian coast

Pollution in India mostly arises from land-based sources - industrial & domestic wastes and agricultural run-off. Shipping and associated shipbuilding, breaking and port activities are becoming increasingly significant. The crop of recently started coastally located industries use seawater as a resource and the coastal domain as a sink of altered seawater [temperature and density]. These pose newer, more direct threats to sensitive eco areas. Estuaries are natural transport centers providing good, often shallow natural harbours and link sea with rivers. The waste from inland, released into adjacent waters eventually reaches the estuary through canals and rivers. The regular change of tides will often carry the waste out into the sea. All these have made the seas the final dumping ground of wastes (Vinith Kumar, 2001).

1.4 Major coastal areas and cities of India are all situated adjacent to estuaries/

Gujarat

Industries manufacture bulk chemicals, dyes, pharmaceuticals and phosphorus pesticides / and discharge over 200 MLD of effluents, which are acidic, oxygen depleted and sediment laden. The effluents contain heavy metals, phenols, nitrogen and phosphorous. This has affected the water quality of the Narmada, Tapti and Mahi rivers.

Mumbai

The River Kalu, north of Mumbai, flowing through the industrial towns of Ambarnath, Ulhasnagar and Kalyan has a mercury concentration exceeding 100 ppm. Thana creek in Mumbai receives effluents of over 50 MLD, where high mercury levels are present in the water, sediments and living organisms.

Kochi

The Periyar river receives chemical industry effluents and untreated sewage. Incidents of ulceration in shrimp and fish, and frequent fish mortality have affected traditional fishing, with no pollution abatement efforts made.

Goa

Estuarine and coastal waters are "clean", though there is high sediment load from mining activities. The Mandovi-Zuari estuaries receive over 30 MLD of partly treated domestic sewage and 15 MLD of industrial and agricultural effluents.

Calcutta → Need not be [illegible]

The Hoogly River carry effluents that have contaminated fish and shell fish with heavy metals such as Ni, Cu, Cd and Zn. The sediments near Haldia have up to 10 µg/g of pesticides. E.coli, shigella, salmonella and other human pathogens contaminate these river waters - indication of severe sewage contamination. Escherichia coli

The data, to date, indicate that the Indian coasts have well circulated oxygenated waters, and that hot spots remain contained within reasonable limits.

1.5 The major rivers in India may be classified as:

(1) Himalayan rivers

(ii) Peninsular rivers

(iii) Coastal rivers

(iv) Rivers of the inland drainage basin

The Himalayan Rivers are perennial as they are generally snow-fed and have reasonable flow throughout the year. During the monsoon, the Himalayas receive very heavy rainfall and the rivers discharge the maximum quantity of water causing frequent floods. The Peninsular rivers are generally rain-fed and, therefore, fluctuate in volume. A large number of the streams are non-perennial. The streams of the inland drainage basin of western Rajasthan are few and far between. Most of them are of an ephemeral character. They drain towards the individual basins or salt lakes like the Sambhar or are lost in the sands having no outlet to the sea. The Luni is the only river of this category that drains into Rann of Kuchch. The Ganga sub-

basin, which is a part of the larger Ganga-Brahmaputra-Meghana basin, is the largest in India receiving waters from an area, which comprises about one-quarter of the total area of the country. The Ganga flows through Uttar Pradesh, Bihar and West Bengal in India and enters Bangladesh thereafter. It has two main headwaters in the Himalayas: the Bhagirathi and the Alaknanda, the former rising from the Gangotri glacier at Gomukh and the latter from a glacier short of the Alkapuri glacier. The Ganga is joined by a number of the Himalayan Rivers including the Yamuna, Ghagra, Gomti Gandak and Kosi. The western-most river of the Ganga system is the Yamuna, which rises from the Yamunotri glacier and joins the Ganga at Allahabad. Among important rivers flowing north from central India into the Yamuna/ Ganga are the Chambal, Betwa and Sone. The Brahmaputra and the Barak flowing from east to west in north-eastern region are international rivers and have immense water resources potential which is still in the initial stages of development.

The Godavari in the southern Peninsula has the second largest river basin covering 10 percent of the area of India. Next to it is the Krishna basin in the region, while the Mahanadi has the third largest basin. The basin of the Narmada in the uplands of Deccan flowing to the Arabian Sea and of the Kaveri in the south falling into the Bay of Bengal are about the same size, though with different character and shape. Two other river systems, which are small but agriculturally important, are those of the Tapti in the north and Pennar in the south. These west coast rivers are of great importance as they contain as much as 11 percent of the country's water resources while draining

about 50 percent of the land area.

A compilation of the type and quantum of pollutants into the coastal ecosystem of India are given below:(Elrich de Sa, 2001).

No	Input / pollutant	Quantum- Annual
1.	Sediments	1600 million tonnes
2.	Industrial effluents	50 x 10^6 m^3 tonnes
3.	Sewage - largely untreated	0.41 x 10^9 m^3 tonnes
4.	Garbage and other solids	34 x 10^6 tonnes
5.	Fertilizer - residue	5 x 10^6 tonnes
6.	Synthetic detergents - residue	1,30,000 tonnes
7.	Pesticides - residue	65,000 tonnes
8.	Petroleum hydrocarbons (Tar balls residue)	3,500 tonnes
9.	Mining rejects, dredged spoils & sand extractions	0.2x10^6 tonnes

Of the world's total crude oil and its products that amounts to 20000 metric tonnes annually, a major part is transported by the sea route. Of this approximately 60% were shipped along the oil tanker routes across the Indian Ocean. Oil spills along the routes will have serious deleterious effects on the water quality of the marine environment and the fishery resources. The

Arabian Sea is a major oil tanker route to south east Asia, and beyond, probably accounting for the tar like residues deposit on the west coast of India. This chronic problem is however a seasonal feature and is largely regulated by the monsoons and associated winds. Metals, being a conservative pollutant, need careful monitoring since they remain indefinitely in the environment without breakdown. As yet our waters are relatively clear. There are urgent needs to be addressed at the regional and local scale. The decline in fisheries, the increasing pollution by heavy metals, PCBs & pesticides are local effects produced by anthropogenic influence. However, not enough data exists to relate these to changes in the earth system. Such effects are however keenly felt and must be dealt with scientifically to ameliorate local fallout.

1.6 Problem proposed for present study

Although pollution from toxic metals and pesticides are well studied, reports on pollution by Polycyclic Aromatic Hydrocarbons (PAHs) which are established potential carcinogens is scanty. This is an aspect, which calls for urgent systematic study and constant monitoring, as incidence of different types of cancer is going up in the country as a result of modern urban life. Oil tankers emptying residual crude to coastal harbour waters, other hydrocarbons from land and other sources all contribute to this pollution. This study proposes to take up a systematic study (~~perhaps the first of its kind~~) along our entire west coast. As the problem is of gigantic magnitude, the aspects and the variables to be studied are also correspondingly large. An attempt is made here to study the salient aspects of the problem within the

scope of a large study on the pollution profile of our coastal seas. The water, sediments and selected four species of fishes available round the year, are studied for the purpose.

The study also covers the pollution of our coastal waters with metals like Hg, Pb, Cd, Cu, Zn and Ni. The seasonal changes in the concentration of these metals along the coast with special emphasise on the waters off Cochin was also studied as a part of this study. In the present study an attempt was made to determine the distribution of trace metals in the tissues of four species of edible fishes from the West Coast of India.

1.7 Objectives of the study

1. To collect base line data on the concentration of PAHs in seawater and sediment from the west coast of India
2. To study the concentration of PAHs in four species of fishes from the west coast
3. To study the comparative levels of PAHs in fish and in the aquatic environment of the west coast of India
4. To study the influence of sediment characteristics on the concentration of PAH in sediment
5. To study seasonal changes in PAH concentration in water, sediment and fish
6. To provide a baseline concentration of trace metals in water, sediment and fish from the west coast of India
7. To study the seasonal change in the content of selected trace metals in water, sediment and fish from the west coast of India

Chapter 2

REVIEW OF LITERATURE

REVIEW OF LITERATURE

Polycyclic Aromatic Hydrocarbons are wide spread contaminants in the marine environment (Blumer, 1976; Suess, 1976; Harvey, 1996). These are compounds consisting of two or more aromatic rings and two adjacent benzene rings that share two carbon atoms. They contain many structural isomers. So far, over 100 PAHs have been detected in the environment. On the basis of their properties and their molecular weight, two classes of PAHs can be distinguished, i.e the two and three ring aromatics from naphthalene to anthracene and the four to six ring aromatics from fluoranthene to indeno (1,2,3-c,d) pyrene. These compounds have- been widely studied (Neff, 1979; Mc Elroy *et al.*, 1989) because of their carcinogenic and mutagenic character. PAHs containing 24 or fewer ring carbons have been chosen as target compounds for environmental monitoring of their biological effects. Most of these groups have mutagenic effects in some bacterial mutation tests, and roughly 60% of the PAHs have been found to be carcinogenic in mammals (Sivasami *et al.,* 1990). Numerous reports indicate that carcinogenic PAHs are immunotoxicants. The main environmental significance of PAHs are their carcinogenic potential as established by several workers (Marvin *et al.*, 1995; Hall and Glower, 1990). In 1965, Doll *et al.* demonstrated that most human cancer might be attributable to environmental carcinogens, especially through the daily diet. The carcinogenic risk to man from these chemicals in the environment can in principle evaluated only from epidemiological studies (Zander, 1968). International Agency for Research on

Cancer publication has been dedicated to analysis of cancer in processes, which involve exposure to PAHs (Anon, 1983; 1987). Since there is no adequate information regarding carcinogenicity of individual PAHs to human beings from epidemiological studies, data from animal bioassays were extrapolated to estimate human cancer risks (Anon, 1993a). A quantitative cancer potency factor has thus far been developed for benzo (a) pyrene only (Anon, 1992). It is 7.3 per mg/kg/ day and is based on animal studies.

Hydrocarbons in aquatic environments originate from several sources, which has been grouped into the following categories (Anon, 1982; Clark, 1997). 1). Petroleum inputs 2) Hydrocarbons especially PAHs arise from the incomplete combustion of organic matter in flames, engines and industrial processes (Hites *et al.,* 1977; Wakeham *et al.*, 1980); 3) Natural sources of PAHs include forest fires, natural petroleum seeps 4) post depositional transformation of biogenic precursors (Young and Cerniglia, 1995) and 5) biosynthesis of hydrocarbons by marine or terrigenous organisms. Biological sources include land plants, animals, bacteria, macro-algae and micro-algae.

Once formed, PAH are known to enter the near-shore marine environment through the spillage of petroleum, industrial discharges atmospheric fall outs, shipping activities, storm water drains and urban run-off (Neff, 1979; Gevao *et al.,* 1998). Because of their low water solubility, and their hydrophobic nature, PAH in the aquatic environment rapidly become associated with inorganic and organic suspended particles (Gearing *et al.,* 1980; Gearing *et al.*, 1976; Chiou *et al.,*

1998) and subsequent deposition in sediments. The favourable partition coefficients and greater persistence of sedimentary PAH compared to PAH in solution, means that in general, sediments contain a PAH concentration which is a factor of 1000 or more times higher than in overlying water column (Witt, 1995; Law and Biscaya, 1994). Therefore sediments are important in monitoring of PAH inputs into aquatic environment. The importance of sediments as reservoirs for PAH is well documented (Naes *et al.*, 1995; Prahl *et al.,* 1984; Maher and Aislabie, 1992). Once deposited in sediments PAHs are subjected to low photochemical or biological oxidation. Thus PAH level is more or less persistent in sediments (Lizia Guzella *and* Paolis, 1994).

PAHs have also been found in phytoplankton, plant leaves, river sediments, suspended solids and worms (Lake *et al.*, 1979). This aquatic biota serves as a food source for all aquatic animals (Andelman and Suess, 1970). A variable proportion of sediment associated PAH is available for uptake by demersal fish. A major factor determining this is the amount of organic carbon present (De Witt *et al.*, 1992; Livingston *et al.*, 1993). The life style and feeding habits of the organism are also important factors in the bioaccumulation of these compounds. As PAH solubility decreases with increasing molecular weight, bioaccumulation of PAH from sediments by marine organisms is generally greater for the lower molecular weight and more water-soluble compounds than for the higher molecular weight compounds.

Some invertebrates are able to degrade and excrete PAH and PAHs are very efficiently metabolized by phase 1 enzymes of cytochrome P450 in fish liver and excreted in bile. Thus although they are exposed to sedimentary PAH via several routes, they do not generally accumulate these compounds at very high levels. Only very high concentrations can be lethal to fish. According to Roberts *et al.* (1989) LC50 values for PAH recorded are 81-3220 µg/g dry weights. But many carcinogenic and mutagenic intermediates such as diol epoxides are produced by cytochrome P-450 while metabolizing the PAH (Vander Oost *et al.*, 1994). The environmental concern of PAH is due to their potential to form carcinogenic and mutagenic derivatives such as diols and epoxides (Woodhead *et al.*, 1999).

Concentration of total PAH as low as 1-3 µg/g dry weight are able to induce cytochrome P-450 enzyme in Winter flounder and Spout (Payne *et al.*, 1988). Carcinogenesis and liver neoplasia have been reported in brown bullhead catfish at total PAH concentrations as low as 0.1 µg/g and as high as 41 µg/g (Baumann *et al.*, 1995). Relatively high concentrations of PAH can be lethal to invertebrates also.

Studies on PAHs in Indian waters are limited. Mithlesh *et al.* (2004) studied Petroleum Hydrocarbons (PHC) in the marine environment of Bassein Mumbai. He reported that concentration of PHCs in the water off Mumbai varied widely from 2.9- 39.2 µg/l. Chouksey (2002) studied the migration and fate of selected contaminants from anthropogenic discharges in coastal marine

environment. Fondekar and Alagarsami (1984) reported the petroleum hydrocarbon contamination along the oil tanker routes in the Arabian Sea. The distribution of petroleum Hydrocarbons in the Goa coastal waters was reported by Fondekar *et al.* (1980). Petroleum Hydrocarbons in the sediments from Bombay harbour, Dharamtar creek and Amba River was done by Ingole *et al.* (1989). Petroleum hydrocarbon residues in the marine environment of Bassein – Mumbai were reported by Mithlesh *et al.* (2004). Ingole *et al.* (1995) studied the concentration of Petroleum hydrocarbons in inter tidal eco system along the Bombay coast. In his study, the concentration of PHC in the intertidal sediment and water samples collected at Madh, Worli and Colaba were in the ranges 2.9-10.3 µg/l. Petroleum Hydrocarbon concentration in some regions of the northern Indian Ocean was investigated by Sengupta *et al.* (1980). A survey of the petroleum hydrocarbon concentrations in the shelf regions and adjacent waters of the west coast of India was made by Sengupta *et al.* (1978)

Fondekar et al. (1980) reported the effects of oil spill in the Goa coast. The environmental impact of Bombay High oil spill was also estimated by Fondekar *et al.* (1980). State of oil pollution in the Northern Arabian Sea after the 1991 Gulf oil spill was investigated by Sengupta *et al.* (1993). Topgi *et al.* (1982) studied the dissolved petroleum Hydrocarbons along the oil tanker routes in the Southern Bay of Bengal.

Studies on Petroleum Hydrocarbon concentration in selected species of fishes and prawn from north west coast of India was carried out by Mehta *et al.*

(1994). According to his study, the concentration of PHCs in 6 fish and prawn species sampled at 10 transects from Veraval and Ratnagiri ranged from 0.2- 10 2µg/g wet weight. Variation of PAHs in sediments in sediments of shrimp farms in Cochin are was studied by Ashraf *et al*, (2003). Indra Jasmine *et al.* (2003) studied Polyaromatic hydrocarbons in seafood. Accumulation and release of Petroleum hydrocarbons by *Mytilopsis sallei* from harbour waters of Visakhapatnam was done by Raghuprakash (2003). Investigations on the stress effects of petroleum hydrocarbons on *Metapenaeus dobsoni* were done by Miriam (2002). Jehosheba (2004) studied the biochemical effects of petroleum hydrocarbons on the tropical teleost *Oreochromis mossambicus*.

The occurrence of inorganic contaminants mainly, metals in surface seawater continue to be one of the most important environmental issues of our time. Though metals have exerted a profound influence on the course of biological evolution, their modern day industrial usage, mainly during the course of last fifty years has led to their bioaccumulation in the environments (Moore and James, 1992). Many of these metals find their way into the living systems through air, water and food and tend to accumulate in the body Some of them even in minor concentrations threaten to affect the metal dependent enzyme catalyzed reactions in the body. At least 11 metals are known to be essential for living organisms and these are Fe, Cu, Zn, Co, Mn, Cr, Mo, V, Se, Ni and Sn. Essential metals always function in combination with organic molecules and most commonly with proteins either tightly bound in metalloproteins or more loosely

bound in metal protein complexes (Williams, 1981; Brouwer *et al.,* 1986). There is little evidence that marine organisms ever suffer from metal deficiencies and presumably the optimum concentrations are those that occur naturally.

Trace metals reach the marine environment via river run-off carrying discharged heavy metals from industries, mining activities, shipping, dredging activities and through other anthropogenic inputs (Manhan, 1994). From surrounding seawater, food and through the imbibed seawater these get accumulated in marine organisms directly (Depledge and Rainbow, 1990). They are accumulated to body concentrations, orders of magnitudes higher than the concentrations in an equivalent weight of seawater (Eisler *et al.*, 1981; Rainbow *et al.*, 1990). In aquatic environments, metals have been termed as conservative pollutants because once added to the environment they remain there for considerably long time if not forever. These metals cannot be broken down to harmless substances by bacterial action. They are leached into the aquatic system as a result of weathering of rocks and volcanic eruptions and as a result of human activities. These processes and activities change the natural concentrations of metals in the seawater resulting in 10 or even 100 fold increase near the point of effluent discharge. The discharge of toxic heavy metal industrial wastes into the sea through rivers and streams result in accumulation of pollutants in the marine environment especially fishes and bio availability of the trace metal is the key factor determining tissue metal concentration (Goldberg *et al.,* 1976). In marine organisms, trace metal uptake occurs directly from the

surrounding seawater across the permeable body surface from food and imbibed seawater entering the gut (Depledge *et al.*, 1990). The fishes form an important target for biomagnification of the metals as they are at the top of the food pyramid and act as a possible transfer media to human beings. Elevated levels of toxic metals like Cd, Hg, Pb, As, etc; have been observed in various fishery products, particularly molluscan shellfish, from various parts of the world (Lakshmanan, 1989; Kurihara *et al.*, 1993).

Fishes coming towards the top of the food pyramid, there is maximum possible biomagnification in them, which will get transferred to human beings. Even though a good amount of data on the distribution of trace metals in the Indian seas are available (Braganca and Sanzgiri, 1980; Sanzgiri and Braganca, 1981; Rajendran *et al.*, 1985; Satyanarayana *et al.*, 1985), not much work has been done on the concentration of these metals in fishes from the Indian coast, for evaluating the levels of contamination from the natural environments (Matakar, *et al.,* 1981; Singbal, *et al.,* 1982; Kureishy, *et al.,* 1983). The most important works on trace metal concentrations are of Windom and Smith (1972), Abdulla *et al.* (1972), Chestner and Stoner (1974), Chestner and Stoner (1975), Bender and Gagner (1976). Danielsson (1980) studied trace metals from surface waters from different depths of Indian Ocean. Matakar (1981) studied the concentration of trace metals in Bombay harbour bay. Studies on trace metals in seawater from Sourashtra coast has been done by Kesava Rao and Indusekhar (1986). In the Arabian Sea, the most important works are those of Sengupta *et*

al. (1978), Sanzgiri and Moraces (1979) and Braganca and Sanzgiri (1980), Kureishy *et al.* (1983). Studies in Cochin coast has been done by Mohapatra (1994), Meenakumari and Nair (1984), Nair and Rao (1980), Nair *et al.* (1990), Meenakumari (1989), Radhakrishnan (1993). Asha Jyothy and Vijayalakshmi (1999) studied concentration of metals in fishes from Thane and Bassein creeks of Bombay, India. Maheswary *et al.* (1997) reported heavy metals in fishes from coastal waters of Cochin.

Study of the physico chemical parameters of the seawater is essential to get background information about the pollution in the marine environment. Earlier works on the physico chemical properties of sea water in the Arabian sea have been done by Gupta and Pylee (1964), Qasim and Sankaranarayanan (1969) Meenakumari (1989), Zingde (1985) and Harvey (1926). Distribution of dissolved oxygen in the Western Bay of Bengal was reported by Naqvi *et al.*(1979). Studies on the nutrient fraction and stoichiometric relationship in the Arabian Sea were done by Sen Gupta *et al.* (1978). The noteworthy contributions pertaining to Cochin backwaters are those of Wallershaus (1972) on the hydrography, Ramamritham and Jayaraman (1963) on the hydrohraphical conditions around Willingdon Island, Haridas *et al.* (1973) on salinity, temperature, oxygen and zooplankton biomass of the backwater, Balakrishnan and Shynamma (1976) on the diurnal variation of physico chemical parameters during the south west monsoon, Joseph (1974) on nutrient distribution of harbour.

The preceding review of literature on PAHs and trace metals in the marine environment indicates that there is a paucity of data on the west coast of India in the west coast. In view of the great concern in the water quality of the Arabian Sea and the safety of the food fishes, the current investigations are aimed to fill the lacunae in information on trace metal levels and PAHs levels in water, sediment and fishes from the west coast of India.

Chapter 3

MATERIALS AND METHODS

3.1 Area of Investigation

Samples were collected from west coast of India during the cruises namely 181,191, 197, and 204 of the Fisheries Oceanographic Research Vessel "Sagar Sampada" under the Department of Ocean Development, Govt. of India during the period from February 2000 to October 2003. The operational area covered lat. 8° -21° N and long. 69° -75° E. Since the numbers of cruises of Sagar Sampada were limited in the west coast, samples were taken from the off Cochin area from shallower waters, for two years to get enough data for the study so that a comparison can be made between the two. Monthly samples of the water, sediments and fishes were collected between 2000-2002 from off Cochin area from MFB "Matsyakumari" of Central Institute of Fisheries Technology (CIFT), Cochin. The sampling was done at a depth of 20-25m. The operational area covered latitude 9° 54' 28"N to 10° 02' 58"N and Longitude 76° 05' 58"E to 76° 12' 47"E. The details of the study area are given in Table 3.1-3.7and in figures 3.1-3.5.

Cruise No.181

The fishing was conducted along the coastal waters off Gujarat from latitude 20° 18' to 21° 31'N and longitude 69° 10'- 70° 33' E. at a depth range of 50-100m during February 2000 in the premonsoon season (Table 3.1 & Fig. 3.1).

Cruise No. 184

Area covered during the cruise was from latitude 8° 30'-22° 00'N and longitude 69° 20'- 76° 29'E, from off Quilon to off Gujarat during May 2000 in the

monsoon season (Table 3.2, 3.3 & Fig. 3.2). The entire area of study was divided into 4 zones and samples were collected from each zone.

Cruise No. 191

Cruise was conducted between latitude 8°47'-11°47'N and longitude 74° 27'- 76° 27'E from off Quilon to off Manglore during the period from 8th August 2001 to 24th August 2001 in the monsoon season (Table 3.4 & Fig. 3.3).

Cruise No.197

Area covered during the cruise was from latitude 9° 08' – 11° 46'N longitude 74° 25'- 76° 00' E from off Cochin to off Manglore during the period from 4th January 2002 to 24th January 2002 in the pre monsoon season (Table 3.5 & Fig. 3.4).

Cruise No.204

The cruise covered the area between latitude 8°14'N and longitude 73° to 74° E during 20th October 2002 to 6th November 2002 in the post monsoon season (Table 3.6 & Fig. 3.5).

3.2 Stations in the off Cochin area

Vembanad lake is a perennial and extensive backwater system stretching 75 km to the south and 40 km to the north of Cochin harbour with innumerable canals branching out from the lake forming an extensive complex of inland water ways. The port of Cochin is located near the confluence of the Vembanad Lake with the Arabian Sea. Vembanad Lake maintains connection with Arabian Sea through a narrow opening, 365 m broad between the mainland of Cochin and the

Vypeen Island. Several rivers originating from the Western Ghats empty into the Vembanad Lake, the major ones being the Periyar and Muvattupuzha river. There are many factories such as a major fertilizer plant producing K- P- N fertilisers an oil refinery, a rare earth element processing factory and Zn smelters on the banks of the Periyar river and a News Print factory on the Muvattupuzha riverbank. Cochin is located at latitudes 9°58' N and 76° 14' E and is an all weather major port on the southwest coast of India. The maximum rainfall in this region occurs in May, June, July and August and average rainfall is 3000 mm (Soman, 1997).

Seven stations were selected for the present study in the area. The details of the stations are given in Table 3.7. Sampling was done monthly in different seasons for two years (2000-2002).

3.3 Methods of sampling and analysis

From FORV Sagar Sampada water samples (both surface and bottom) were collected using Niskin bottles attached to Conductivity Temperature Depth (CTD) instrument. Temperature and salinity of the water samples were measured using the CTD. pH of the water samples measured using precision pH meter (Jackson, 1973). Salinity of water samples collected from off Cochin area was analysed by the method of Strickland and Parson (1972). Dissolved Oxygen was measured by the Winkler method (Grasshoff, 1983).

Sediment samples were collected from different stations using Smith & Mac Intyre grab for the analysis of trace metals and Polycyclic Aromatic

Hydrocarbons (PAH). The samples were kept in freezer maintained at -15° C in polythene bags until analysis. The sediment organic carbon was determined using the method of Walkly and Black (Allison, 1965). Sediment characteristics were determined using the Robinson combined sieve and pipette method, (Day, 1965). Analysis of nitrite-N, Phosphorous and total nitrogen was carried out by standard methods (Grasshoff, 1983).

3.4 Analysis of PAH in sediment

For PAH analysis, sediment samples (50 gm) were dried under vacuum at room temperature and extracted using dichloromethane. The organic layer was separated and was passed through anhydrous sodium sulphate. The process was repeated three times for the complete extraction of the PAHs. The extract was concentrated to a small volume using rotary evaporator and cleaned up using alumina: silica columns using 1:1 dichloromethane: hexane eluent. The samples were evaporated to dryness and redissolved in a fixed volume of high purity acetonitrile. The quantification of PAH was carried out using in HPLC (Hew lett Packard model 1090) fitted with Emerck PAH column. The maximum elution time was 30 minutes. The samples were analysed for sixteen PAH constituents viz. naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluorene, pyrene, benzo (a) anthracene, chrysene, benzo (k) fluoranthene, benzo (a) pyrene, dibenzo (a, h) anthracene, benzo (g, h, I) perylene and indeno (1,2,3-cd) pyrene. A mixture of 16 PAHs from Sigma chemicals, USA, was used as standard. Solvents like acetonitrile, n-hexane and

dichloromethane used for extraction were of HPLC grade. A solvent system of 100% acetonitrile pumped at the rate of 1ml per minute was used (Lizia Guzella and Paolis, 1994).

3.5 Analysis of PAH in water

Water samples (1 litre) were extracted using dichloromethane in a separating funnel. The organic layer was collected and concentrated to a small volume and cleaned up using alumina: silica columns using Dichloromethane: hexane (1:1) mixture. The purified samples were redissolved in high purity acetonitrile and fed into the column of HPLC.

3.6 Analysis of PAH in Fish

Four species of edible fishes namely, *Saurida tumbil*, *Nemipterus japonicus*, *Epinephelus diacanthus* and *Sciaenidae* (sp) were selected for the study. These species are found abundantly in all seasons through out the west coast of India. *Nemipterus japonicus* is found abundantly in coastal waters, mainly on mud or sand bottoms usually in schools. They feed mainly on crustaceans, mollusks (mainly cephalopods) polychaetes and echinoderm. Sciaenids are small to moderately large fishes, primarily costal water species. Majority of them are found over muddy bottoms. In India, about 60% of the total marine fish landings corresponds to sciaenids. Most of them feed on small crustaceans, fishes and benthic organisms. *Saurida tumbil* is a highly abundant species along the west coast of India. They are bottom dwelling and fish eaters. The flesh is said to be of good quality and flavour though bony. *Epinephelus*

diacanthus occur mainly on muddy sand or mud substrates, caught in depths of 50 to 100 m along the west coast of India (FAO, 1984; Munro, 2000; Froese and Pauly, 2000). The samples were collected from stations located in the west coast of India by demersal trawling using various demersal trawls developed by Central Institute of Fisheries Technology, Cochin, namely HSDT-II fish version and 51 M Long wing trawl. The fishes collected were identified as per FAO identification sheets (1984). Each fish was inspected for grossly observable lesions involving the skin, the gills, and tissues within the oral cavity.

Five samples of each species of almost same size were kept in polythene bags and stored in the freezer at -25°C until analysis. The fishes were dissected and liver, gills and muscle tissues were separated for analysis of PAH. The tissues were aseptically homogenized with minimum amount of distilled water (Sivasami *et al.*, 1990). Then the samples were extracted thrice with 40 ml of dichloromethane in a separating funnel. The extracts were pooled and 5 g of anhydrous sodium sulphate were added to absorb excess water. The clear supernatant was removed and concentrated to 5 ml under vacuum at 60° C in a rotary evaporator. The concentrate was purified over alumina: silica column using Hexane: dichloromethane 1:1 mixture. The eluent was mixed with 1g sodium sulphates and the supernatant was collected and evaporated to dryness under vacuum in a rotary evaporator. The residue was then dissolved in 3 ml acetonitrile and then filtered through a membrane filter. The resultant extract was then diluted to 3 ml with acetonitrile, transferred to a screw-capped test tube,

labeled and stored in refrigerator. From this, an aliquot of 20 micro litres was injected into HPLC column for identification and quantification (Panalacs, 1976).

3.7 Analysis of trace metals

Reagents, chemicals and glasswares

AnalaR grade acids and reagents were used. All glasswares/plastic bottles were washed first with water and detergent and further cleaned by soaking in 5% nitric acid for 24hr and finally rinsed with deionised water. Metal standards were prepared using pure metals or AnalaR BDH salts.

Methods

3.8 Analysis of trace metals in water

Water samples were filtered using Whatman No.1 filter paper and were analysed for the trace metals using Inductively Coupled Plasma Emission Spectrometer (Labtom 8410) with a wave length range of 160- 820 nm, which allows determination of most elements in the periodic table. The monochromator in the instrument is an optical filter driven by computer controlled stepper motor to locate the optical emission lines and by the software package Slimpac available with the model, data from the emission spectrometer is controlled and managed.

3.9 Analysis trace metals in sediment

Pre-weighed dried sediment samples were heated with conc. Nitric acid and Perchloric acid in the ratio 5:1 (V/V). The samples were heated gently and cautiously at first, until the first vigorous reaction subsides, continued heating,

adding more conc. nitric acid in small portions as needed to prevent charring, until the organic matter was completely digested as indicated by a clear solution. The solution was cooled, filtered through Whatman filter paper, diluted to a definite volume with deionised water in volumetric flasks and kept in polythene bottles for analysis by ICP-AES (AOAC, 1990). A reagent blank was prepared by taking the same amount of acid mixture and other ingredients except the sediment samples.

3.10 Analysis of trace metals in fish

Preparation of tissue homogenate

The fish samples were washed with potable water and the length and weight were measured. The muscle tissue was peeled off and homogenized in a mixer. The samples were then dissected and muscle, gills and liver tissues were separately collected and kept. They were also homogenized in a mixer. An aliquot of the homogenate was pressed within filter paper folds so as to remove water. This was then used for digestion and subsequent analysis. For analysis of trace metals in the whole tissue, the fish samples were weighed and digested whole until it became clear and aliquots taken for metal analysis.

Predigestion of samples

15 ml of conc. nitric acid was added to 20 gm of the homogenized samples and kept overnight for predigestion at room temperature in a fume hood.

Digestion procedure

Digestion was carried out by wet oxidation method (AOAC, 1990), ~~as described above.~~ The filtered solution was diluted to a ~~constant~~ known volume and were analysed using ICP- AES.

Statistical analysis of data for correlation and two- way ANOVA was done using Excel available with Microsoft Office Software.

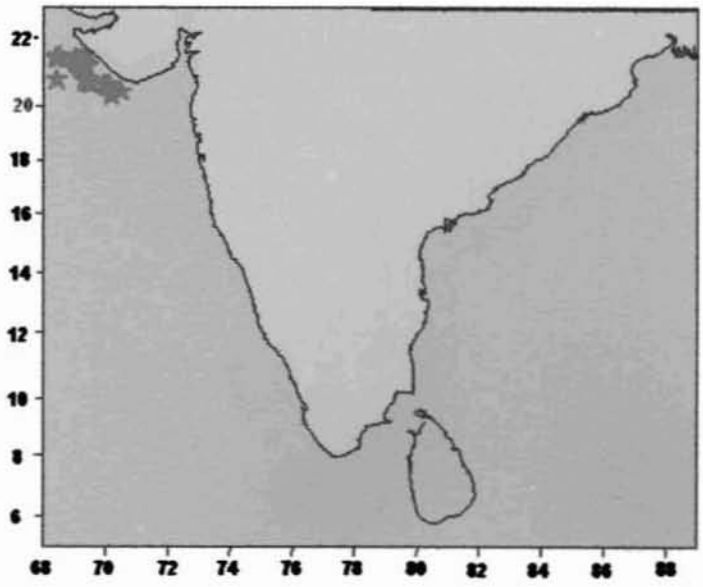


Fig.3.1 Area of investigation –Cruise 181

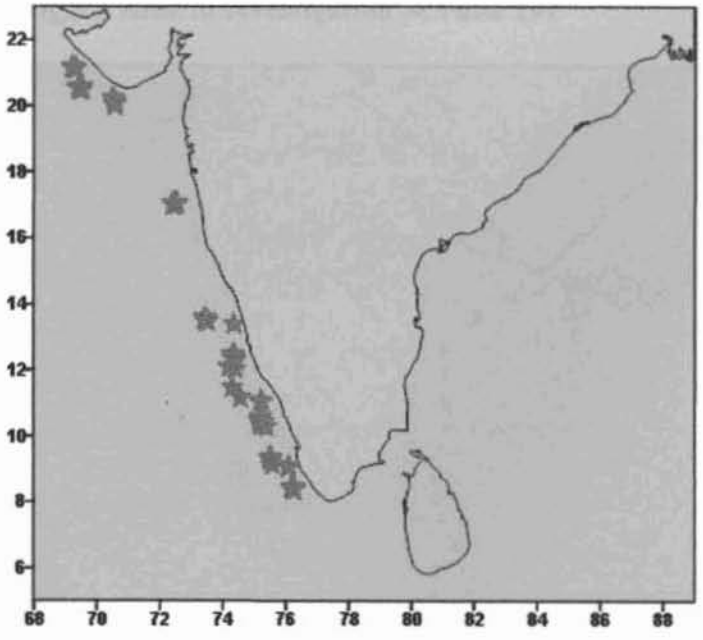


Fig.3.2 Area of investigation –Cruise 184

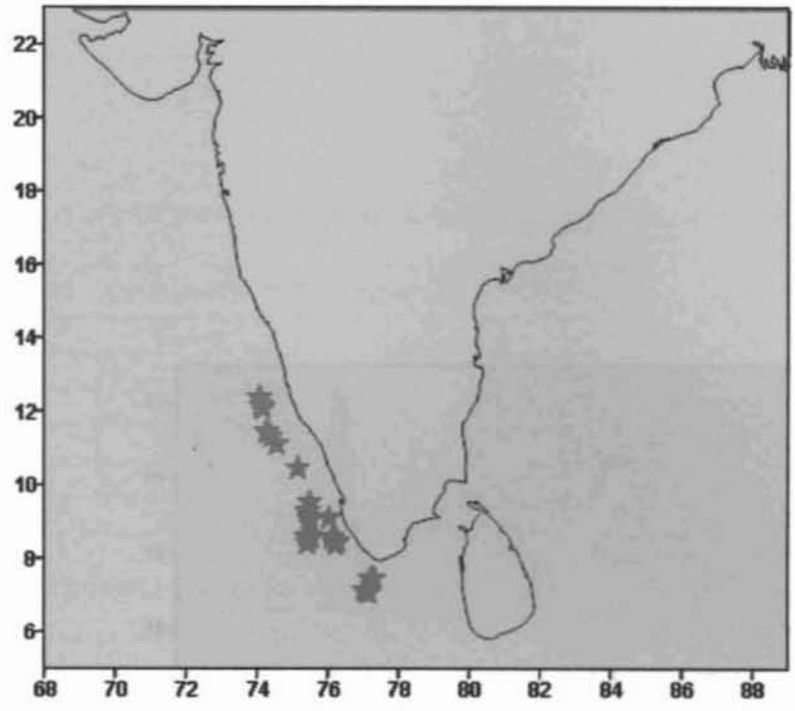


Fig.3.3 Area of investigation –Cruise 191

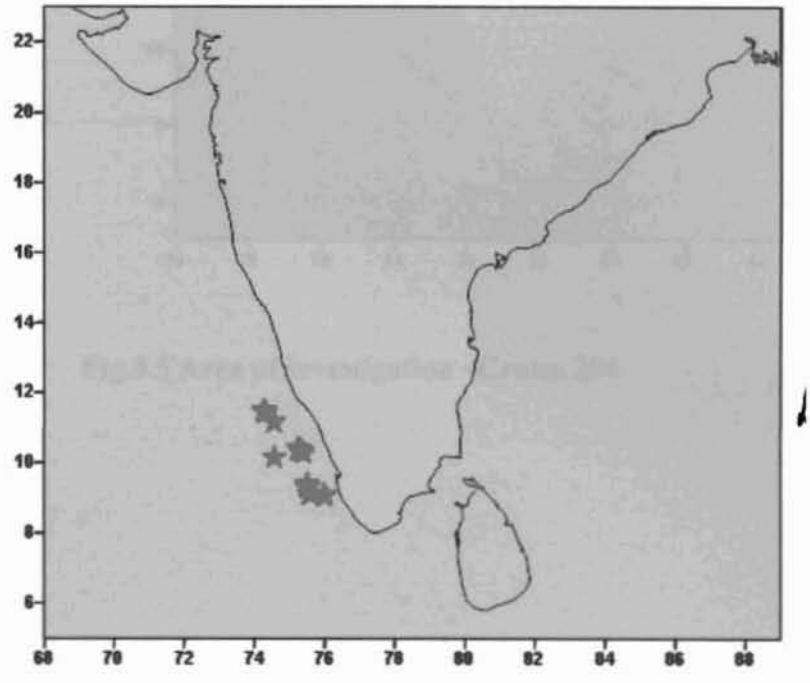


Fig.3.4 Area of investigation –Cruise 197

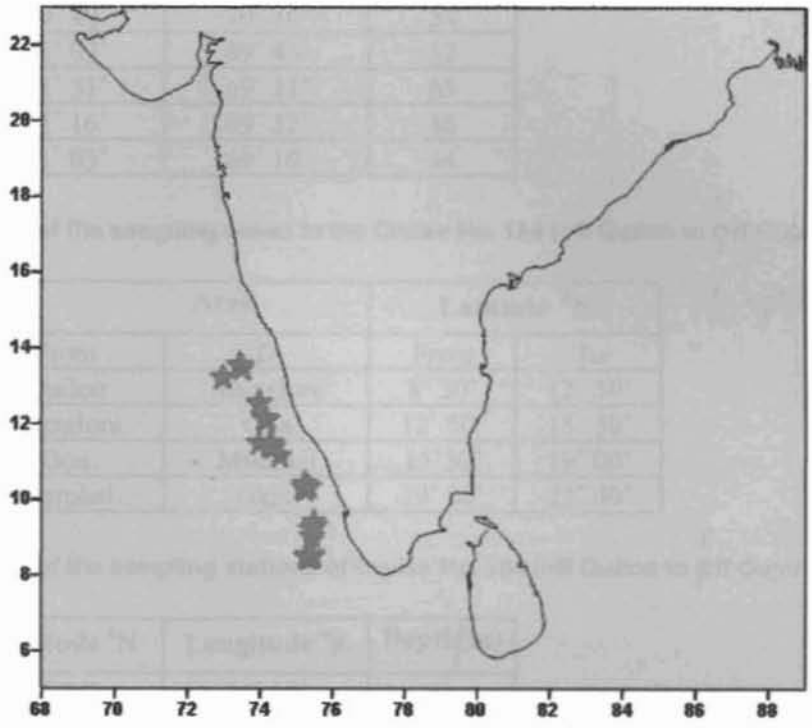


Fig.3.5 Area of investigation –Cruise 204

Table 3.1 Details of the sampling stations in Cruise No. 181 (off Gujarat)

Stations	Latitude °N	Longitude °E	Depth (m)
1	20° 40'	70° 02'	65
2	20° 40'	70° 16'	54
3	21° 02'	69° 43'	52
4	21° 31'	69° 11'	65
5	21° 16'	69° 32'	46
6	21° 03'	69° 10'	44

Table 3.2 Details of the sampling zones in the Cruise No. 184 (off Quilon to Off Gujarat)

Zone	Area		Latitude °N	
	From	To	From	To
1	Quilon	Manglore	8° 30'	12° 50'
2	Manglore	Goa	12° 50'	15° 30'
3	Goa	Mumbai	15°30'	19° 00'
4	Mumbai	Okha	19° 00'	22° 00'

Table 3.3 Details of the sampling stations of Cruise No. 184 (off Quilon to Off Gujarat)

Stations	Latitude °N	Longitude °E	Depth (m)
1	9° 04'	76° 10'	61
2	10° 47'	75°19'	118
3	11° 02'	75° 23'	56
4	12° 32'	74° 41'	56
5	19° 00'	73° 46'	60
6	20° 06'	70° 56'	74

Table 3.4 Details of the sampling stations in Cruise No.191 (off Quilon to off Manglore)

Stations	Latitude °N	Longitude °E	Depth (m)
1	8° 47'	76° 27'	36
2	9° 14'	76° 4'	37
3	9° 56'	75° 56'	35
4	12° 30'	74°10'	200
5	8° 41'	76° 32'	200
6	9° 5'	75° 50'	200

Table 3.5 Details of the sampling stations in Cruise No.197 (off Cochin to off Manglore)

Stations	Latitude °N	Longitude °E	Depth (m)
1	9° 35	76° 00	70
2	9°28	75° 54	79
3	9° 08	76° 00	85
4	10° 26	75° 40	62
5	10° 38	75° 29	78
6	11° 44	74° 31	230

Table 3.6 Details of the sampling stations of the Cruise no 204 (off Quilon to off Maglore)

Station	Latitude °N	Longitude °E	Depth (m)
1	08° 46 49	75° 48 33	300
2	08° 58 42	75° 48 62	330
3	13° 55 02	73° 45 12	75
4	13° 42 05	73° 56 82	60
5	13° 13 89	74° 12 49	56
6	12° 54 37	73° 57 00	268

Table 3.7 Detials of the sampling stations off Cochin

Stn.No	Station Name	Depth (F)	Latitude °N	Longitude °E
1	Fairway	5.2	9° 57' 40"	76° 10' 10"
2	Mundanveli	9	9° 54' 28"	76° 9' 40"
3	Mundanveli	5.6	9° 54' 40"	76° 12' 47"
4	Narakkal	6	10° 02' 58"	76° 09' 15"
5	Narakkal	11.7	10° 02' 37"	76° 05' 58"
6	Malippuram	11.4	10° 00' 02"	76° 06' 05"
7	Malippuram	6.2	09° 59'57"	76° 09' 15"

Chapter 4

HYDROGRAPHY OF THE STUDY AREA

4.1 Introduction

Environmental parameters of the marine environment are gradually influenced by changes in rainfall, ocean currents, winds and other geographical conditions. Seasonal variations of different environmental features in the coastal marine ecosystems will depend on the fresh water inflow, tidal changes and introduction of potentially new physical, chemical and biological changes, thus altering the biological quality. The objectives of this study were to summarise the major physicochemical and biological parameters in the study area during the period from 2000 - 2002, to provide some background information on pollution problems, and to study changes in the selected water quality parameters.

4.2 Materials and Methods

The details of sample collection, sample preservation and analysis for the determination of salinity, dissolved oxygen (D.O), pH and major nutrients are given in chapter 2.

4.3 Results and Discussion

Physico chemical parameters recorded at the study area during the cruises of FORV Sagar Sampada are given in Table 4.1. At stations where the depth was below 200 m, the bottom salinities were only slightly higher than the surface values whereas the difference between surface and bottom salinities were considerably higher at stations of higher depths (>200 m). From the salinity distribution pattern, it is also found that there is an increase in salinity from south to north. The increased salinity in the north has possibly resulted out of the high

saline north Arabian Sea water reaching the area in the southerly flow during the premonsoon period. The decrease in salinity towards the south may be due to the slow spreading of the high saline water southwards losing their high salinity characteristics and also due to the emptying of many rivers into the Arabian Sea near this area. The important rivers draining into Arabian Sea in the south are, Kali river in Karnataka, river Mandovi and Zuari near Goa and around 41 rivers in Kerala. (Pillai, 1991). The salinity of surface water samples during the monsoon season (May- August) is found to be lower (33.38-34.5 ‰ in may and 33.03-34.25 ‰ in August) when compared to that of the other two seasons when the salinity was 35.7-35.98 ‰ in February and 34.8-35.5 ‰ in October. The surface dissolved oxygen ranged from 2.01 ml/l-4.89 ml/l. At stations of depth below 100 m, the range was between 2.3-3.7 ml/l. At higher depths, D.O. as low as 0.1 ml/l was observed.

Macronutrients like nitrite-N, phosphorous and total Nitrogen were relatively lower in surface waters than in the bottom waters. Phosphorous ranged from Non-Detectable level (ND) to 0.07 ppm in surface water and from 0.001-0.05 ppm in the bottom water. Nitrite- N had an average concentration of 0.034 ppm in the surface and 0.040 ppm in the bottom. All these nutrients were relatively lower in the surface, which can be due to uptake of nutrients by phytoplankton at surface and regeneration by microbial oxidation in the bottom sediments and release into the overlying water (Vita Pariente, 1997). Since phytoplankton utilizes phosphate and nitrate simultaneously, the concentrations

of these nutrients fluctuate in a similar manner (Harvey, 1926). Decomposition of organic matter resulting in the release of the thermodynamically stable nitrogen species, *i.e. nitrate*, may be the major factor resulting in higher nitrate concentration at greater depths, where the water is also characterized by low values of dissolved oxygen and temperature.

4.4 Physico chemical parameters of seawater in the off Cochin area

The samples collected from off Cochin area can be grouped as samples collected during premonsoon (January-April), Monsoon (May- August) and Post Monsoon seasons (September – December). The results of physico chemical parameters in various seasons in the study period are given in tables 4.2 – 4.8.

4.4.1 Water Temperature

There were not much fluctuations in surface seawater temperature (S.W.T) between different stations. The variation in surface water temperature in the study period is represented in Fig. 4.1. At station 1 water temperature ranged from 25.5° C (monsoon season) to 28.75° C (pre-monsoon). In station 2 surface water temperatures ranged from 25.5° C in the monsoon to 28.8° C. The highest temperature was noted in pre-monsoon season. In station 3 it was 26.5° C -29.13° C. In station 4, seawater temperature varied from 25.5° C -29.38° C, highest being recorded in the pre monsoon period. In station 5, the range in temperature was from 26.5° C -29.38° C. Station 6 recorded temperature ranging from 26°C -29.5° C and in station 7 surface water temperatures ranged from 26 -29.5° C. In all the stations highest temperature was recorded in the pre-

monsoon season. In the present study the fluctuations of water temperature were in the range of 25-29.5° C. A drop in temperature is noticed in monsoon period and the highest being in pre-monsoon period. Statistical analysis of variance has shown that there was significant variation in seawater temperature in different seasons studied ($p<0.01$) as is recorded by Qasim *et al.*, (1969) and Meenakumari (1989), (Appendix 1, Table 1). When the temperature of the initial year of study was compared with that of the second year there was not much change in the surface water temperature.

4.4.2 Salinity

Of all the hydrographical factors studied salinity was found to fluctuate largely at this area (Fig. 4.2). At station 1 the salinity of the surface water varied from 30.37 ‰ in post-monsoon to 33.52 ‰ in the pre-monsoon. In monsoon season also salinity was lowered to 30.9 ‰. At station 2 the lowest salinity was observed in monsoon season (26.61 ‰) and the highest was in pre-monsoon (33.7 ‰). In station 3, salinity ranged from 21.86 ‰ in monsoon to 33.6 ‰ in pre-monsoon. In station 4, salinity ranged from 32.16 ‰ in monsoon to 33.51 ‰ in pre monsoon season. Salinity ranged from 30.35-34.05 ‰ in station 5 and from 30.08-34.04 ‰ in station 6. In station 7, the range in salinity was from 27.11-33.46. Comparing the average salinities in the initial year of study with that of the second year there was a slight increase in salinity for the second year of study in most of the stations. The annual rainfall data indicated that the rainfall in year 2002 in Ernakulam district was comparatively lower than that in the year 2001

(Guhatha, 2006). This fact correlates well with the increase in salinity observed in surface water in the second year of study. Analysis of Variance showed that there is highly significant variation in salinity in different studied seasons ($p<0.01$), (Appendix 1, Table 2). Recording of high salinity in the pre-monsoon months was due to low amount of rainfall and high rate of evaporation in the shallow coastal areas owing to high atmospheric temperature. Erlansen (1936) reported that the salinity of the surface water in the estuary becomes almost fresh in the active monsoon period. A drop in salinity in the monsoon might be due to the increased fresh water inflow by the rivers and also by the heavy rainfall.

4.4.3 pH

There was no spatial variation in the case of the pH level of water at these seven stations (Fig. 4.3). The pH was comparatively lower during the monsoon season. It ranged from 8.00-8.31 in station 1, 8.11-8.3 in station 2, 7.90-8.29 in station 3, 8.11-8.3 in station 4, 8.19-8.31 in station 5, 8.12-8.31 in station 6 and from 8.07-8.32 in station 7. Statistical analysis showed a significant variation in pH in different seasons of the year ($p< 0.01$), (Appendix 1, Table 3). In the monsoon and post monsoon season pH was relatively low. pH fluctuations are mainly due to fresh water discharge. Low pH was usually observed during the period when salinity values were lower indicating the influence of fresh water drainage on pH.

4.4.4 Dissolved Oxygen

In the study area, horizontal distribution of dissolved oxygen (D.O) in surface waters did not show much variation (Fig. 4.4). The dissolved oxygen ranged from 3.5 ml/l-7.2 ml/l in station 1, 5.3-7.06 ml/l in station 2 and 4.9-7.53 ml/l in station 3. Lower values were observed during monsoon season. In station 4, dissolved oxygen ranged from 6-7.9 ml/l, 6.66-7.15 ml/l in station 5, 6.33-7.6 ml/l in station 6 and 5.7-7.6 ml/l in station 7. Lower values were observed in monsoon and higher values in post-monsoon season. Oxygen variations were dependent on the extent of mixing of the water and the photosynthetic activity of the phytoplankton. Fairly high values of oxygen were observed for most part of the year. Statistical analysis (Appendix 1, Table 4) showed that there is significant variation in dissolved oxygen in different season ($p < 0.01$) the lower being in the monsoon. There was no significant spatial variation in dissolved oxygen between stations.

4.4.5 Nutrients

The concentration of phosphorous in the water sample fluctuated from month to month (Fig. 4.5). There was no uniform pattern for the distribution of the nutrient over the different stations. The highest phosphate concentration observed at station 1 was 0.27 ppm in the post-monsoon season. In station 2, the phosphorous values ranged from 0.06 ppm-0.31ppm. At station 3, the concentration of phosphorous ranged from 0.08-0.28 ppm. The concentration of phosphorus in station 4 was 0.1-0.2 ppm and in station 5 the range was 0.03-

0.30ppm. Phosphorus concentration in station 6 ranged from 0.09 ppm in post monsoon period to 0.29 ppm in monsoon and the range was between 0.05-0.24 ppm in station 7. Statistical analysis showed a significant variation in phosphorus in different seasons studied ($p < 0.01$), (Appendix 1 Table 6). Higher values of phosphorus were observed in the monsoon season. The earlier reported values for phosphates in the Cochin area ranged from 0.01- 3.22 µg/l by Meenkumari (1989), 0.85- 1.6 µg/l by Manikoth and Salih (1974). Higher values obtained for total phosphorus in the present study may be attributed to the enrichment of phosphate by land run-off and land drainage (Qasim, 1969).

Nitrite was found in traces in all the seven stations and not pronounced as that of total phosphorus. An increase in concentration was observed for the post monsoon period. The decline in concentration in the other seasons can be attributed to the higher planktonic productivity in these months (Gupta and Pylee, 1964). Qasim and Sankaranarayanan (1969) reported that the Nitrite-N was more during monsoon period contrary to what has been observed in this study. Total nitrogen varied from 1.55 ppm to 3.1 ppm at station 1, the highest recorded concentration was in pre-monsoon season. At station 2 the total Nitrogen varied from 1.9 ppm to 3.32 ppm in surface water. In station 3 the range was from 1.6 – 3.31 ppm, in station 4, from 1.32- 2.65 ppm. The concentration of total nitrogen varied from 1.9- 3.59 ppm in station 5, 1.5- 2.6 in station 6 and from 1.95- 2.64 ppm in station 7. There was a significant variation in Total nitrogen concentration in surface water in the different seasons studied ($p < 0.05$) (Appendix 1, Table, 7)

but such a significant variation was not observed for nitrite nitrogen (Appendix 1, Table 5). Relatively high value of nutrients in the study area indicated the prevailing unhealthy water quality of the area.

Environmental conditions in most tropical coastal areas are governed by marked seasonal changes induced by the monsoonal cycles, rain fall, wind, fresh water inflow and introduction of new physical, chemical and biological changes. The study of the hydrography of the coastal waters of Cochin shows that prevailing southwest and northeast monsoons considerably influences the chemical and physical factors. The increased dependency of agriculture on chemical fertilizers and pesticides in the catchment areas of rivers and estuaries and increased population pressure and fast urbanization give rise to the heavy sewage effluents are the possible anthropologic factors leading to high concentration of nutrients in the area studied.

Table 4.1 Physico chemical parameters recorded at the study area during the cruises of FORV Sagar Sampada.

Cruise	Area	Temperature(°C)	Salinity(‰)	D.O(ml/l)	pH	P(ppm)	NO_2 –N(ppm)
181	Surface	24-26.73	35.57-35.98	3.28-4.89	8.07-8.18	ND-0.034	ND-0.001
	Bottom	23-24.8	35.52-36.01	3.76-2.3	8.09-8.11	0.015-0.038	ND-0.002
184	Surface	28.3-28.96	33.4-34.52	3.13-4.8	8.11-8.56	ND-0.072	ND-0.089
191	Surface	28.22-28.77	33.03-34.25	2.011-4.16	8.05-8.76	0.01-0.034	ND-0.03
	Bottom	14.55-27.96	33.86-35.23	0.122-3.8	8.04-8.55	0.01-0.036	ND-0.08
197	Surface	27-28.5	33.45-34.38	2.7-4.5	8.11-8.9	0-0.001	ND-0.021
	Bottom	15.25-22.33	34.5-34.95	0.21-2.4	8.31-8.87	0.003-0.005	ND-0.032
204	Surface	26-27.8	34.8-35.6	2.5-4.5	8.9-8.97	0.019-0.034	0.02-0.034
	Bottom	23-24.5	33.5-34.78	0.5-3.25	7.97-8.76	ND-0.05	ND-0.052

Table 4.2 Physico chemical parameters of surface water from stations in off Cochin area during postmonsoon season (2000)

Stn.	D.O(ml/l)	Salinity(‰)	PH	NO_2-N(ppm)	P(ppm)	S.W.T(° C)	Total N ppm
1	5.8	30.99	8.17	0.02	0.07	26.5	1.55
2	6.5	29.14	8.23	0.03	0.06	26.3	1.99
3	5.9	32.79	8.15	0.03	0.08	27	1.77
4	6	32.94	8.15	0.035	0.1	26	1.32
5	6.86	33.12	8.27	0.025	0.03	26	2.44
6	6.33	34.29	8.26	0.024	0.09	26.5	1.98
7	6	32.52	8.17	0.05	0.05	26.5	1.98

Table 4.3 Physico chemical parameters of surface water from stations in the off Cochin area during pre monsoon season 2001

Stn.	D.O(ml/l)	Salinity(‰)	PH	NO2-N(ppm)	P(ppm)	S.W.T(° C)	Total N ppm
1	6.8	33.52	8.28	0.036	0.16	28.75	1.99
2	7.1	33.75	8.3	0.03	0.17	28.88	3.32
3	6.95	33.60	8.29	0.02	0.15	29.13	1.98
4	7.55	33.51	8.29	0.02	0.14	29.38	2.65
5	7.15	34.04	8.31	ND	0.15	29.38	3.32
6	6.95	34.05	8.31	0.014	0.13	29.5	2.65
7	7.6	33.46	8.32	0.016	0.17	29.5	1.98

Table 4.4 Physico chemical parameters of surface water from stations in the off Cochin area during monsoon season in the year 2001

Stn.	D.O(ml/l)	Salinity(‰)	pH	NO_2-N(ppm)	P(ppm)	S.W.T(° C)	Total N ppm
1	3.5	30.99	8.01	0.01	0.22	25.5	2.27
2	5.3	26.61	8.11	0.05	0.175	26	2.44
3	4.9	21.86	7.91	ND	0.2	26.5	1.61
4	6	32.16	8.11	ND	0.215	25.5	2.43
5	7	30.35	8.19	ND	0.17	26.5	3.59
6	6.5	30.08	8.13	0.01	0.14	26	2.91
7	5.7	27.11	8.07	0.01	0.16	26	2.61

Table 4.5 Physico chemical parameters of surface water from stations in the off Cochin area during postmonsoon season in the year 2001

Stn.	DO(ml/l)	Salinity(‰)	pH	NO_2-N(ppm)	P(ppm)	S.W.T(° C)	Total N (ppm)
1	7.2	30.37	8.31	ND	0.27	26.7	2.42
2	7.06	31.92	8.28	0.03	0.31	28.8	1.95
3	7.53	32.52	8.29	ND	0.28	27	2.65
4	7.93	32.28	8.3	0.11	0.2	26.5	1.54
5	6.93	31.61	8.3	0.02	0.3	26	1.99
6	7.6	31.37	8.32	0.01	0.29	27	2.20
7	7.8	32.1	8.33	0.03	0.24	27	2.41

Table 4.6 Physico chemical parameters of surface water from stations in the off Cochin area during premonsoon season in the year 2002

Stn.	DO(ml/l)	Salinity(‰)	pH	NO_2-N(ppm)	P(ppm)	S.W.T(° C)	Total N (ppm)
1	6.06	33.3	8.26	ND	0.18	26.5	3.17
2	6.33	29.9	8.28	0.006	0.04	26.83	2.30
3	5.8	33.06	8.22	0.023	0.01	26.83	1.96
4	6.2	33.24	8.25	ND	0.50	27.66	2.20
5	6.66	33.01	8.33	0.02	0.28	27	2.20
6	7.2	32.08	8.33	ND	0.13	27	2.04
7	6.06	31.82	8.19	ND	0.19	27	2.64

Table 4.7 Physico chemical parameters of surface water from stations in the off Cochin area during monsoon season in the year 2002

Stn.	DO	pH	Salinity(‰)	P(ppm)	NO_2-N(ppm)	Total N (ppm)	S.W.T(° C)
1	6.8	8.2	33.42	0.25	ND	2.9	27.5
2	6.2	8.3	26.2	0.08	ND	2.01	28
3	7.2	8.23	34.33	0.02	0.05	2.01	28
4	7.4	8.1	33.96	0.8	ND	1.98	29
5	5.2	8.3	32	0.38	0.03	1.9	28
6	7	8.3	33	0.2	ND	1.5	28
7	7.6	8.2	32.4	0.3	ND	1.98	28

Table 4.8 Physico chemical parameters of surface water from stations in the off Cochin area during postmonsoon season in the year 2002

Stn.	DO (ml/l)	pH	Salinity ‰	P(ppm)	NO_2-N(ppm)	Total N (ppm)	S.W.T(° C)
1	7.2	8.22	30.71	0.19	ND	1.32	28
2	7.4	8.25	31.98	0.23	ND	1.9	28
3	6	8.23	33.96	0.28	ND	3.31	28
4	7.2	8.26	32.88	0.15	ND	1.32	30
5	7.2	8.23	33.42	0.34	0.03	2.65	29
6	7.2	8.25	32.7	0.26	0.05	1.32	29
7	6.4	8.29	33.6	0.23	ND	1.95	29.5

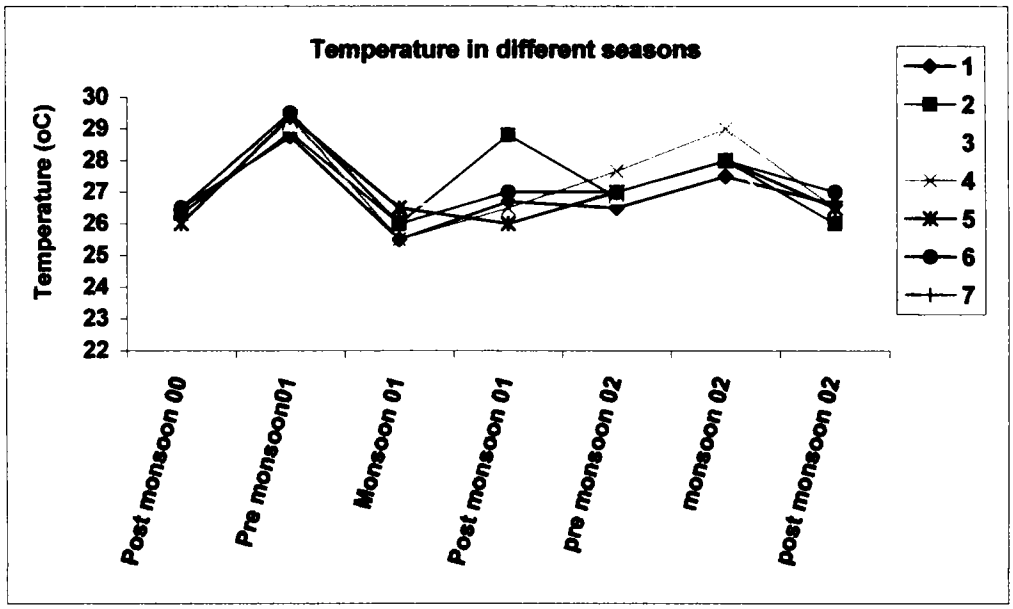


Fig. 4.1 Seasonal variations of Sea Water Temperature at the study area (7 stations) during 2000-02

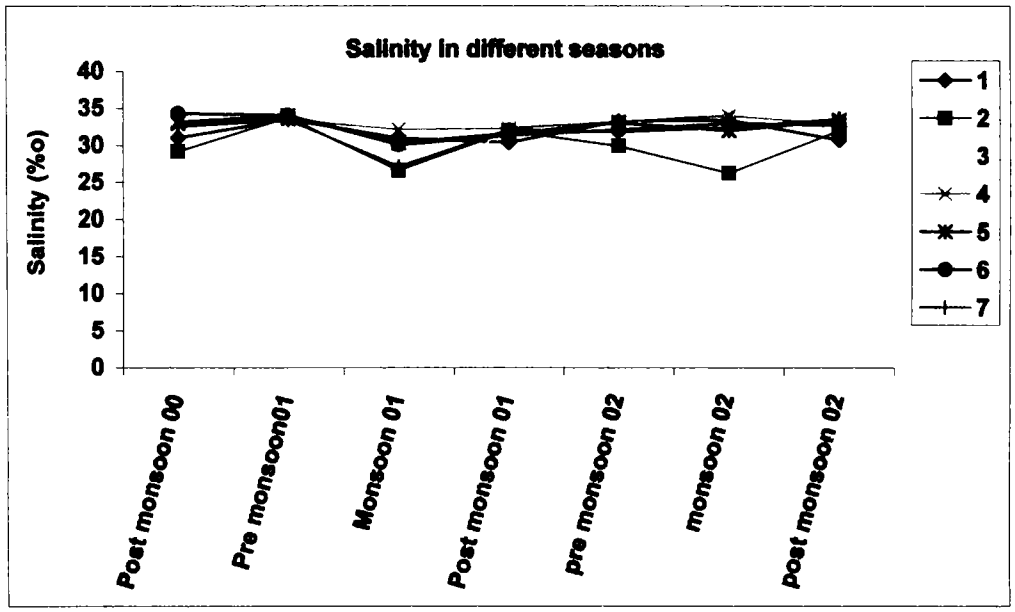


Fig. 4.2 Seasonal variations of salinity at the study area (7 stations) during 2000-02

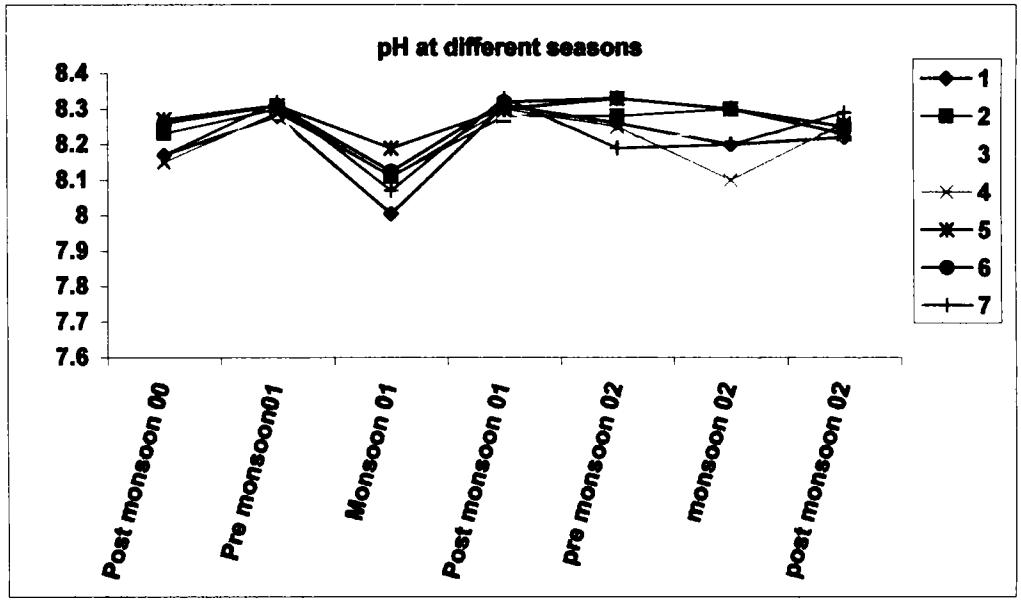


Fig. 4.3 Seasonal variations of pH in sea water at the study area (7 stations) during 2000-02

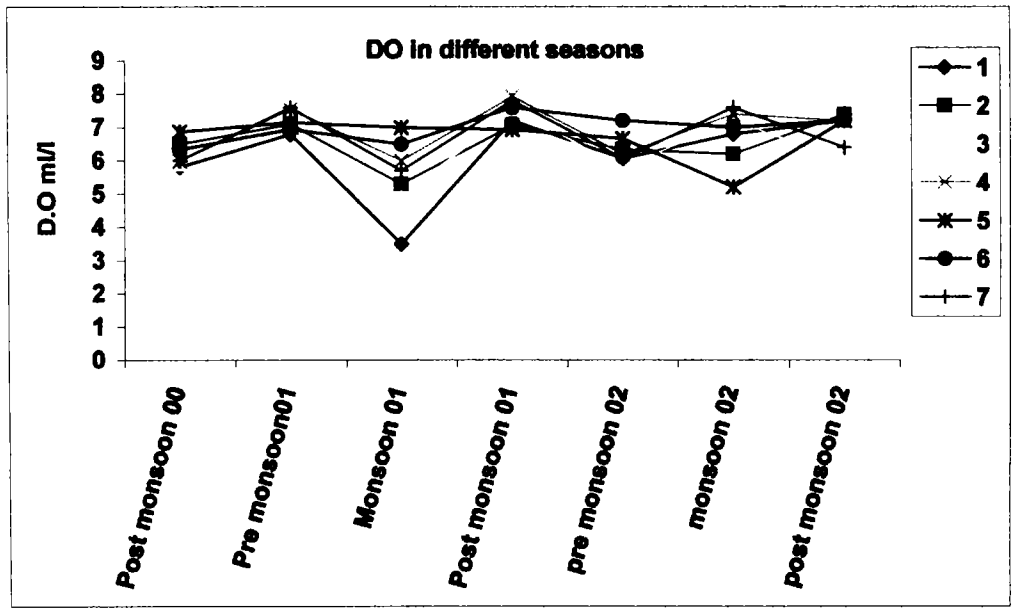


Fig. 4.4 Seasonal variations of D.O.in sea water at the study area (7 stations) during 2000-02

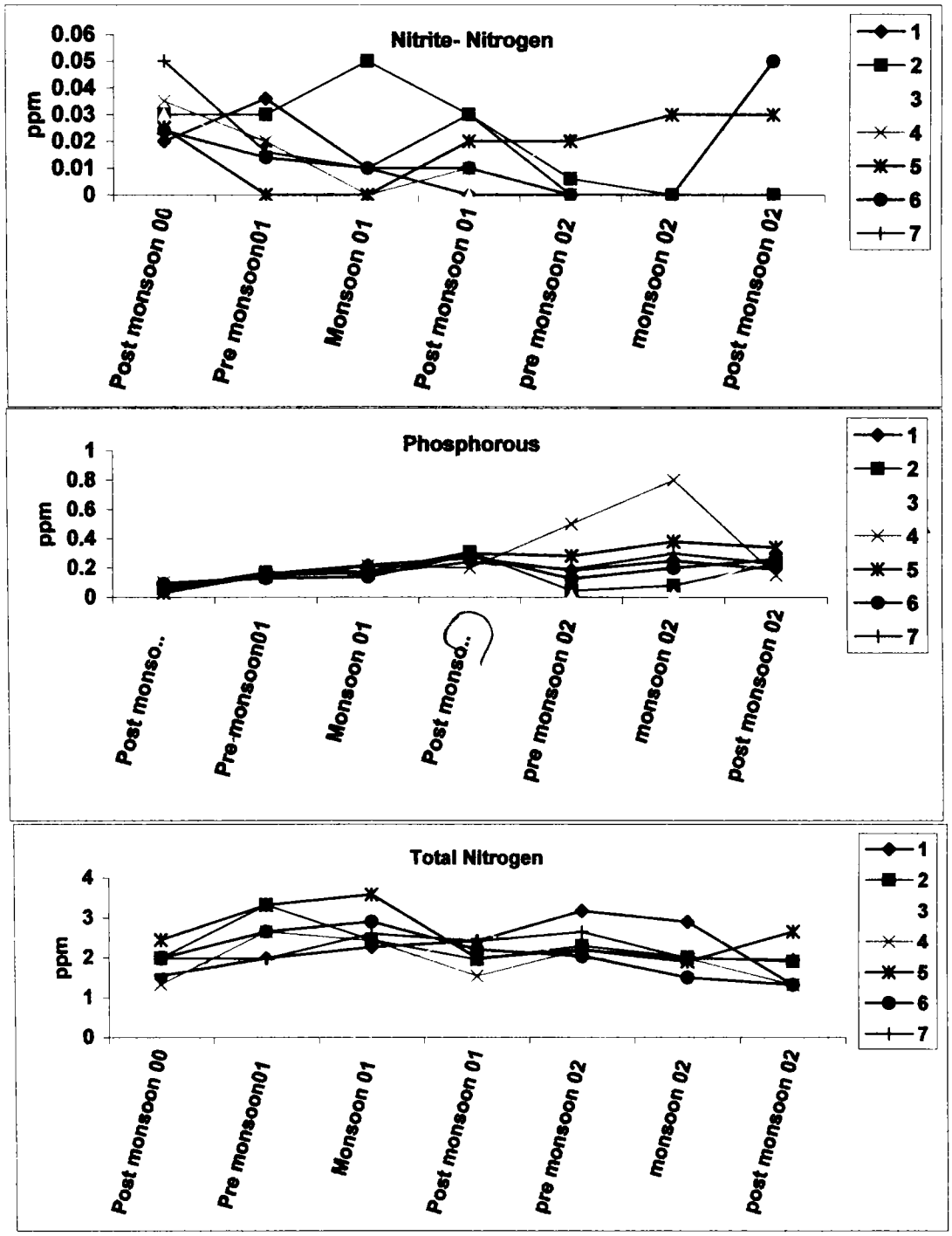


Fig. 4.5 Seasonal variations of nutrients in the sea water at the study area (7 stations) during 2000-02

Appendix I

Table1 Results of two way ANOVA on seawater temperature (off Cochin) in different seasons

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	0.634281	5	0.126856	0.35277	0.875567	2.602988
Columns	43.58221	5	8.716443	24.23927	7.65E-09	2.602988
Error	8.990003	25	0.3596			
Total	53.2065	35				

Table 2 Results of two way ANOVA on salinity (off Cochin) in different seasons

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	24.21832	6	4.036386	1.018504	0.444555	2.661302
Columns	103.4476	3	34.48254	8.700999	0.00088	3.159911
Error	71.33498	18	3.963055			
Total	199.0009	27				

Table 3 Results of two way ANOVA on pH of water (off Cochin) in different seasons

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	0.032536	6	0.005423	2.527279	0.059367	2.661302
Columns	0.24741	3	0.08247	38.43615	4.93E-08	3.159911
Error	0.038621	18	0.002146			
Total	0.318567	27				

Appendix I con...

Table 4 Results of two way ANOVA on dissolved oxygen (off Cochin) in different seasons

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	4.006971	6	0.667829	1.934124	0.129933	2.661302
Columns	15.79803	3	5.26601	15.2511	3.47E-05	3.159911
Error	6.215171	18	0.345287			
Total	26.02017	27				

Table 5 Results of two way ANOVA on nitrite nitrogen in water (off Cochin) in different seasons

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	0.003401	6	0.000567	1.192204	0.354302	2.661302
Columns	0.001638	3	0.000546	1.148317	0.356589	3.159911
Error	0.008559	18	0.000476			
Total	0.013599	27				

Table 6 Results of two way ANOVA on phosphorus in water (off Cochin) in different seasons

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	0.00238	6	0.000397	0.431718	0.84816	2.661302
Columns	0.145171	3	0.04839	52.65853	4.12E-09	3.159911
Error	0.016541	18	0.000919			
Total	0.164093	27				

Table 7 Results of two way ANOVA on total nitrogen in water (off Cochin) in different seasons

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	2.261862	6	0.376977	1.837372	0.148066	2.661302
Columns	2.345955	3	0.781985	3.811366	0.028215	3.159911
Error	3.693094	18	0.205172			
Total	8.300911	27				

Chapter 5

POLYCYCLIC AROMATIC HYDROCARBONS IN SEAWATER AND SEDIMENTS

5.1 Introduction

Every year 230000 tonnes of Polycyclic Aromatic Hydrocarbons reach the marine environment and these compounds are ubiquitously distributed world wide (Law, 1986). The investigation of these compounds is of great scientific interest, since several of them show high carcinogenic and mutagenic activity (Liptou and Saliot, 1991). The major source of PAH in the environment is atmospheric deposition based on pyrolysis of fossil fuels. Combustion derived PAHs are mainly transported to the sea by two routes, via the atmosphere and rivers (Lipitou and Albaiges, 1994). Other sources are domestic and industrial wastewater, continental run-off and spillage of petroleum and petroleum products by ships. The solubility of PAHs in water is low and decreases with increasing molecular weight. Due to their hydrophobic nature, the concentrations of dissolved PAHs in water is low and they are easily associated with particulate matter and finally deposited in sediments. Microbial degradation, photo oxidation and chemical oxidation are thought to be the major processes contributing to the decomposition of PAHs (Lee and Ryan, 1983). A major part of the world's total crude oil is shipped along the oil tanker routes across the Indian Ocean. Of the world's total crude oil and its products that amounts to 20000 metric tones annually, a major part is transported by the sea route. The Arabian Sea is a major oil tankers route to south east Asia and beyond, probably accounting for the tar like residues deposited on the west coast of India. More over a large number of rivers empty into the Arabian Sea.

Hence, establishing a base line concentration of these compounds in the Arabian Sea is of great significance.

PAH levels in the world oceans have been reported by several workers (Witt, 1995; Law *et al.*, 1997; Law *et al.*, 2002; Woodhead *et al.*, 1999; Licia Guzzella *et al.*, 1994).

At present, only a few facts are available on the contamination of the Indian seas with PAHs. Most of the works are limited to specific areas in the Indian Ocean and are dealing with contamination of the Seas with Petroleum Hydrocarbons (PHC) (Sengupta *et al.*, 1978; Fondekar *et al.*, 1980; Sengupta *et al.*, 1980; Fondekar *et al.*, 1984; Topgi *et al.*, 1982; Ingole *et al.*, 1989; Sengupta *et al.*, 1993; Ingole 1995; Chouksey, 2002; Mithlesh *et al.*, 2004). Variation of PAHs in sediments of shrimp farms of Cochin were studied by Ashraf *et al.* (2003). The present study reports the findings of a comprehensive study conducted to assess the extent of PAH contamination in water, sediments and biota of the marine environment of the west coast of India. As mentioned earlier, PAH is a major pollutant along the Arabian Sea coast which has great public health significance, also on account of the mutagenic and carcinogenic properties of some of them. Though pollution by pesticides and heavy metals have been studied rather extensively, data on PAH pollution along the Indian west coast is scanty. This is perhaps the first of such a comprehensive study taking the entire west coast.

5.2 Materials and Methods

The chemical structure of the studied PAHs are given in Annexure 1. The methods of collection of samples, sample preparation and determination of PAH levels in them by High Performance Liquid Chromatography and procedure adopted are described in detail in chapter 2. Statistical analysis was carried out using two way ANOVA to determine the significant variations if any between different stations and different seasons. Correlation analysis was also carried out for comparing the levels of the PAHs in various trophic levels.

5.3 Results and discussion

5.3.1 PAH in sea water from Off Gujarat (Pre monsoon)

Concentration of individual PAHs in water samples is given in Table 5.1. All the 15 PAHs studied were undetectable in water samples from certain stations. The sum of the concentrations of all the PAH components (ΣPAH) in present study ranged from ND- 8.966 ng/l in surface water and from ND-11.50 ng/l in bottom water. Two and three ring aromatics like naphthalene, acenaphthylene and phenathrene predominated in all the samples where as the six-ring component benzo (a) pyrene was present in water samples in minor quantities, below 1 ng/l. The concentration of naphthalene in surface water ranged from non-detectable level to 6.62 ng/l and the highest was observed in station 5 followed by station 1. Naphthalene concentration in the bottom water ranged from non-detectable level to 7.50 ng/ l. The range of acenaphthylene in

surface water was nondetectable- 3.0 ng/l and in surface water the range was nondetectable to 3 ng/l in bottom water. Benzo (a) pyrene in the surface water ranged from nondetectable level to 0.50 ng/l and in bottom from non-detectable level to 0.17 ng/l. Bottom waters showed compararatively higher concentration of PAHs than in surface water. Statistical analysis of correlation was carried out between the concentration in surface and bottom water and a strong positive correlation was obtained for the surface water concentration and bottom water concentrations (r = 0.68).

Two and three ring aromatics like naphthalene, acenaphthylene and phenathrene predominated whereas the concentration of the higher molecular weight compounds remained below 0.6 ng/l. Concentration of PAH was higher in seawater near sea floor than in surface water. The elevated concentrations in the bottom water may be attributed to the contribution of resuspended sediment particles.

5.3.2 PAH in sediment from Off Gujarat (Pre monsoon)

The sediment type, organic carbon content and ΣPAH concentration are given in Table 5.2. The pattern of distribution of individual PAH components in the sediment are given in Table 5.3. The sediment characteristics showed that in most of the stations it was silty clay and some were sandier in nature. The samples contained high amount of organic carbon. The concentration of ΣPAH in the different sediments showed wide variations, depending on the kind of sediment. In the sediments, higher molecular weight and more hydrophobic

PAHs were present in higher levels (Table 5.3). Naphthalene in stations ranged from 2.65 ng/g to 70.3 ng/g. Acenaphthylene ranged between 199- 603 ng/g. Concentration of fluorene ranged from non-detectable levels to 193 ng/g indicating that among the low molecular weight components, this compound generally occurs in low concentration. Among the two and three ring aromatics, acenaphthylene showed higher levels. Among the four and five ring components, chrysene was present in higher levels. Its concentration ranged from non-detectable to 812 ng/l. Benzo (a) pyrene in the sediment samples ranged from non-detectable level to 25 ng/g. The total PAH in the sediment ranged from 315 ng/g to 1323 ng/g.

The sum of the lower molecular weight two and three ring aromatics occurred in concentrations between 203- 967 ng/g. Statistical analysis of correlation was carried out to investigate the relationship between the concentrations of PAH and the percentage of organic carbon. But a significant correlation was not obtained. The concentration of total PAHs was comparatively lower in the sandy stations. The higher values of total PAHs were seen in station 1 and 2. This could be a result of continuous deposition of PAHs derived from urban run-off and the riverine input via the river Narmada. Pollution of the Narmada river begins downstream of Bharuch where it is joined by its tributary, Amlakhadi. This tributary carries effluents from Ankleshwar, Jhagadia and Panoli industrial estates, the constituent units of which have high pollution potential. A survey done in the five districts of Gujarat, namely,

Valsad, Surat, Bharuch, Vadodara and Ahmedabad by the Central Pollution Control Board (CPCB) in 1996 had identified 1349 units generating and disposing off heavy metals, toxic organic compounds, oils and emulsions, spent chemicals and incineration ash on land.

The PAH contents in the investigated surface sediments were higher by a factor 10^5 to 10^6 than the concentrations of PAHs in the overlying water column.

5.3.3 PAH in sea water from off Quilon to off Gujarat, Cruise No. 184 (Pre – monsoon season)

Concentration of PAH in water samples is given in table 5. 4. Total PAH (ΣPAH) in water samples in present study ranged from 2.66- 32.43 ng/l in surface. Two and three ring aromatics like naphthalene, phenathrene, anthracene, fluorene and fluoranthene predominated in all the samples whereas the four ring compound pyrene, the five ring compound chrysene and six ring component benzo (a) pyrene were present in water samples in minor quantities, below 1 ng/l. The concentration of naphthalene in surface water ranged from 0.26-19.83 ng /l and the highest was observed in station 7 followed by station 2. The range of anthracene was 0.026- 2.5 ng/l in surface. Level of phenanthrene ranged from nd- 4.5 ng/l, fluorene from ND – 9.6 ng/l, fluoranthene from ND to 0.86 ng/l. Benzo (a) pyrene in the surface water ranged from nondetectable level to 0.05 ng/l.

Two and three ring aromatics like naphthalene; anthracene, fluorene, fluoranthene and phenathrene predominated whereas the concentration of the higher molecular weight compounds remained below 0.1 ng/l.

5.3.4 PAH in sediment from off Quilon to off Gujarat, Cruise No. 184 (Monsoon season)

The sediment type and organic carbon content of the sediment are given in Table 5.5. The pattern of distribution of individual PAH components are given in Table 5.6.

The sediment characteristics showed that in most of the stations it was silty clay and others were sandier in nature. Organic carbon content of the fine sediment fractions was higher. The concentration of ΣPAH in the different sediments showed wide variations, depending on the kind of sediment. In the sediments higher molecular weight and more lipophilic and hydrophobic PAH predominated. Among the two and three ring compounds acenaphthylene and naphthalene predominated. Naphthalene in stations ranged from Non-detectable level to 140 ng/g. Acenaphthylene ranged between Non-detectable level- 871 ng/g. Concentration of fluorene ranged from non-detectable levels to 690 ng/g. Benzo (a) pyrene in the sediment samples ranged from non-detectable level to 10ng/g. The total PAH in the sediment ranged from 423 ng/g to 1542ng/g.

The sum of the lower molecular weight two and three ring aromatics occurred in concentrations between 225- 937 ng/g. Statistical analysis of correlation was carried out to investigate the relationship between the concentrations of PAH and the percentage of organic carbon. A significant correlation was obtained (r=0.640). According to several authors (Lee *et al.*, 1978; Neff, 1979) PAHs in sediment are associated with the organic matter. Here in this study a linear relationship was obtained for the percentage of organic carbon and concentration of PAH in sediments. This suggests that high amounts of PAH occur in sediments with a high Total Organic Carbon (Evans *et al.*, 1990). The concentration of total PAHs was comparatively lower in the stations, which were sandier. The higher values of total PAHs were seen in station 3, which is near to Mangalore and in station 4, which is off Mumbai. This could be a result of continuous deposition of PAHs derived from urban run off and the riverine input and in the Mumbai region due to the influence of the Mumbai harbour activities. The PAH contents in the investigated surface sediments were higher by a factor 10 to 10 than the concentrations of PAHs in the overlying water column. In a recent study by Rockne *et al.* (2002) PAHs were preferentially associated with the lower density fractions in sediments containing detrital plant rather than soot carbon. PAHs associated with coal-derived fractions appeared to be bound very strongly and desorption rate is very slow. In contrast, desorption from the heavier clay/silt fraction is more which indicate a higher bioavailability and PAHs associated with this fraction

getting more easily degraded. The unavailable PAH fraction associated with coal-derived fraction in the sediments pose less environment risk than those associated with clay/silt fractions.

5.3.5 PAH in sea water from Quilon to Mangalore area, Cruise 191 (Monsoon)

The results of analysis of PAH in water from Quilon to Mangalore area in cruise 191 are given in Table 5.7. The sum of the concentration of all the PAH components (ΣPAH) in the present study ranged from 1-67 ng/l in surface water. In the bottom water the concentration ranged between 8- 69.5 ng/l. Two and three ring aromatics like naphthalene, phenanthrene, anthracene, fluorene and fluoranthene predominated in all the samples where as the four ring compound pyrene, the five ring compound chrysene and six ring component benzo (a) pyrene were present in water samples in minor quantities, below 1 ng/l. In surface water from station 1, dibenzo (a, h) anthracene was detected (28 ng/l). The concentration of naphthalene in surface water ranged from 0.47-26.52 ng /l and the highest was observed in station 1 followed by station 3. In bottom water the range in concentration of naphthalene was 2.7- 30.88 ng/l. The range of anthracene was 0.066-0.45 ng/l in surface and 0.1-0.7 ng/l in bottom water. Level of phenanthrene ranged from 0.25- 4.6 ng/l in surface water and from 0.88- 5.2 ng/l in bottom water, fluorene in surface water ranged from 0.05- 2.95 ng/l and in bottom water from, 0.09 – 2.7 ng/l. Fluoranthene in surface water ranged from ND to 1.77 ng/l. Benzo(a) pyrene in the surface

water ranged from nondetectable level to 0.05 ng/l. Benzo(b)fluoranthene in surface water ranged from 0.03- 0.05 ng/l

Two and three ring aromatics like naphthalene, anthracene, fluorene, fluoranthene and phenanthrene predominated whereas the concentration of the higher molecular weight compounds remained below 0.1 ng/l.

Stations 1, 2, 3 are in the south west coast of India between Quilon and Cochin and the depth of sampling stations ranged from (30-50 m). Stations 4, 5, 6 are away from shore and of greater depths (150-200 m). The sampling was done at the end of the monsoon season. The concentrations of PAHs in the near shore stations were higher compared to the far away stations. When the levels of PAHs in water in the monsoon season is compared with that of the other two seasons, the levels were found to be higher in the monsoon. This could be due to the increased river input of the domestic wastage and other pollutants during this period. The great turbulence caused due to the wave action in this season might have increased the dispersion of PAH components from the bottom sediments into the overlying water.

5.3.6 PAH in sediment from Quilon to Mangalore area, Cruise 191 (Monsoon)

The sediment characteristics (Table 5.8) showed that in stations 1,2 and 4 silt and clay were predominant while in stations 3, 5 and 6 the bottom was sandier. In stations where the bottom was more muddy, contained a high

amount of organic carbon. In the sediments the proportion of higher molecular weight, hydrophobic PAH was high (Table 5.9). Higher molecular weight compounds are more adsorbed on to sediments and are more persistant (Mackay *et al.*, 1992). Among the two and three ring compounds Naphthalene, phenanthrene and fluorene predominated. Naphthalene in stations ranged from 55 to 2121 ng/g. Acenaphtylene was not detected in any of the samples. Concentration of fluorene ranged from non-detectable levels to 90 ng/g. Benzo (a) pyrene in the sediment samples ranged from 10.22- 131 ng/g. By comparing the results of this study with the one reported for the Baltic Sea along the coastal area of Germany (Witt, 1995), it may be concluded that the concentrations of anthracene, fluorene, pyrene, Benzo (a) pyrene and chrysene in the sediment collected from Quilon to Mangalore area were very much closer to that from the Baltic Sea. The total PAH in the sediment ranged from 327 ng/g to 2763 ng/g.

The sum of the lower molecular weight two and three ring aromatics occurred in concentrations between 102- 2446 ng/g. Statistical analysis of correlation was carried out to investigate the relationship between the concentrations of PAH and the percentage of organic carbon. A significant correlation was obtained (r=0.94). Here in this study a linear relationship was obtained for the percentage of organic carbon and concentration of PAH in sediments. This suggests that high amounts of PAH occur in sediments with a high TOC (Evans *et al.*, 1990). The concentration of total PAHs was

comparatively lower in the sandy stations. The higher values were seen in stations of lower depths near to the shore. A significant positive correlation was obtained for the percentage of silt and clay with the concentration of total PAH in sediments (r=0.72).

5.3.7 PAH in sea water from off Cochin to Mangalore, Cruise No 197 (Pre – monsoon)

The total PAH in water (ΣPAH), in present study ranged from 2 – 24. 2 ng/l in surface water, (Table 5.10). Two and three ring aromatics like naphthalene, phenanthrene, anthracene, fluorene and fluoranthene predominated in all the samples where as the four ring compound pyrene, the five ring compound chrysene and six ring component Benzo (a) pyrene were present in water samples in minor quantities, below 1 ng/l. The concentration of naphthalene in surface water ranged from 1.3 – 16.4 ng /l and the highest was observed in station 4 followed by station 6. The range of anthracene was 0.05 – 0.22 ng/l in surface water. Level of phenanthrene ranged from 0.16 – 3.08 ng/l in surface water. Fluorene in surface water ranged from 0.09 – 3 ng/l. Fluoranthene in surface water ranged from non-detectable level to 1.26 ng/l. Benzo (a) pyrene in the surface water was nondetectable. Benzo (b) fluoranthene in surface water was 0.609 and was present in only one sample. Benzo (a) anthracene ranged from non-detectable level to 0.05 ng/l.

Two and three ring aromatics like naphthalene; anthracene, fluorene and phenanthrene predominated whereas the concentration of the higher molecular weight compounds remained below 0.1 ng/l. The concentrations of PAHs in the near shore stations were higher compared to the far away stations.

5.3.8 PAH in sediment from off Cochin to Mangalore (Pre monsoon).

The sediment characteristics showed that in most of the stations silt and clay were predominant while in stations 3 and 6 the bottom was sandier (Table 5.11). In stations where the bottom was more muddy, contained a high amount of organic carbon. Among the two and three ring compounds Naphthalene, phenanthrene, anthracene and fluorene predominated. Naphthalene in stations ranged from 299 to 4833 ng/g, (Table 5. 12). Acenaphthylene was not detected in any of the samples. Concentration of fluorene ranged from non-detectable levels to 248 ng/g. Benzo (a) pyrene was non detectable in the samples. The total PAH in the sediment ranged from 490 ng/g to 6255 ng/g. The total PAH in sediments in this study period was found to be higher in sediments when compared with all other study periods. A possible explanation could be the increased atmospheric input of PAHs in this season (Jenson, 1983). These seasonal distribution patterns are more significant for the low molecular weight PAHs (two-three rings) due to their higher sensitivity to photo oxidation and microbial degradation, whereas the four to six ring compounds did not show significant differences due to their high persistence for microbial degradation (Witt, 1995). During this season, the planktonic growth and productivity gets

increased and a high amount of detrital material is produced that might effectively scavenge PAHs and transfer them to the sea floor. An algal bloom was observed in this study area during this period. This supports the above argument.

The sum of the lower molecular weight two and three ring aromatics occurred in concentrations between 487- 5738 ng/g. The sum of the concentrations of four- six ring compounds ranged from 2.5-516 ng/g. Statistical analysis of correlation was carried out to investigate the relationship between the concentrations of PAH and the percentage of organic carbon. A significant correlation was obtained (r= 0.96). Here in this study a linear relationship was obtained for the percentage of organic carbon and concentration of PAH in sediments. This suggests that high amounts of PAH occur in sediments with a high Total Organic Carbon (Evans *et al.*, 1990). There is a significant positive correlation between silt and clay percentage to the total PAH in sediments (r=0.747). The concentration of total PAHs was comparatively lower in the sandy stations. The higher values were seen in stations of lower depths near to the shore.

5.3.9 PAH in sea water from off Quilon to Mangalore area (post monsoon)

The sum of the concentration of all the PAH components (ΣPAH) in the present study ranged from 4-13 ng/l in surface water (Table 5. 13). In the bottom water, the concentration ranged between 9- 28 ng/l. Two and three ring aromatics like naphthalene, phenanthrene, anthracene and fluorene

predominated in all the samples where as the four ring compounds fluoranthene, pyrene, the five ring compound chrysene and six ring component benzo (a) pyrene, benzo(a)anthracene and benzo(b) fluoranthene were present in water samples in minor quantities, below 1 ng/l. The concentration of naphthalene in surface water ranged from 1-10.2 ng /l and the highest was observed in station 1 followed by station 6. In bottom water the range in concentration of naphthalene was 1.2- 22.5 ng/l. The range of anthracene was 0.066-0.45 ng/l in surface and 0.1-0.7 ng/l in bottom water. Level of phenanthrene ranged from 0.25- 4.6 ng/l in surface water and from 0.88- 5.2 ng/l in bottom water, fluorene in surface water ranged from 0.05- 2.95 ng/l and in bottom water from, 0.09 – 2.7 ng/l. Fluoranthene in surface water ranged from non detectable to 1.77 ng/l. Benzo(a) pyrene in the surface water ranged from nondetectable level to 0.05 ng/l. Benzo(b)fluoranthene in surface water ranged from 0.03- 0.05 ng/l. Two and three ring aromatics like naphthalene; anthracene, fluorene, fluoranthene and phenanthrene predominated whereas the concentration of the higher molecular weight compounds remained below 0.1 ng/l.

The sediment characteristics showed that most of the stations were sandier and in these stations percentage of organic carbon in the sediment was lower (Table 5. 14). Stations 1 and 2 were of greater depths (>200m). In the sediments, higher molecular weight and hydrophobic PAH predominated. Among the two and three ring compounds naphthalene, phenanthrene and

fluorene predominated. Naphthalene in stations ranged from 221- 1225 ng/g. Concentration of fluorene ranged from non-detectable levels to 179 ng/g. Benzo (a) pyrene in the sediment samples ranged from non-detectable level to 0.5 ng/g. The total PAH in the sediment ranged from 547 ng/g to 1618 ng/g (Table 5. 15).

Statistical analysis of correlation was carried out to investigate the relationship between the concentrations of PAH and the percentage of organic carbon. A significant correlation was obtained. In this present study a linear relationship was obtained for the percentage of organic carbon and concentration of PAH in sediments. According to Upal Ghosh *et al.* (2002) 62% of total PAH in sediments were associated with coal-derived particles and remaining 38% is associated with clay/silt fraction of the sediment. In the present study, the concentration of total PAHs was comparatively lower in the sandy stations. A significant positive correlation was obtained for the percentage of silt and clay with the concentration of total PAH in sediments.

5.4 PAH in the marine environment-Off-Cochin area

Concentration of PAH in water samples in various seasons of the studied year is given in Table 5.16. Two and three ring aromatics like naphthalene; fluorene, phenathrene and anthracene predominated in all the samples where as the five-ring component benzo (a) pyrene was present in water samples in minor quantities, below 0.1 ng/l. In some samples dibenzo (a, h) anthracene was also detected. During pre monsoon season the

concentration of total PAHs ranged from1.7 ng/l to 6.40 ng/l (Table 5. 16). During the monsoon season, the total PAHs in water ranged between 1 ng/l to 193 ng/l. In the post monsoon period, the range was from 0.7- 4.405 ng/l. The results from different seasons were compared (Fig. 5. 1). The concentration of PAHs in surface water in the monsoon season was higher than during the post monsoon and pre monsoon periods. But a significant variation was not observed for PAH concentration in water during the different seasons studied (Appendix II, Table 1). In monsoon season at stations 7 and 4, fairly high concentrations of PAHs were noted and in these samples acenaphtilene and naphthalene were the predominant components.

The sediment characteristics showed that in most of the stations percentage of silt and clay predominated for most part of the year and contained a high amount of organic carbon (Fig 5. 2- 5.5). There was a significant variation in the organic carbon content of the sediments in different seasons ($p< 0.01$) and the higher percentages were observed in the pre monsoon and post monsoon seasons (Appendix II, Table 2). The concentration of ΣPAH in the different sediments showed wide variations, depending on the kind of sediment. Naphthalene in stations ranged from non-detectable level to 10831 ng/g, (Table 5. 17). The highest concentration was observed in the pre monsoon period. Acenaphtilene ranged between 0- 347 ng/g. Concentration of fluorene ranged from non-detectable level to 393 ng/g. Among the two and three ring aromatics naphthalene, acenaphthene and

fluorene showed higher levels. Among the four and five ring components, benzo (a) anthracene and pyrene were present in higher levels. Their concentration ranged from non detectable- 116ng/g, and non-detectable level to 720 ng/g respectively. Benzo (a) pyrene in the sediment samples ranged from non-detectable level to 24.3 ng/g. The total PAH in the sediment ranged from 616 ng/g to 11453 ng/g. A significant variation in total PAH in all the stations studied was not obtained in different seasons studied; but comparatively higher values were obtained for the pre monsoon period, (Appendix II, Table 3). The variations in total PAH in different seasons studied are given in Fig. 5. 6.

The results of analysis showed that these stations located near to the shore (shallower), contained greater proportions of PAH components. In the sediment, high percentage of organic carbon were present (3.3- 8.5%). This might be a cause of the high concentration of PAHs in them. A significant positive correlation was observed for percentage of organic carbon and Total PAH in sediments in different stations (r= 0.85 in Stn 1, r= 0.87 in 2, r= 0.99 in station 3, r= 0.63 in station 4, r= 0.82 in station 5, r= 0.92 in station 6). The influence of the port of Cochin which is located near the confluence of the Vembanad lake with the Arabian sea is another factor that might attribute to this high concentration of organic compounds. Oil pollution in this area is common by operational discharges and bilge and bunker washings of tankers on their way to the Gulf ports for loading the cargo of oil. Vembanad Lake maintains connection with Arabian Sea through a narrow opening, 365 m broad between

the mainland of Cochin and the Vypeen Island. Several rivers originating from the Western Ghats empty into the Vembanad Lake. Of these, the Periyar River needs special mention because of the large number of chemical industries draining their wastes into the river.

This study documents a comprehensive analysis of PAHs in water and surficial sediments in the Arabian Sea. In the surficial sediments from the off shore locations in the Arabian Sea, the total PAH concentration ranged from 340 ng/g to 6255 ng/g dry weight. Similar values were reported from the sediments of the Baltic Sea (720- 1871ng/g) and also by Notar *et al.* (2001). Relative to other urbanized coastal areas world wide, the measured PAH content in the off shore sites in the Arabian sea sediments can be considered to low to moderately contaminated. The concentration of PAHs obtained for the near shore sediments from the off Cochin area was found to be higher than this (616 ng/g to 11453 ng/g). Woodhead *et al.* (1999) reported concentration similar to this in sediments around England and Wales. (Non-detectable - 102471 ng/g). Similar works from the Indian waters are scarce. Ingole *et al.* (1995) reported petroleum hydrocarbon concentrations ranging from 5.7- 7 µg/g in sediments along the Bombay coast. Compared to the concentrations in water, the contents of the sediments were higher by several orders. PAH group profile in the sediment showed the predominance of 2-3 ring PAH in all samples and proportion of higher molecular weight components in sediments were higher in sediments than in water. This suggests a petrogenic source of origin.

The dominant source of PAH appear to be combustion process through run off, industrial and sewage discharges, atmospheric input rather than by oil pollution. But the ratio of pyrollitic to petrogenic source might be continuously changed to the intense tanker traffic in the Arabian Sea. The lower values obtained for the monsoon months may be due to PAH values in water column of the Arabian Sea in the offshore stations are still low in ecotoxicological level. Witt (1995) obtained similar values for the Baltic Sea (3.85 ng/l- 14.1) and in the North Sea levels of PAH reported were, 0.63 ng/l- 3.51 ng/l. Fondekar *et al.* (1984) reported values ranging from non-detectable level to 41.6 µg/l for petroleum hydrocarbons in the Arabian Sea. Ingole *et al.* (1995) reported petroleum hydrocarbon concentrations in the range of ND - 18.5 µg/l along the Bombay coast. Fondekar *et al.* (1980) reported petroleum hydrocarbon concentrations ranging from 16.8-42.8 µg/l in Goa coastal waters.

Elevated levels of PAHs were found in the coastal water near Cochin area, indicating higher pollution due to industrial wastes. Even though a highly significant variation was not observed for concentration of PAH in water in different seasons of study, comparatively higher concentration was in the monsoon season. Long-term exposure to low concentrations of PAHs found in water samples can result in sublethal effects for aquatic organisms. Due to these toxicity risks it is necessary to monitor PAHs in the Indian waters.

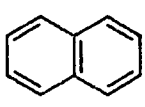
5.5 Ecotoxicological significance of PAH concentration in sediment

Elevated concentrations of PAH found in some locations in the near shore area can be acutely toxic to certain sediment dwellers and the levels in other locations might cause chronic effects including the induction of neoplastic liver disease in fish. Although they are exposed to sedimentary PAH via several routes, fish do not generally accumulate very high levels. Only very high concentrations can be lethal to fish (Roberts *et al.,* 1989 LC_{50} 81000-3220000 ng/g dry weight total PAH), but many carcinogenic and mutagenic intermediates such as diol epoxides are produced by cytochrome P450 while metabolising the PAHs (Vander OoSt *et al.,* 1994; Van Shooten *et al.,* 1995). Concentration of total PAH as low as 1000-3100ng/g dry weight are able to induce Cytochrome P450 enzyme in Winter flounder and Spout (Payne *et al.,* 1988; Van Veld *et al.,* 1990). Total PAH concentrations as low as 181 and as high as 41200 ng/g have been associated with carcinogenesis and liver neoplasia in brown bullhead catfish (Baumann *et al.*, 1995, Klamer and Fomsgaard, 1993). Relatively high concentrations of total PAH can be lethal to invertebrates also.

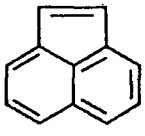
ANNEXURE - I

STRUCTURE OF POLY CYCLIC AROMATIC HYDROCARBONS STUDIED

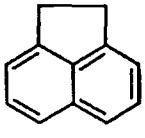
1. Naphthalene (Naph)



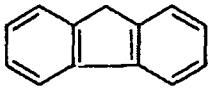
2. Acenaphtylene



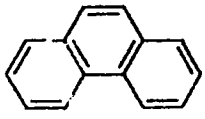
3. Acenaphthene (Ace)



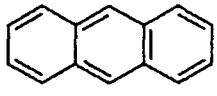
4. Fluorene (Fl)



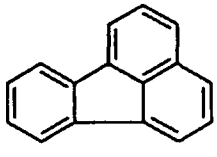
5. Phenanthrene (Phe)



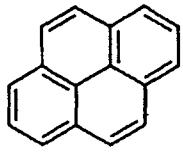
6. Anthracene (Ant)



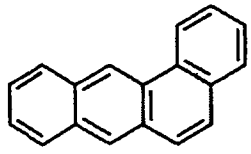
7. Fluoranthene (Flu)



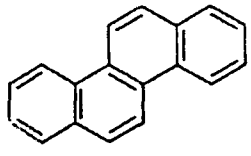
8. Pyrene (Pyr)



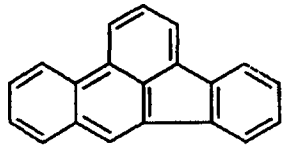
9. Benzo(*a*)anthracene (BaA)



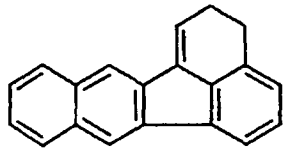
10. Chrysene (Chr)



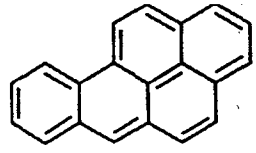
11. Benzo(*b*)fluoranthene (BbF)



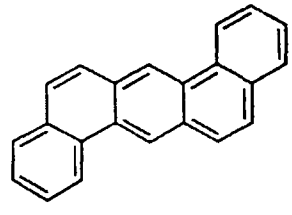
12. Benzo(*k*)fluoranthene (BkF)



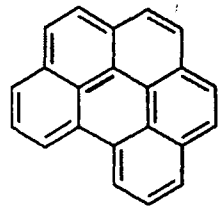
13. Benzo (a) pyrene (BaP)



14. Dibenzo(*a,h*)anthracene (DBA)



15. Benzo(*g,h,i*)perylene (BghP or BP)



16. Indeno(1,2,3-*c,d*)pyrene (InP)

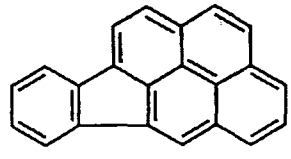


Table 5.1 Concentration of individual PAH (ng/l) in water collected during Cruise No.181

Stn. No	Area	Naphthalene	Acenaphthylene	Benzo(a)pyrene	Phenanthrene	ΣPAH
1	Surface	0.99	ND	0.19	ND	1.18
	Bottom	7.50	3.50	0.50	ND	11.50
2	Surface	ND	ND	ND	ND	ND
	Bottom	2.40	1.25	ND	ND	3.65
3	Surface	ND	ND	ND	ND	ND
	Bottom	ND	ND	ND	ND	ND
4	Surface	ND	ND	ND	0.10	0.10
	Bottom	2.01	0.05	ND	ND	2.06
5	Surface	ND	ND	ND	ND	ND
	Bottom	ND	ND	ND	ND	ND
6	Surface	5.80	3.00	0.17	ND	8.97
	Bottom	5.02	ND	ND	2.60	7.62

ND= Not detectable

Table 5.2 Sediment chatacteristics and concentration of total PAH (ng/g) from Cruise No.181

Stn. No	pH	Silt+clay %	Sand%	Organic Carbon %	ΣPAH
1	9.37	78	22	1.90	1040.1
2	9.56	75	25	2.40	1323.2
3	9.55	76	24	2.15	315.1
4	9.49	65	31	2.41	603.8
5	9.38	67	35	1.77	1129.1
6	9.56	77	23	2.40	842.9

Table 5.3 Concentration of individual PAH (ng/g) in sediment collected during Cruise No.181

Stn. No	Naphthalene ng/g	Acenaphthylene	Fluorene	Phenathrene	Chrysene	ΣPAH
1	2.65	225.39	ND	ND	812.03	1040.07
2	70.23	603.72	193.01	123.90	332.35	1323.21
3	8.75	248.65	ND	57.75	ND	315.15
4	6.90	179.89	ND	87.49	329.50	603.79
5	3.20	226.83	ND	88.55	810.51	1129.09
6	12.50	199.20	ND	65.04	566.15	842.89

ND= Not detectable

Table 5.4 Concentration of individual PAH (ng/l) in water collected during Cruise No.184

Stn No	Naphthalene	Phenantrene	Anthracene	Fluorene	Fluoranthene	Pyrene	Chrysene	Benzo (a) pyrene	Total PAH
1	4.976	0.69	0.026	ND	0.351	0.17	0.029	ND	6.242
2	12.02	2.411	0.11	2.706	0.87	0.788	0.048	0.047	19
3	1.78	4.85	0.3	0.85	0.86	0.99	0.056	0.04	9.72
4	0.267	1.1	0.39	0.5	0.63	0.05	0.022	0.01	2.96
5	0.45	0.98	0.29	0.402	0.466	0.02	0.06	ND	2.66
6	1.31	0.86	0.414	0.86	ND	0.08	ND	ND	3.52
7	19.83	ND	2.5	9.6	ND	0.5	ND	ND	32.43
8	11.1	ND	0.4	3.2	ND	0.8	ND	ND	15.5

ND= Not detectable

Table 5.5 Deatails of the sediment chatacteristics and total PAH (ng/g) from Cruise No.184

Stn. No	pH	Silt+clay %	Sand%	Organic Carbon %	ΣPAH
1	9.32	72	22%	0.5	423.1
2	9.17	77	25%	1.88	925.4
3	9.06	83	15%	2.853	1542.2
4	9.21	65	31%	2.14	1435.6
5	9.49	67	35%	1.34	690.6
6	9.16	70	25%	2.6	558.68

Table 5.6 Concentration of individual PAH (ng/g) in sediment collected during Cruise No.184

Stn. No	Naphthalene	Phenantrene	Anthracene	Fluorene	Acenaphthylene	Pyrene	Chrysene	Benzo(a)anthracene	Total PAH
1	140.00	ND	1.10	ND	282.00	ND	ND	ND	423.10
2	34.60	ND	ND	19.80	871.00	ND	ND	ND	925.40
3	44.00	139.80	ND	283.98	372.00	nd	420.87	281.50	1542.15
4	26.97	249.77	ND	377.00	284.00	0.01	286.77	211.06	1435.58
5	ND	ND	ND	690.60	ND	ND	ND	ND	690.60
6	ND	ND	ND	ND	225.88	ND	120.00	212.80	558.68

ND= Not detectable

Table 5.7 Concentration of individual PAH (ng/l) in water collected during Cruise No.191

Stn. No	Area	Naphthalene	Phenantrene	Anthracene	Fluorene	Fluoranthene	Pyrene	Chrysene	Benzo(a)pyrene	Benzo(a) anthracene	Benzo(b)fluoranthene	Didenz(a,h) anthracene	ΣPAH
1	Surface	26.520	4.659	0.459	2.950	1.770	2.24	ND	0.04	ND	ND	28.65	67.0
	Bottom	30.880	5.280	0.317	1.970	2.070	ND	ND	ND	0.964	ND	ND	43.0
2	Surface	2.330	0.890	0.066	0.060	Nd	0.41	ND	ND	0.048	0.047	ND	4.0
	Bottom	17.470	2.040	0.130	0.910	0.420	48	0.1	ND	0.48	ND	ND	69.5
3	Surface	15.050	2.250	0.380	0.850	ND	0.99	0.089	0.04	0.08	0.035	ND	20.0
	Bottom	24.760	4.340	0.420	2.700	1.660	2.09	1.07	ND	1.44	ND	ND	38.0
4	Surface	0.470	0.550	0.264	0.490	0.450	0.25	0.079	0.027	0.003	0.057	ND	5.0
	Bottom	12.500	1.200	0.400	1.400	1.900	2	0.21	0.05	ND	ND	ND	20.0
5	Surface	1.190	0.880	0.229	0.450	0.820	0.39	ND	ND	ND	ND	ND	4.0
	Bottom	10.500	1.100	0.500	1.200	1.300	0.5	0.07	0.02	ND	ND	ND	15.0
6	Surface	0.500	0.250	0.100	0.050	ND	ND	0.45	Nd	0.02	ND	ND	1.0
	Bottom	2.700	0.880	0.700	0.900	1.200	0.6	0.6	0.5	0.08	ND	ND	8.0

ND= Not detectable

Table 5.8 Deatails of the sediment chatacteristics and total PAH (ng/g) from Cruise No.191

Stn. No	pH	Silt+clay %	Sand%	Organic Carbon %	ΣPAH
1	9.1	72%	22%	1.28	2586
2	9.2	65.00%	35%	1.25	2624
3	9.01	51%	49%	0.62	342
4	9.2	60%	40%	1.2	2763
5	9	35%	65%	0.5	423
6	9	58%	42%	0.8	327

Table 5.9 Concentration of individual PAH (ng/g) in sediment collected during cruise no.191

Stn. No	Naphthalene	Phenantrene	Anthracene	Fluorene	Fluoranthene	Pyrene	Chrysene	Benzo(a)pyrene	Benzo(a)anthracene	Benzo(b)fluoranth	ΣPAH
1	1590.9	398.09	30.82	90.23	186.4	163.13	13.35	94.94	8.28	10.35	2586
2	2121.3	265.39	ND	60.15	ND	108.75	9	54.44	5.52	ND	2624
3	123.92	9.65	8.85	ND	26.67	ND	10.2	55	5.75	102	342
4	1832.9	247	28.6	94	100.2	88.8	12.52	131.57	4.4	223.35	2763
5	109.45	52.76	12.47	8.94	49.05	62.4	62.8	10.22	40.7	15	423
6	55	24.32	20.94	2.53	51.36	43.76	15.35	34.44	21.78	58.25	327

ND= Not detectable

Table 5.10 Concentration of individual PAH (ng/l) in water collected during Cruise No.197

Stn. No	Naphthalene	Phenantrene	Anthracene	Fluorene	Fluoranthene	Pyrene	Chrysene	Benzo(a) pyrene	Benzo(a) anthracene	Benzo(b)fluoranthene	ΣPAH
1	1.341	0.163	ND	0.095	ND	0.1044	ND	0.001	ND	ND	1.7
2	1.814	0.975	0.075	0.69	0.58	0.215	ND	0.002	0.057	ND	4.4
3	5.28	0.888	0.055	1.114	1.26	0.653	0.097	ND	0.053	ND	9.4
4	16.4	3.08	0.202	3	ND	0.922	0.028	ND	0.04	0.609	24.3
5	2.15	2.1	0.22	0.15	ND	ND	0.14	ND	ND	ND	4.76
6	6.7	1.3	0.13	0.55	0.22	ND	ND	ND	0.002	ND	8.9

ND= Not detectable

Table 5.11 Deatails of the sediment chatacteristics and total PAH (ng/g) from Cruise No.197

Stn. No	pH	Silt+clay %	Sand%	Organic Carbon %	ΣPAH
1	9.1	71	28%	1.5	2418
2	9.2	80	20%	2.7	6255
3	9.01	60	40%	0.8	490
4	9.2	75	25%	2.2	4808
5	9	65	35%	2.6	4532
6	9	58	42%	1	1518

Table 5.12 Concentration of individual PAH (ng/g) in sediment collected during Cruise No.197

Stn. No	Naphthalene	Phenantrene	Anthracene	Fluorene	Fluoranthene	Pyrene	Chrysene	Benzo(a)pyrene	Benzo(a) anthracene	Benzo(b)fluoranthene	ΣPAH
1	2066	ND	96.84	ND	249.36	5.8	ND	0.89	ND	ND	2418
2	4833	102	610	193.6	495.8	ND	20.6	ND	ND	ND	6255
3	299.78	22.5	165.4	ND	ND	2.5	ND	ND	ND	0.02	490
4	4082	221	46.2	180	265	12.5	ND	1	0.67	0.43	4808
5	3906	101	100.3	248.4	176.8	ND	ND	ND	ND	ND	4532
6	1030	55	55	215	150	2.8	10.3	ND	ND	ND	1518

ND= Not detectable

Table 5.13 Concentration of individual PAH (ng/l) in water collected during Cruise No.204

Stn. No	Area	Naphtalene	Phenanthrene	Anthracene	Fluorene	Fluoranthene	Pyrene	Chrysene	Benzo(a)pyrene	Benzo(a) anthracen	Benzo(b)fluoranthen	ΣPAH
1	Surface	10.2	1.2	ND	1.2	ND	ND	0.088	0.02	ND	ND	13
	Bottom	22.5	2	0.9	1	0.78	0.3	0.1	0.03	0.1	0.2	28
2	Surface	2.2	0.2	0.1	2.5	ND	ND	ND	ND	0.1	ND	5
	Bottom	7.8	0.3	0.23	5.2	0.2	0.14	0.11	0.01	0.25	0.3	15
3	Surface	1.1	ND	0.3	1.6	1.1	0.2	0.04	ND	0.15	ND	4.5
	Bottom	2.1	0.5	0.12	2.2	2.3	0.5	0.56	0.01	0.2	0.6	9
4	Surface	1	ND	ND	2	3.2	0.32	0.02	0.03	ND	0.21	7
	Bottom	1.2	0.32	0.23	2.2	6.2	0.65	0.1	0.2	0.12	0.25	11
5	Surface	2.1	1.3	ND	0.5	ND	ND	ND	0.02	0.1	ND	4
	Bottom	7.4	1.5	0.52	1.1	0.86	ND	0.2	0.05	0.8	0.32	13
6	Surface	3.5	0.5	ND	0.2	0.6	ND	0.05	ND	ND	ND	5
	Bottom	4.2	0.6	ND	0.32	0.76	0.21	0.2	0.2	0.54	0.26	13

Table 5.14 Deatails of the sediment chatacteristics and total PAH (ng/g) from Cruise No.204

Stn. No	pH	Silt+clay %	Sand%	Organic Carbon	ΣPAH
1	9.1	63	37	1.1	1618
2	9.2	70	30	1.5	1176
3	9.01	62	38	0.8	1042
4	9.2	58	42	0.5	547
5	9	70	30	1.6	1475
6	9	62	38	1.1	839

Table 5.15 Concentration of individual PAH (ng/g) in sediment collected during Cruise No.204

Stn. No	Naphtalene	Phenantrene	Anthracene	Fluorene	Fluoranthene	Pyrene	Chrysene	Benzo(a)pyrene	Benzo(a) anthracene	Benzo(b)fluranthene	ΣPAH
1	1225	52	23	89	221	6.2	2.2	0.2	ND	0.02	1618
2	556	26.3	124	145	322.3	1	1.4	0.53	ND	ND	1176
3	740	65	230	ND	ND	3.2	3.4	ND	ND	0.01	1042
4	221	12.3	45	132	124	11	1.5	0.2	ND	0.05	547
5	1023	64	89	144	154	ND	0.8	ND	ND	ND	1475
6	451	32	12	179	164	1.1	ND	ND	ND	ND	839

ND= Not detectable

Table.5.16 Seasonal Variation of PAH in water (ng/l) from stations off Cochin

	Post Monsoon					
Stn.no	Naphthalene	Fluorene	Phenanthrene	Anthracene	Benzo(b)fluoranthene	Total PAH
1	2.74	0.341	0.06	0.16	ND	3.30
2	0.55	ND	ND	0.08	ND	0.63
3	1.83	ND	ND	0.11	ND	1.94
4	5.20	0.12	ND	0.20	ND	0.32
5	2.00	ND	ND	0.19	ND	0.19
6	1.00	ND	ND	0.17	ND	0.17
7	1.00	ND	ND	0.20	ND	1.20
	Pre Monsoon					
Stn.no	Naphthalene	Fluorene	Phenanthrene	Anthracene	enzo(a)pyren	Total PAH
1	1.20	0.17	0.5	0.12	0.01	2.00
2	2.85	0.12	ND	0.11	ND	3.07
3	4.50	0.31	0.2	0.05	0.01	5.07
4	6.35	ND	ND	0.06	ND	6.41
5	5.98	ND	ND	0.10	ND	6.08
6	2.01	0.06	ND	0.03	ND	2.10
7	3.60	0.10	ND	0.04	ND	3.74

	Monsoon								
	Naphthalene	Fluorene	Phenathrene	Anthracene	Pyrene	Acenaphthylene	Fluoranthene	Dibenz(a,h antracene)	Total PAH
1	2.10	0.5	0.06	0.245	ND	ND	ND	ND	2.90
2	1.00	ND	ND	ND	ND	ND	ND	ND	1.00
3	3.76	ND	ND	0.039	ND	ND	ND	ND	3.80
4	16.99	2.12	3.25	0.693	18.55	ND	26.58	0.06	68.24
5	1.10	ND	ND	ND	ND	ND	ND	ND	1.10
6	0.50	ND	ND	ND	ND	ND	ND	ND	0.50
7	19.82	1.528	1.08	6.61	1.10	160.25	2.74	0.02	193.95

Table.5.17 Seasonal Variation in PAH in sediment (ng/g) from stations off Cochin

Post monsoon

Stn. No	Naphthalene	Fluorene	Phenanthrene	Anthracene	Pyrene	Chrysene	Acenaphthylene	Fluoranthene	Acenaphthene	Benzo(a) anthracene	Total PAH
1	16	122.03	106.86	ND	100.05	193.29	347.07	ND	398.98	ND	2769.13
2	ND	102.84	295.00	76.90	32.30	ND	ND	ND	ND	ND	2275.68
3	ND	394.85	136.62	25.00	ND	1605.60	91.80	37.85	569.40	62	680.50
4	ND	ND	134.58	21.00	ND	2414.45	57.62	21.43	120.37	ND	1382.91
5	ND	530.65	131.89	15.25	720.18	2816.97	76.91	12.12	211.55	ND	1583.48
6	ND	101.00	746.00	15.06	60.16	2419.49	140.08	ND	ND	ND	2831.48
7	ND	57.63	220.80	11.00	180.00	1760.50	60.00	21.16	ND	ND	150.00

PreMonsoon

Stn. No	Naphthalene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Benzo(a) anthracene	Benzo(a) pyrene	Didenz(a, h)an	Benzo(ghi) perylene	Total PAH
1	8113.10	172.47	73.52	ND	143.63	47.81	24.30	61.37	ND	8636.20
2	12150.00	169.54	105.05	ND	161.98	116.62	ND	57.91	ND	12761.10
3	6720.28	73.635	173.27	27.49	98.38	16.79	1.15	24.31	87.35	7178.97
4	10831.77	134.35	197.87	17.46	117.84	104.85	ND	48.96	1	11453.59
5	4947.86	113.84	87.78	6.96	40.73	24.41	ND	15.29	101.97	5287.84
6	1264.32	102.21	65.50	ND	29.79	15.17	ND	10.10	89.69	1586.88
7	1359.11	72.08	262.89	ND	135.30	28.41	ND	12.23	67.61	1937.63

Monsoon

Stn. No	Naphthalene	Fluorene	Phenanthrene	Anthracene	Pyrene	Chrysene	Acenaphthylene	Fluranthene	Acenaphthene	Benzo(a)pyrene	Total PAH
1	2270	120	10	ND	ND	ND	ND	ND	ND	ND	2400
2	447	ND	9.5	ND	ND	ND	ND	ND	ND	ND	456.5
3	4050.53	217.55	251.06	42.86	ND	ND	ND	ND	ND	20.96	4582
4	727.54	172.4	34.59	10.26	ND	ND	ND	ND	ND	9.28	954
5	4125	215	30	25	ND	ND	ND	ND	ND	ND	4395
6	2829.54	159.14	128.59	ND	ND	ND	ND	ND	ND	ND	3117
7	520	120	10	ND	ND	ND	ND	ND	ND	ND	650

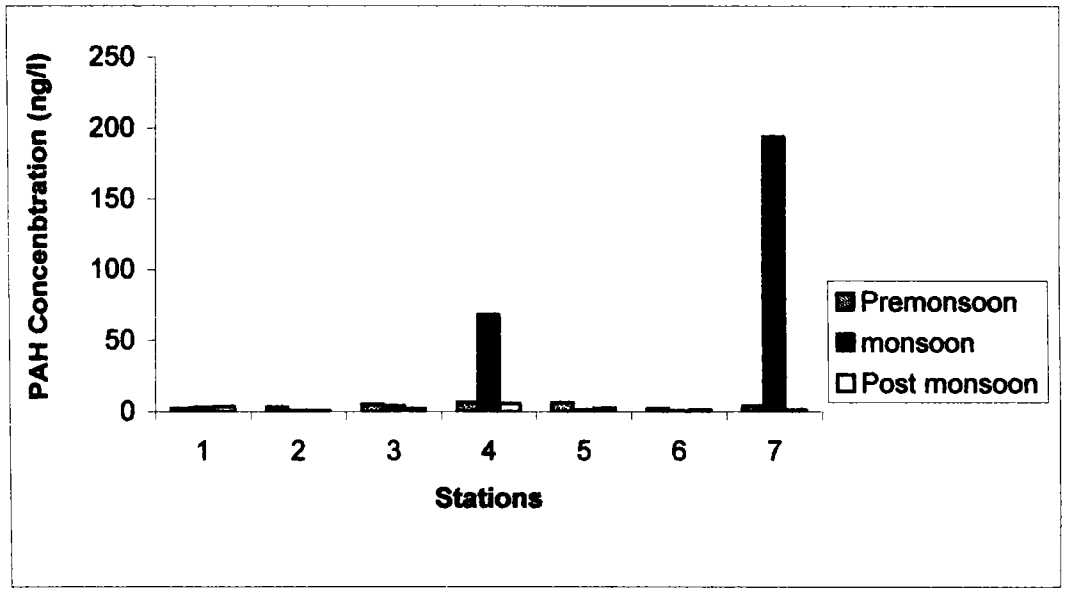


Fig.5.1 Seasonal changes in total PAH concentration in water from stations off Cochin

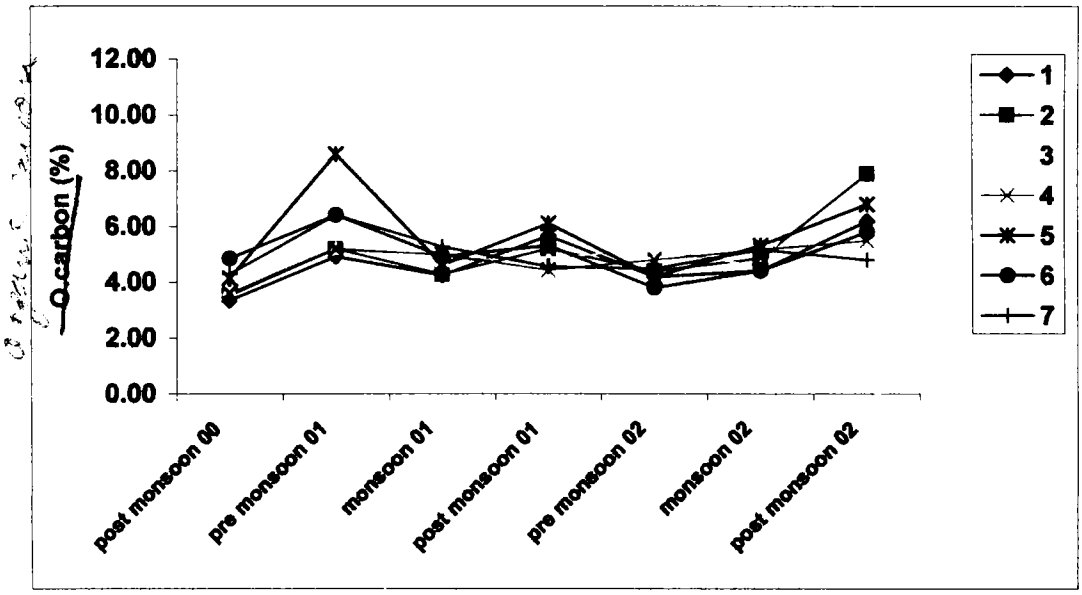


Fig. 5.2 Seasonal Variation in Organic Carbon in sediment from stations off Cochin

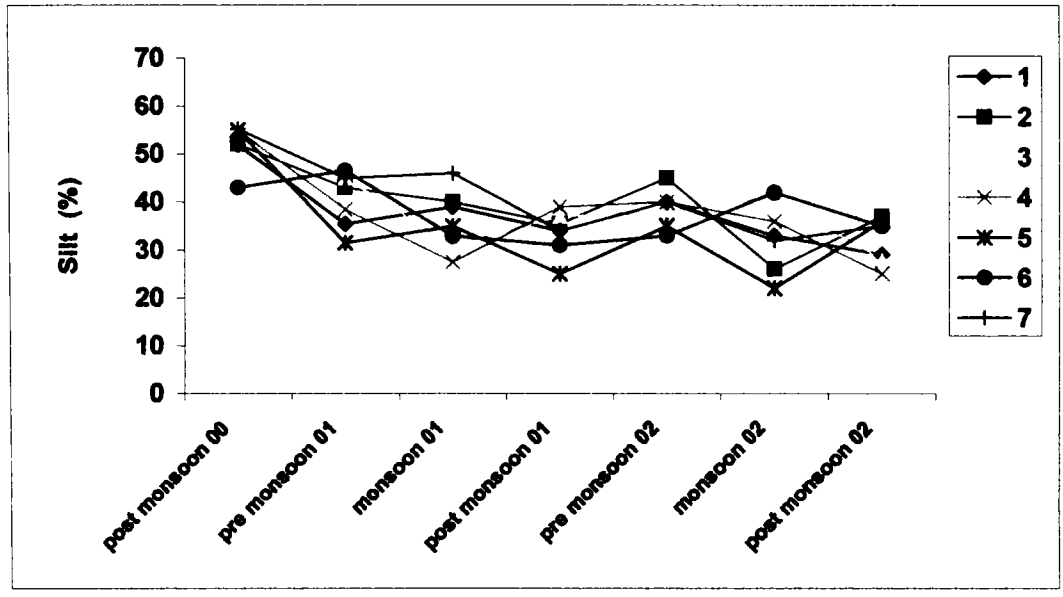


Fig.5.3 Seasonal Variation in percentage of silt in sediment from stations off Cochin

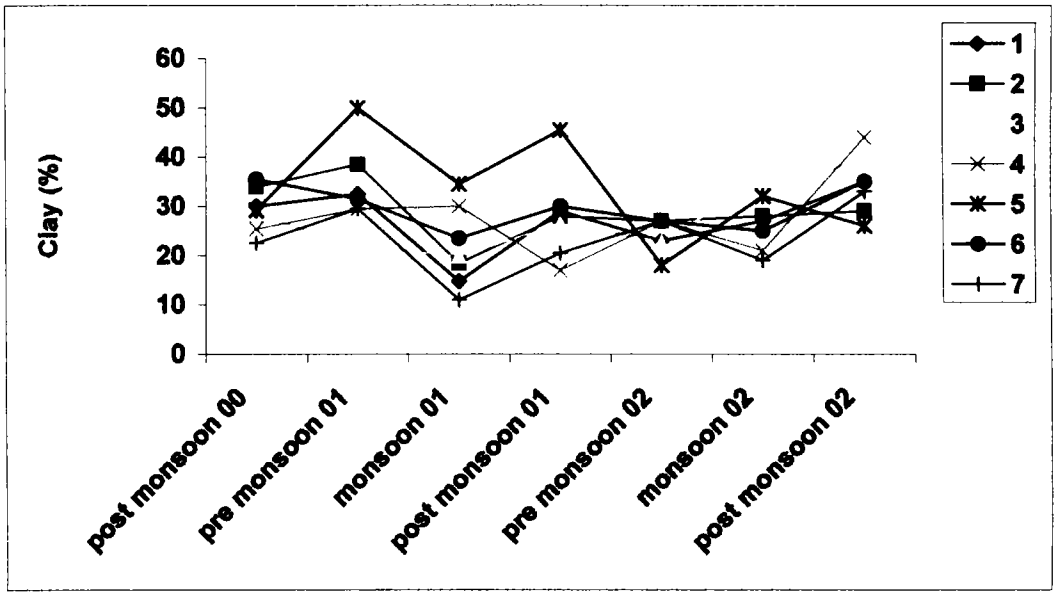


Fig.5.4 Seasonal Variation in percentage of clay in sediment from off Cochin

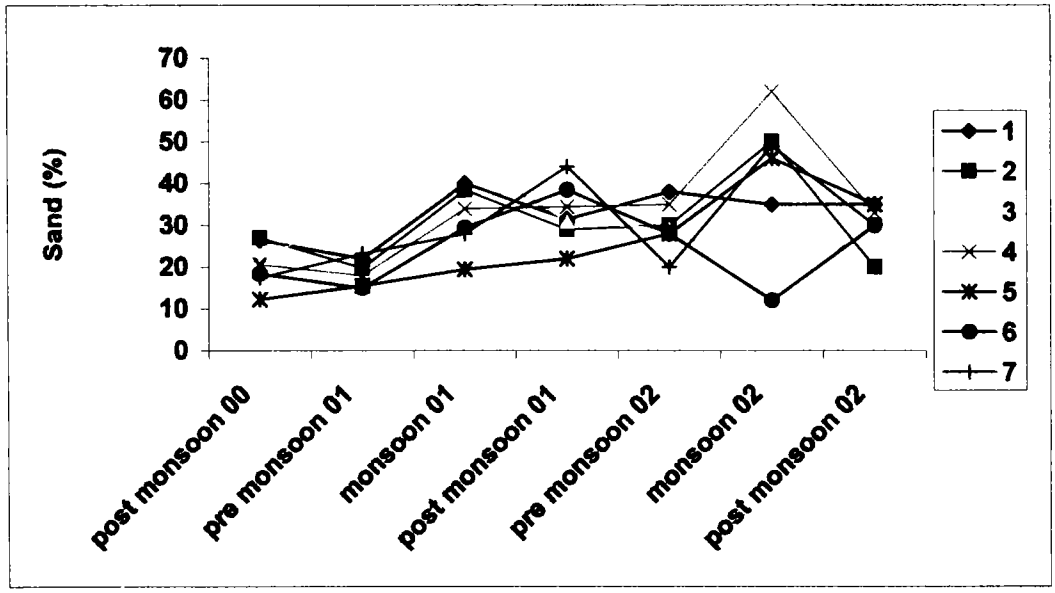


Fig.5.5 Seasonal Variation in percentage of sand in sediment from stations off Cochin

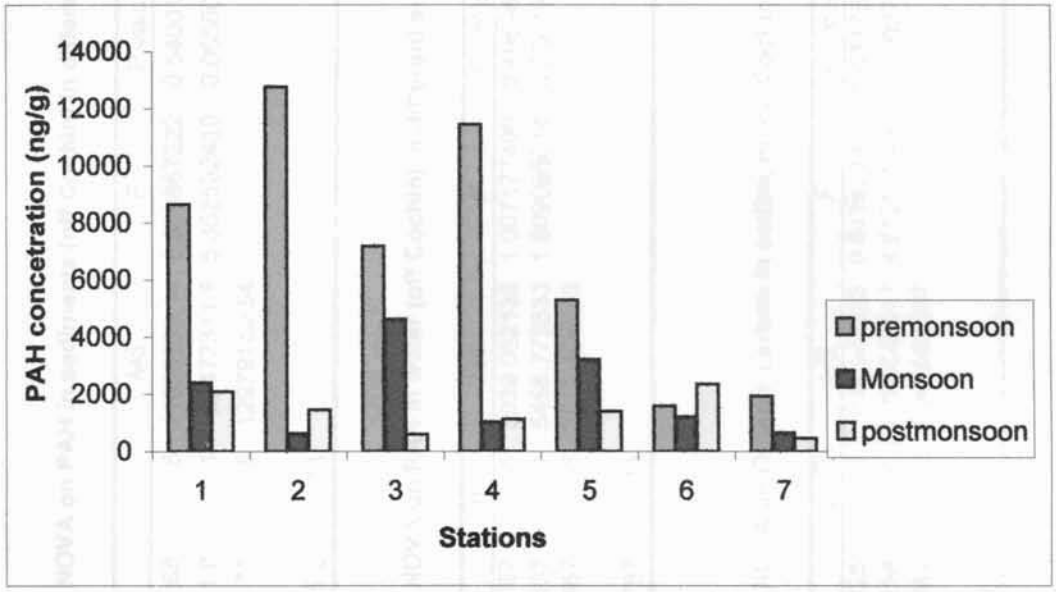


Fig.5.6 Seasonal changes in total PAH concentration in sediments from stations off Cochin

Appendix II

Table 1 Results of two -way ANOVA on PAH in sediments (off Cochin) in different seasons

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	59046695.68	5	11809339.14	0.909867222	0.54001425	5.050338814
Columns	69472311.8	1	69472311.8	5.352592439	0.06860144	6.607876912
Error	64895947.71	5	12979189.54			
Total	193414955.2	11				

Table 2 Results of two- way ANOVA on PAH in water (off Cochin) in different seasons

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	15195.31067	5	3039.062133	1.007177499	0.49696468	5.050338814
Columns	5458.773633	1	5458.773633	1.809095614	0.23639956	6.607876912
Error	15087.02357	5	3017.404713			
Total	35741.10787	11				

Table 3 Results of two- way ANOVA on Organic carbon in sediment (off Cochin) seasonal change

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	4.24206425	5	0.84841285	0.843633165	0.53176808	2.602988047
Columns	23.53171258	5	4.706342517	4.679828496	0.0037525	2.602988047
Error	25.14163992	25	1.005665597			
Total	52.91541675	35				

Chapter 6

POLYCYCLIC AROMATIC HYDROCARBONS IN FISH

6.1 Introduction

Polycyclic Aromatic Hydrocarbons (PAH) may exert toxic effects on organisms at tissue concentrations of only a few μg/g for marine invertebrates (Smith *et al.,* 1984) and a few μg/g for fish (Klaasen, 1996). Some PAHs can also damage a wide range of trophic components, even at very low levels (Neff, 1979). Being a major component of the aquatic food web and a main food resource for humans, fish have received special attention with respect to ecotoxicological analysis. Recently, interest has grown in research on the organ specific distribution of PAHs in aquatic organisms, but the pattern of accumulation of PAHs in fish tissues remains unknown. Very few reports have appeared that quantitatively describe the patterns of bioaccumulation of PAH in fish organs (Awad, 1987; Mohammad, 2000). Generally it is assumed that PAH congeners are depurated quite rapidly from fish tissues by metabolic activities and thus their concentrations have not been measured.

When an organism is exposed to organic contaminants, the concentration of these xenobiotics in its tissues varies until it reaches a steady state level. This apparent constant concentration results from a balance between uptake and depletion. The uptake of a contaminant is governed by its bioavailability, which in the case of a neutral organic compound is related to its water solubility. Hydrophobic contaminants such as PAHs tend to adsorb on to particles. Their hydrophobic character is represented by the octanol water

partition coefficient (Kow). The bioavailability of aromatic compounds adsorbed on particles decreases as Kow increases (solubility decreases). As PAH solubility decreases with increasing molecular weight, bioaccumulation of PAHs from sediments by marine organisms is generally greater for the lower molecular weight and more water soluble PAHs than for the higher molecular weight compounds (Porte and Albaiges, 1993). Different profiles of contaminants have been observed in organisms of different trophic levels (Broman *et al.,* 1990, Leonards *et al.,* 1997) and these differences were attributed to a partial biotransformation of the contaminants in the organisms of higher trophic levels. In the present study an attempt has been made to study the levels of PAHs in seawater, sediment and also in some of the important fish species available in the Indian waters.

6.2 Materials and methods

The details of sample collection, sample preparation and determination of PAH in them and procedure adopted are described in detail in chapter 2. Statistical analysis was carried out using two way ANOVA to determine the significant variations if any between different stations and seasons.

6.3 Result and discussion

Samples from Off Gujarat in pre monsoon season (Cruise No. 181)

The concentration of PAH in three different species of fish from the off Gujarat area is given in Table 6.1. The total PAH in fish muscle ranged from 432 ng/g - 3752 ng/g on wet weight basis, the highest concentration was

observed in *Saurida tumbil*. In *Epinephelus diacanthus*, the highest concentration of total PAH observed was 1288 ng/g while *Nemipterus japonicus* showed the highest concentration of 3714 ng/g. The mean total concentrations of PAH in these fishes from different stations were 1722 ng/g in *Nemipterus japonicus*, 818 ng/g in *Epinephelus diacanthus* and 1959 ng/g (wet weight) in *Saurida tumbil*.

Considering the concentration of individual PAH components, Naphthalene and phenanthrene were the most predominant ones. The four ring components, fluoranthene, pyrene and chrysene were also present in lower concentration in the fish. Benzo (a) pyrene, benzo (b) fluoranthene and benzo (a) anthracene were also detected in the samples analysed.

A comparison of PAH in water, sediments and fish muscle are given in Fig. 6.1. Statistical analysis of correlation was carried out for correlating the concentration of PAHs in fish to that in water and sediment. There is strong positive correlation between the PAH concentration in two species of fish studied namely, *Saurida tumbil* and *Nemipterus japonicus* with that in sediment (r= 0.84 and r= 0.86 respectively). In *Epinephelus diacanthus* such a correlation was not observed. The possible explanation is that, the two species *Nemipterus japonicus* and *Saurida tumbil* are more bottom dwelling fishes and voracious feeders. Hence their accumulation of PAH will be enhanced. A similar positive correlation was observed for the concentration of PAHs in these

two species and the concentration of PAHs in bottom water (r= 0.94 and r = 0.88 respectively). The carcinogenic benzo (a) pyrene was found in concentrations up to 2.5 ng/g in *Saurida tumbil.*

Samples from Quilon to Manglore area in monsoon season (Cruise No. 184)

The results of the analysis of samples from the entire west coast in the monsoon season (Cruise No. 184) is presented in Table 6.2. The total mean PAH in fish muscle varied from 813 - 1399 ng/g. The highest concentration was observed in *Nemipterus japonicus* followed by *Saurida tumbil.* Naphthalene was found in concentration ranging from 290-1041 ng/g in ~~*Nemipterus sp*~~, 220-880 ng/g in ~~*Epinephelus sp.*~~ and 212-1285 ng/g in *Saurida tumbil.* The sum of the concentrations of two and three ring compounds ranged from 666-3430 ng/g in *Nemipterus sp.*, 936- 1708 ng/g in *Epinephelus sp.*, and from 339-1082 ng/g in *Saurida tumbil.* Concentration of the higher molecular weight components varied from 123 ng/g- 333 ng/g in *Nemipterus sp*, 60- 255 ng/g in *Epinephelus sp* and 227- 321-ng/ g in *Saurida sp.* Among the four ring compounds, pyrene and fluoranthene were the predominant PAHs.

PAH in water, sediment and fish muscle are given in Fig. 6.2. Correlation studies revealed that no significant correlation existed between the concentration of PAHs in sediment and that in fish tissues during this period. This might possibly due to the great turbulence produced due to wave action in the monsoon period and the PAHs in sediment might have been distributed

over a greater area due to this. However a strong linear relationship was found between the levels in seawater and *Nemipterus sp.* (r= 0.75).

Samples from Quilon to Manglore area, monsoon season (Cruise No. 191)

The PAH concentration in three different species of fish are given in Table 6.3. The total PAH in fish muscle ranged from 113 ng/g – 1562 ng/g, where the highest concentration was observed in *Nemipterus japonicus*. In *Epinephelus diacanthus,* the highest concentration of total PAH observed was 1222 ng/g. The mean total concentrations of PAH in these fishes from different stations were 791 ng/g in *Nemipterus japonicus* and 470 ng/g in *Epinephelus diacanthus*. Considering the concentration of individual PAH components, Naphthalene and anthracene were the most predominant ones. The four ring components, fluoranthene, pyrene and chrysene were also present in lower concentration in the fish studied. Benzo (a) pyrene, benzo (b) fluoranthene and benzo (a) anthracene were also detected in the samples analysed.

PAH in water, sediment and fish muscle are given in Fig. 6.3. Statistical analysis of correlation was carried out for correlating the concentration of PAHs in fish to that in water and sediment. There was no significant correlation between the PAH concentration in two species of fish studied namely, *Epinephelus diacanthus* and *Nemipterus japonicus* with that in sediment. But a significant positive correlation was observed for the concentration of PAHs in

these two species and the concentration of PAHs in water (r= 0.92 and r= 0.74 respectively).

Samples from Cochin to Manglore area pre monsoon season (Cruise No. 197)

Results of analysis of PAH in fish samples collected from Cochin to Manglore during premonsoon (cruise no.197) are presented in table 6.4. The total mean PAH in fish muscle varied from 371- 1628 ng/g. The highest mean concentration was observed in *Nemipterus japonicus* followed by *Saurida tumbil*. Naphthalene was found in concentration ranging from 215-1018 ng/g in *Nemipterus sp*, 87- 1112 ng/g in *Epinephelus sp* and 128-1010 ng/g in *Saurida tumbil*. The sum of the concentrations of two and three ring compounds ranged from 249-1299 ng/g in *Nemipterus sp.*, 114-1469 ng/g in Epinephelus sp., and from 140- 1033 ng/g in *Saurida tumbil*. PAH in water, sediment and fish muscle are given in Fig. 6.4. Correlation analysis showed that a significant positive correlation existed between concentrations of PAH in sediment and that in the muscle tissue of *Nemipterus japonicus* only (r= 0.53).

Samples from Quilon to Manglore area, post monsoon season (Cruise No. 204)

Results of analysis of samples from Quilon to Manglore area in the post monsoon season are presented in Table 6. 5. The total PAH concentration in fish muscle was comparatively lower in all the stations studied during this

period. The range in concentration was from 60-569 ng/g. The highest concentration was found in *Saurida tumbil.* This comparatively lower concentration in fish tissues could be associated with the relatively lower concentration of PAHs in sediment during this season. It is found that the levels of lower molecular weight PAH especially naphthalene is lowered during this period. Statistical analysis of correlation showed that concentration of PAH in sediment and that in fishes namely, *Saurida tumbil* and *Epinephelus diacanthus* had a strong linear relationship (r= 0.94,and r= 0.63 respectively). A strong positive correlation existed between the levels of PAHs in bottom water and that in *Epinephelus diacanthus* and *Saurida tumbil* (r= 0.91, 0.95 respectively).

Swapan *et al.* (2000) reported a mean concentration ranging from 0.2 - 13.6 µg/g dry weight in 11 species of fishes from the Hiroshima Bay. The maximum concentrations of PAHs in fish were reported as 160µg/g dry weight in Puget Sound (Landlot *et al.,* 1987). Nicholson *et al.* (1994) reported levels of 55.7-µg/g dry weight in Port Philip Bay, Australia. Dou Abul *et al.* (1997) reported 118 µg/g of PAHs in Arabian Gulf and 49.2 µg/g in the Red sea coast of Yemen (Dou Abul *et al.,* 1997). The values obtained in the present study are below these reported values in all species of fishes studied. Law *et al.* (2002) reported total PAHs values in mussels ranging from 57- 6450 ng/g. The concentration obtained for PAHs in the present study was coming under this range. The PAH concentrations in edible fish muscle are coming within the

range of values as reported by Takatsuki *et al.* (1985) for zones defined as unpolluted elsewhere (2- 592 µg/g dry weight). The lower molecular weight PAHs were present at higher concentrations in fish tissues. But in sediments higher molecular weight components predominated. A similar observation was given by Swapan *et al.* (2000) and Baumard *et al.* (1998). This could possibly be due to greater bioavailability of these compounds due to their more water soluble nature. Higher molecular weight compounds are biotransformed at higher rates than lower molecular weight compounds and the low levels of high molecular weight compounds could be an effect of such selective biotransformation in fish tissues. The safe level of benzo (a) pyrene for human consumption is given as 4 ng/g dry weight (for consumption of 50g fish per week), 1 ng/g for the consumption of 200 gm fish per week. None of the samples studied here contained levels above this. The levels of PAHs in fishes were found to vary in different seasons, which could be due to changes in the levels of PAHs in the aquatic environment, variations in filtration, PAH concentration of the prey they feed on and the reproductive cycle of the fish.

Significant correlation was obtained for concentration of PAHs in fish and sediment levels in all seasons except in monsoon. In monsoon season due to the wave action and heavy rainfall PAHs might have dispersed into the surrounding areas. The higher concentrations of PAHs were observed in the premonsoon season.

At present very few quantitative information is available as to whether the accumulated PAHs in fish organs pose a risk to humans. Data on human exposure to PAHs including the levels causing adverse reproductive changes should be obtained.

6.4 Seasonal change of PAH in fish from off Cochin area

As found earlier, the concentration of PAH was more in the pre monsoon period. In *Nemipterus* the concentration of total PAH obtained in the post monsoon period was 683 ng/g. In *Epinephelus diacanthus* the total PAH was 463 ng/g and in *Sciaenids* the concentration was 890.45 ng/g. Benzo (a) pyrene was detected in all the three species studied but was below 1 ng/g. Naphthalene was the predominant component detected in the three species. The concentration of higher molecular weight compounds was more in these samples than that from the off shore study areas.

In pre monsoon period, Naphthalene was present in very high concentrations in the fish muscles. The total PAH concentration in *Nemipterus japonicus* was 6723 ng/g, in *Epinephelus diacanthus* the concentration of total PAH was 8706 ng/g and in *Sciaenids* it was 5588 ng/g. In *Nemipterus japonicus*, benzo (a) pyrene concentration was 1.1ng/g and in others it was below 1 ng/g. Fishes have a greater metabolic capacity and they biotransform the higher molecular weight PAHs with greater efficiency (Livingstone, 1992).

This explains the higher proportions of low molecular weight PAHs in fish tissues than the higher molecular weight components.

In Monsoon period, the concentration of total PAHs in fish ranged from 698 ng/g to 818 ng/g. The lowest concentration of PAH found in fish muscle was in the monsoon season. Naphthalene was the predominant component in this season also. Among the higher molecular weight components, benzo (a) pyrene and Didenz (a, h) anthracene were present in levels below 1 ng/g.

Statistical analysis of correlation showed that the levels on PAHs in sediment and that in fish were highly correlated. For Nemipterus the correlation coefficient r = 0.99, for Epinephelus diacanthus r= 0.99 and for Sciaenids r= 0.99. Swapan *et al.* (2000) reported values ranging from 440-12300-ng/ gm of naphthalene in fish tissues from Hiroshima Bay. Osuna *et al.* (2002) reported total PAH of 120- 3520 ng/g in oysters from Pacific coast of Mexico. In the study by Indra Jasmine *et al.* (2003), the highest concentration of chrysene observed in *Sardinella gibbosa* was 1.18 mg/g and the lowest was in silver bellies 0.01 mg/g. In marine catfish from Tuticorin coast the concentration of chrysene was 0.04 mg/g and in *Rastrelliger kanagurta*, the reported value was 0.61 mg/g wet weight basis (Indra jasmine *et al.,* 2003). Cocchieri *et al.* (1990) reported 13 mg/kg of chrysene in razor fish. Sivasami *et al.* (1990) reported chrysene values as 18.57 mg/g in salted dried *Trichurus lepturus*. The values obtained for fishes from the off Cochin area are lower than these reported values from the Indian coast. The reported values in the

present study are similar to that reported in oysters by Osuna *et al.* (2002) which are not directly responsible for fish kills, but may induce a key step in mechanism of malignant transformation through the formation of DNA adduct (Tran,1996;Mathieu *et al.*, 1998).

Table 6.1 PAH concentration ng/g wet weight in fishes from off Gujarat (Cruise No.181)

Nemipterus japonicus

Stn No	Naphtalene	Phenantrene	Anthracene	Fluorene	Fluoranthene	Pyrene	Chrysene	Benzo(a)pyrene	Benzo(a)anthracene	Benzo(b)fluoranthene	ΣPAH
1	1030.32	99.36	25	ND	191.11	21.4	ND	ND	8.25	0.99	1376.43
2	3210.96	156.6	13.39	ND	211.01	99.3	ND	ND	10.5	12.65	3714.41
3	550.8	25.3	8.5	1.3	49	68.2	2.5	0.5	0.89	2.1	709.09
4	809.22	65.43	3.3	0.58	106.3	100.6	ND	ND	0.55	2.5	1088.48

Epinephelus diacanthus

Stn No	Naphtalene	Phenantrene	Anthracene	Fluorene	Fluoranthene	Pyrene	Chrysene	Benzo(a)pyrene	Benzo(a)anthracene	Benzo(b)fluoranthene	ΣPAH
1	908.28	113.29	6.662	ND	213.5	2.1	15.2	1.1	22.2	1.1	1283.432
2	420.3	102.3	12.25	3.3	152.5	ND	10.2	0.58	12.2	10.5	724.13
3	625	98.5	6.6	ND	65	10.5	13.2	0.25	11.5	2.3	832.85
4	256	110	5.5	1.1	22.3	7.2	9.8	1.1	18.3	1.7	433

Saurida tumbil

Stn No	Naphtalene	Phenantrene	Anthracene	Fluorene	Fluoranthene	Pyrene	Chrysene	Benzo(a)pyrene	Benzo(a)anthracene	Benzo(b)fluoranthene	ΣPAH
1	1132	109	32	10	185	35	1.2	2.5	37	2	1545.7
2	3312	106	12.5	ND	185	102	ND	ND	12.5	22.4	3752.4
3	625	28.2	10.4	2.5	88	112	5.7	0.5	11.4	10.2	893.9
4	975	212	125	1.2	112	176	12	ND	10.2	8.2	1631.6

Table 6.2 PAH concentration in fishes (ng/g wet weight) from off Quilon-Gujarat (Cruise No.184)

Nemipterus japonicus

Stn No	Naphtalene	Phenantrene	Anthracene	Fluorene	Fluoranthene	Pyrene	Chrysene	Benzo(a)pyrene	Benzo(a)anthracene	Benzo(b)fluoranthene	ΣPAH
1	1041	290	44	20	ND	25	2.5	1.1	ND	0.5	1424.1
2	356	1010	22.5	320	ND	98	ND	ND	12	1.2	1819.7
3	480	202	40.9	214	58	116	ND	ND	11.4	5.5	1127.8
4	290	212	58	550	28	94	15	ND	10.2	4.2	1261.4

Epinephelus diacanthus

Stn No	Naphtalene	Phenantrene	Anthracene	Fluorene	Fluoranthene	Pyrene	Chrysene	Benzo(a)pyrene	Benzo(a)anthracene	Benzo(b)fluoranthene	ΣPAH
1	880	190	12	ND	ND	22	5.6	1.2	0.5	0.6	1111.9
2	550	255	68	1.2	2.5	10.2	1.1	ND	0.5	ND	888.5
3	220	103	11	5.5	1.3	0	10.5	ND	22.1	ND	373.4
4	265	312	8.8	65	3.2	1.1	0.29	ND	225	ND	880.39

Saurida tumbil

Stn No	Naphtalene	Phenantrene	Anthracene	Fluorene	Fluoranthene	Pyrene	Chrysene	Benzo(a)pyrene	Benzo(a)anthracene	Benzo(b)fluoranthene	ΣPAH
1	1285	290	15.5	1.3	ND	14	0.89	0.55	ND	ND	1607.24
2	336	550	12.5	128	4.5	1.8	0.6	0.5	0.45	0.25	1034.6
3	250	124	15	5.5	2.2	0.1	12.5	ND	21.1	0.08	430.48
4	212	102	12.5	20.5	2.8	0.5	1.25	ND	41.1	0.58	393.23

Table 6.3 PAH concentration in fishes (ng/g wet weight) from off Quilon -Mangalore(Cruise No.191)

Nemipterus japonicus

Stn No	Naphtalene	Phenantrene	Anthracene	Fluorene	Fluoranthene	Pyrene	Chrysene	Benzo(a)pyrene	Benzo(a)anthracene	Benzo(b)fluoranthene	ΣPAH
1	1356.67	ND	141.59	65.54	ND	ND	0.6	0.002	ND	ND	1564
2	525	23.8	74	ND	89	ND	ND	0.01	ND	0.2	712
3	132	1.32	12	ND	5	ND	0.2	ND	ND	0.3	150
4	660	5.1	21	11	41	ND	ND	ND	ND	ND	738

Epinephelus diacanthus

Stn No	Naphtalene	Phenantrene	Anthracene	Fluorene	Fluoranthene	Pyrene	Chrysene	Benzo(a)pyrene	Benzo(a)anthracene	Benzo(b)fluoranthene	ΣPAH
1	862	104.9	10	23	220.65	0.45	1.1	0.01	ND	ND	1222
2	252	0.5	4.2	1.5	2.5	ND	ND	ND	0.21	0.1	261
3	110	1.2	0.5	ND	0.1	ND	1	ND	0.1	ND	113
4	285	2.8	ND	1.3	ND	ND	ND	ND	ND	ND	289

Table 6.4 PAH concentration in fishes (ng/g) from off Cochin-Mangalore (Cruise No.197)

Nemipterus japonicus

Stn No	Naphtalene	Phenantrene	Anthracene	Fluorene	Fluoranthene	Pyrene	Chrysene	Benzo(a)pyrene	Benzo(a)anthracene	Benzo(b)fluoranthene	ΣPAH
1	1018	221	5.2	55	1.2	1.1	0.5	0.001	0.5	ND	1302
2	1150	130	125	112	100	1.5	10.2	ND	ND	ND	1628
3	215	12	12	10	2	ND	21	0.3	ND	ND	272
4	350	2.6	13	1.2	ND	2.5	ND	ND	1.3	0.2	371

Epinephelus diacanthus

Stn No	Naphtalene	Phenantrene	Anthracene	Fluorene	Fluoranthene	Pyrene	Chrysene	Benzo(a)pyrene	Benzo(a)anthracene	Benzo(b)fluoranthene	ΣPAH
1	1078	15	5.2	28	1	0.5	ND	ND	0.2	ND	1127
2	1112	225	6.3	126	2.4	1.1	ND	ND	ND	ND	1472
3	99	21	1.4	43	5.3	2.1	ND	ND	ND	ND	172
4	87	4	2	21	1.2	ND	ND	ND	ND	ND	115

Saurida tumbil

Stn No	Naphtalene	Phenantrene	Anthracene	Fluorene	Fluoranthene	Pyrene	Chrysene	Benzo(a)pyrene	Benzo(a)anthracene	Benzo(b)fluoranthene	ΣPAH
1	1010	22	1.2	ND	ND	ND	ND	0.01	ND	ND	1033
2	254	35	ND	ND	ND	ND	ND	0.2	ND	0.25	289
3	212	15	ND	ND	ND	ND	ND	ND	ND	0.08	227
4	128	12	ND	ND	ND	ND	ND	0.2	ND	0.58	141

Table 6.5 PAH concentration in fishes (ng/g) from off Quilon-Mangalore (Cruise No.204)

Nemipterus japonicus

Stn No	Naphtalene	Phenantrene	Anthracene	Fluorene	Fluoranthene	Pyrene	Chrysene	Benzo(a)pyrene	Benzo(a)anthracene	Benzo(b)fluoranthene	ΣPAH
1	52	13	1	0.2	1.5	0.1	0.1	0.01	ND	0.1	68
2	12	12	ND	1.1	2.1	0.01	0.3	ND	ND	ND	28
3	25	5	ND	ND	ND	0.05	0.05	0.01	ND	ND	30
4	35	7	ND	1.1	ND	ND	ND	0.2	ND	ND	43

Epinephelus diacanthus

Stn No	Naphtalene	Phenantrene	Anthracene	Fluorene	Fluoranthene	Pyrene	Chrysene	Benzo(a)pyrene	Benzo(a)anthracene	Benzo(b)fluoranthene	ΣPAH
1	48	14	12	0.6	21	ND	0.5	1.1	ND	0.5	98
2	12	12	1.3	0.8	ND	ND	0.2	1.2	ND	0.5	28
3	15	10	ND	1.7	ND	ND	0.3	0.25	ND	0.5	28
4	36	5	1.1	ND	0.5	ND	ND	0.5	ND	1	44

Saurida tumbil

Stn No	Naphtalene	Phenantrene	Anthracene	Fluorene	Fluoranthene	Pyrene	Chrysene	Benzo(a)pyrene	Benzo(a)anthracene	Benzo(b)fluoranthene	ΣPAH
1	550	12	5.1	1.1	ND	ND	0.1	ND	0.8	ND	569
2	220	22	2.7	0.3	ND	ND	0.2	ND	0.8	ND	246
3	120	42	ND	0.2	ND	ND	ND	ND	0.5	ND	163
4	48	10	1.2	ND	ND	ND	0.1	ND	1	ND	60

Table 6.6 PAH in fish muscle (ng/g wet weight) in different studied seasons from off Cochin (Average for the 2 years)

Post monsoon

	Naphthalene	Fluorine	Phenanthrene	Anthracene	Pyrene	Chrysene	Acenaphthilene	Fluranthene	Benzo(a) anthra	Benzo(a) pyrene	ΣPAH
N.japonicus	550	15	12	ND	100.05	2.1	1.1	2.3	0.1	0.5	683.15
E.diacantus	385	22	25	2	25.1	1.1	1	2.1	0.1	0.2	463.6
Sciaenid sp.	726	35	95	2.5	28.5	1	0.5	1.5	0.2	0.25	890.45

Premonsoon

	Naphthalene	Fluorine	Phenanthrene	Anthracene	Fluoranthene	Benzo(a) anthra	benzo(a) pyrene	Didenz(a,h)an	ΣPAH
N.japonicus	6550	120	46	2	2.5	1.5	1.1	0.2	6723.1
E.diacantus	8570	100	23	1.3	1.3	10.2	0.5	0.1	8706.3
Sciaenid sp.	5500	45	25	7	1.2	10	0.2	0.05	5588.4

Monsoon

	Naphthalene	Fluorine	Phenanthrene	Anthracene	Pyrene	Chrysene	Fluranthene	benzo(a)pyrene	Didenz(a,h)an	ΣPAH
N.japonicus	620	30.5	10	ND	25.2	1	12	0.1	0.05	698.85
E.diacantus	780	13	9.5	ND	12	0.6	2.6	0.1	0.2	818
Sciaenid sp.	450	18.6	251.06	42.86	10	1.1	7.1	0.2	0.3	781.22

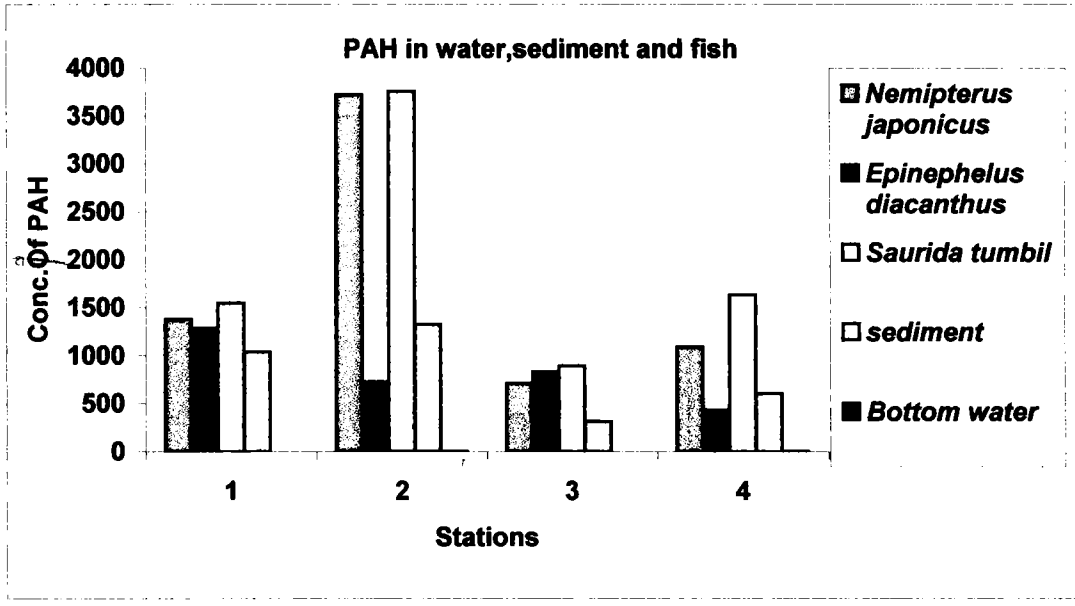


Fig. 6.1 Comparative levels of PAH in water (ng/l), sediments and fish (ng/g) from 4 stations in Cruise 181

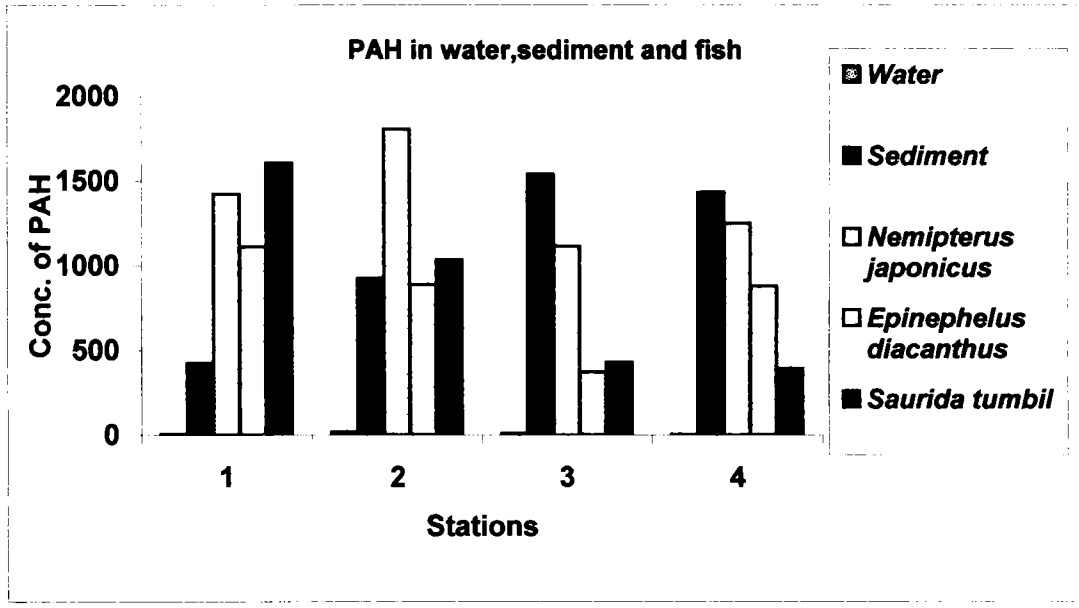


Fig. 6.2 Comparative levels of PAH in water (ng/l), sediments and fish (ng/g) from 4 stations in Cruise 184

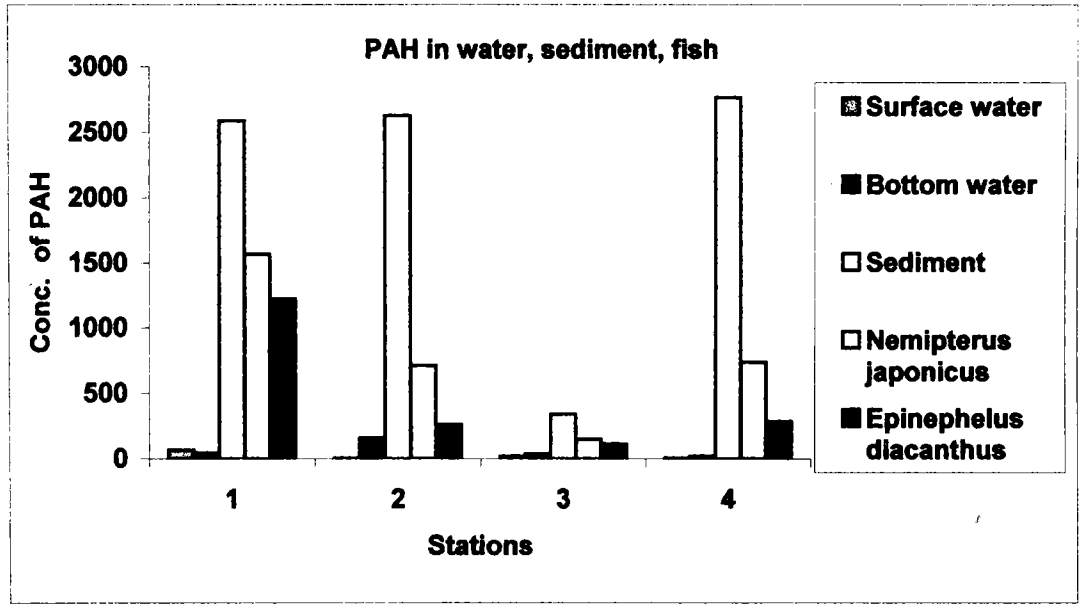


Fig. 6.3 Comparative levels of PAH in water (ng/l),sediments and fish (ng/g) from 4 stations in Cruise 191

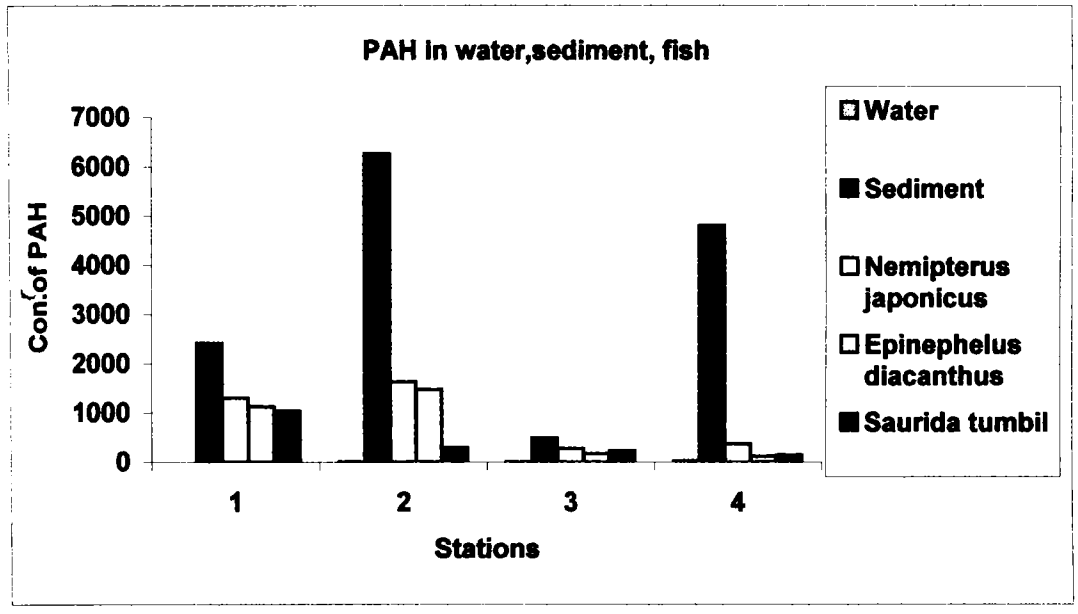


Fig. 6.4 Comparative levels of PAH in water (ng/l),sediments and fish (ng/g) from 4 stations in Cruise 197

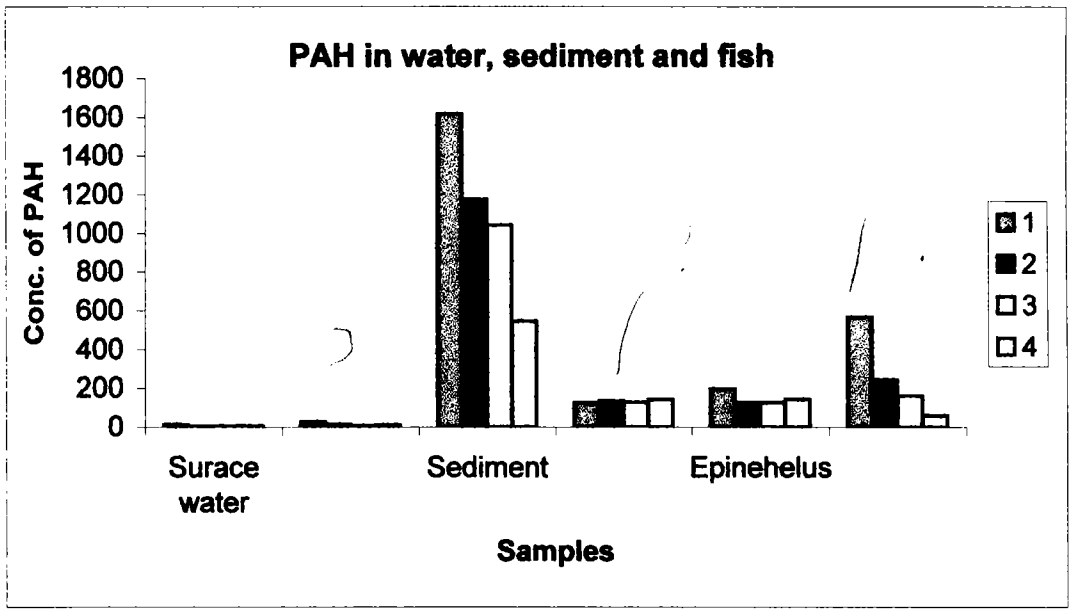


Fig. 6.5 Comparative levels of PAH in water, sediments and fish from 4 stations in Cruise 204

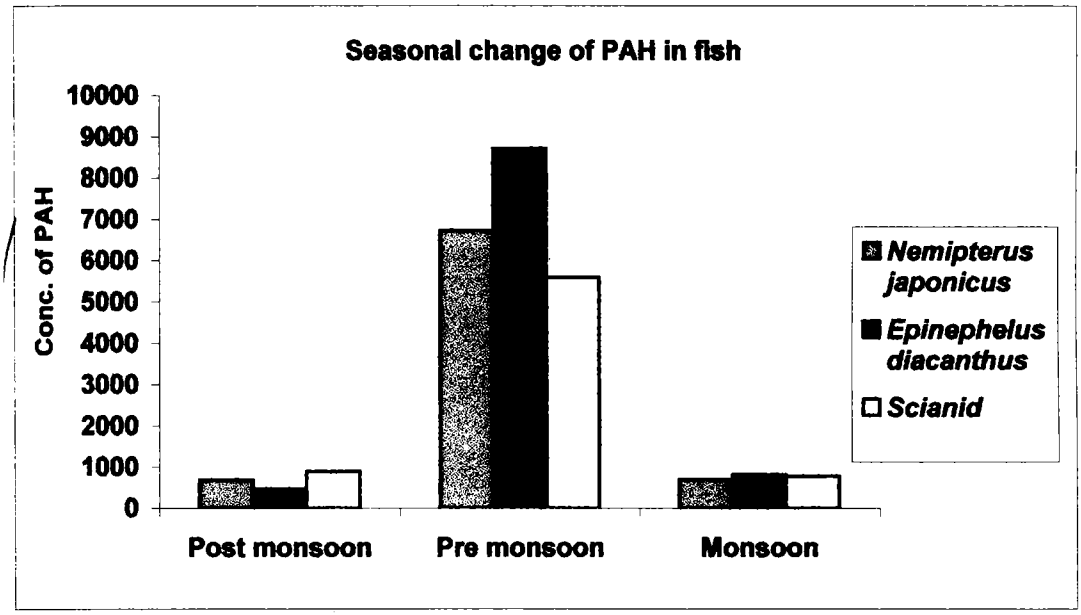


Fig. 6.6 PAH concentration in fishes in different seasons of study from off Cochin

Chapter 7

TRACE METALS IN SEAWATER AND SEDIMENTS

7.1 Introduction

Trace metal can be defined as those metals, which are occurring in the environment in trace amounts (>100 ppm). At the appropriate concentrations some trace metals are essential for enzymic activity in the organisms. They form important groups of enzyme inhibitors when their natural concentrations are increased. Metals such as Ag, Hg, Cd, Cu and Pb are particularly toxic and they usually inhibit enzymes by forming mercaptides with the sulfhydril groups (Nair, 1980). Being major seafood exporting nation, India is very much concerned with the quality and safety of seafood products. Even though studies have been made on the levels of trace metals in Indian waters, not much work has been done on the determination of their levels in the aquatic environment and their corresponding levels in fishes.

The most important works on trace metal concentrations are of Windom and Smith (1972); Abdulla *et al.* (1972); Chestner and Stoner (1975); Chestner and Stoner (1975); Bender and Gagner (1976). Danielson (1980). Kremling *and* Peterson (1977) studied trace metals from surface waters of Baltic Sea water, and Danielsson (1980); Subrahmanyam and Ananthalashmi (1990); Kaladharan *et al.* (1990), Jonathan and Ram Mohan (2003), from different depths of Indian Ocean. Matakar (1981) studied the concentration of trace metals in Bombay harbour bay. Studies on trace metals in seawater from Sourashtra coast has been done by Kesava Rao and Indusekhar (1986). In the Arabian Sea, the most important works are those of Sengupta *et al.*,

(1978), Sanzgiri and Moraces (1979) and Braganca and Sanzgiri (1980). Studies in Cochin coast has been done by Mohapatra, (1994), Meenakumari (1989), Radhakrishnan (1993), Lakshmanan, (1998). The purpose of the present study was to establish a baseline trace metal concentration in water, sediment and fish samples collected from the west coast of India during various seasons.

7.2 Materials and Methods

The details of sample collection, sample preparation and determination of metal levels in them by Inductively Coupled Plasma Emission Spectrometer and procedure adopted are described in detail in chapter 2. Statistical analysis was carried out using two way ANOVA to determine the significant variations if any between different stations and seasons.

7.3 Result and discussion

Concentration of trace metals like Cu, Pb, Hg, Zn and Cd found in surface and bottom waters and Cu, Cd and Pb in sediment collected from various stations in the west coast of India are presented in Tables 7.1 to 7.10.

7.4 Trace metals in seawater and sediments from Off Gujarat area (Pre monsoon season)

Copper (Cu) was non detectable in the water samples collected at surface from all the 6 stations whereas traces of copper registered at station 6

(0.013 ppm) in the water samples collected at bottom. Concentration of lead (Pb) in surface water ranged from 0 in station 2 to 0.3 ppm in station 6. Mercury (Hg) values in surface water ranged from non-detectable levels to 0.11 ppm and in bottom water it varied from non-detectable level to 0.12 ppm in station 2. Detectable levels of Hg were also recorded at station 1 in both surface and bottom water (0.07 and 0.11 respectively). But traces of Hg could not be recorded in all other stations. Zinc (Zn) concentration recorded varied from 0.004 ppm in station 5 to 0.06 ppm in station 2 whereas, cadmium was on non detectable level in almost all the stations except in station 1 and 2. Relatively higher levels of Cd have been reported in coastal waters (4.2 µg/l) around the British Isles (Abdulla *et al.,* 1972). Somasundaram *et al,* (1987) reported 1.42 µg/l of Cd in Madras Coast. But in the present study lower concentrations of Cd were detected in water samples.

The trace metal concentrations recorded in the samples collected from the area are given in Table 7.2. Station 1 and 2 recorded higher concentrations of all the metals. Cd concentration varied from 5.3 ppm in station 3 to 6.73 ppm in station 1 while lead (Pb) ranged from 96.3 ppm in station 3 to 122 ppm in station 1. Cu was also present in the sediment samples collected from all the 6 stations where the highest concentration recorded at station 2 (5.4ppm) whereas the lowest registered at station 5 (1.3 ppm). Cu in sediment and organic carbon showed strong negative correlation (r = -0.79).

Significant variation was recorded in concentration of Zn in surface and bottom waters ($P < 0.01$). But there is no significant variation among different stations and also between surface and bottom waters for the concentration of Cu and Pb (Appendix III, Table 1, 2, 3). Correlation studies shows that there is strong positive correlation in the level of Cd in water and sediment ($r=0.88$) and no significant correlation in the concentration of other three metals studied between that in the water and sediment.

Chester and Stoner (1974) found Zinc contents of near shore surface waters range between 0.6 and 12.6 µg/l with an average of 2.5 µg/l. In the present study, higher values were recorded than this both in surface and bottom water (Average in surface water is 0.04 ppm and in bottom water is 0.39 ppm). The Environmental Protection Agency (EPA) recommended safe level for Zn in seawater is 0.1 ppm, Cu is 0.025 ppm, Pb is 0.1 ppm and critical upper limit for Cd is 0.01 ppm (Anon, 1991; Lohani, 1981). Zn recorded in the bottom water samples at station 3 and 4 are slightly above this level. The earlier reported value for average concentration of Cu in Arabian Sea is 0.004 ppm (Topping 1969, Sengupta *et al.*, 1978). The concentration of Cu in the present study is lower than this in all the stations except in the bottom water of station 6.

Cd, Cu, Ni, and Zn, which display a nutrient like behaviour in the ocean, are rapidly released from sediments under oxic bottom conditions, but fixed to them in anoxic bottom waters (Bruland and Franks, 1983). The dissolved

Oxygen in the bottom waters was lower (2.3-3.76 ml/ l). The stations 1 and 2 are marked by the influence of the discharge from the river Narmada. There is a major amount of sediment being delivered from this river into the ocean. (Rangasami and Jing Zhang, 2005). Narmada and Tapti rise in the plateau and fall into the Arabian Sea. Archaen rocks occur on either side of the Narmada and include granites and gneisses and several outcrops of Bijawar rocks. High levels of Cu, Zn was found in Tapti river (Shajan, 2001).

7.5 Trace metals in seawater and sediments from Quilon to Gujarat (monsoon season, Cruise 184)

The results of analysis of trace metals in surface water of the above cruise are given in Table 7.3. Copper was recorded in the water samples collected at surface from all the stations except from station 6. The concentration of Cu ranged from 0.001 to 0.033 ppm where the highest was recorded in station 3 near Manglore. Earlier reported value of Cu from Arabian Sea by Meenakumari (1988) ranged from 0.0002 - 0.01 ppm. The highest concentration obtained in the present study is higher than this reported value. The EPA recommended safe level for Cu in seawater is 0.025 ppm and in station 3 a slightly higher value was observed. Cd was also present in surface water samples from all the stations except in station 3 and 6 and the concentration ranged from ND- 0.007ppm. Sanzgiri and Bragansa (1981) found the range of Cd as 0.0001-0.001 ppm for the Indian Ocean waters. Bryan, (1984) reported concentration of Cd as 0.015- 0.118 µg/l in natural

seawater. The concentration of Cd obtained in the present study is higher than this indicating pollution in the area but it is well below the critical upper limit of 0.01 ppm (Lohani, 1981). In the Indian Ocean, the increase of Cd concentration with age of deep water can be observed on a larger scale in the high deep water concentrations according to Danielsson(1980). Zn in water samples varied from 0.035 to 0.088 ppm and the highest value was registered at station 1. Pb in surface water ranged from 0.039-0.052 ppm and the highest concentration was recorded at station 3.

Trace metals in sediment samples are given in Table 7. 4. The concentration Cu in the sediment ranged from 1.3 ppm in station 5 to 23.06 ppm in station 6. The value was high in station 3 also (21.36 ppm). Concentration of Cd ranged from 1.06 ppm to 2.3ppm where the highest values were recorded at station 3 and 4. The statistical analysis shows that there is significant positive correlation between the concentration of Cu and Zn in water (r=0.78). Cu and Cd showed significant negative correlation in water(r =-0.84). Cd and Zn also recorded strong negative correlation (-0.631).

The study revealed the predominanance of clayey silt at all stations except a few that are away from the shore at higher depths where sand predominates. Organic carbon recorded at stations 3, 4 and 6 were comparatively higher. High inputs of terrigenous materials from effluents and industrial activities could have increased the organic carbon values in the samples close to the shoreline as reported by Jonathan and Ram Mohan

(2003). The total metal content exhibited higher concentration in station 3 and station 6, which is near to Manglore and Okha respectively, near the major industrial out falls. The sampling was done in the monsoon months and hence in the near shore stations there was greater influence by the river run off.

Organic carbon and concentration of the three metals (Cu, Cd and Pb) in sediment showed strong positive correlation. Between Cu and organic carbon the correlation factor r = 0.79, for organic carbon and Cd r = 0.72 and for organic carbon and Pb r = 0.69. The finer sediments like clay, clayey silt showed enrichment of organic matter and also the trace metal studied. Particle size has a significant role in the accumulation and exchange process of metals between sediments and water. The higher concentration in the fine sediments is due to the increase in specific surface area and to the surface properties of clay minerals (Biksham *et al.*, 1991)

7.6 Trace metals in seawater and sediments from off Quilon to Manglore (monsoon season, Cruise 191)

Stations 1, 2, 3 are in the south west coast of India between Quilon and Cochin located at the depth zone of 30-50 m while stations 4, 5, 6 are fixed away from shore at depths range of 150-200 m. The sampling was done at the end of the monsoon season. The total metal concentration was higher in station 1,2, and 3 (Table 7.5). Concentrations of Nickel in surface water ranged from non-detectable level to 0.01 ppm where the highest value was

observed in station 3. In the bottom water, Ni was found in non-detectable level in stations 5 & 6 and the highest values were observed in station 4 (0.004 ppm). The highest value of Ni recorded in water (0.01 ppm) is higher than that reported by Chester and Stoner (1974), for the Indian Ocean where the value was 0.005 ppm and it is above the EPA recommended safe level of 0.005ppm. Copper in surface water ranged from non-detectable level to 0.026 ppm. The highest observed value was in station 4. Cu was non-detectable in the bottom water at stations 5&6 while in the other stations it ranged from 0.006- 0.026 ppm and the maximum value was observed in station 4. The highest concentration obtained was slightly above the EPA recommended safe level of 0.025 ppm. Mercury was non-detectable in almost all the stations except in the bottom water of station 3 where the concentration was 0.0001 ppm. Concentration of Zn varied from 0.01- 0.05 ppm in surface water and from 0.003- 0.01 ppm in bottom water.

Analysis of sediments (Table 7.6) Showed that concentration of Cd ranged from 0.21 ppm in station 6 to 3.36 ppm in station 1. Pb was lowest at station 5 and the concentration ranged from 1.25 ppm to 10.66 ppm in station 1 while copper in sediments ranged from 1.2 ppm to 4.8 ppm with the lowest level at station 5 and the highest at station 1.

Statistical analysis showed that there is strong positive correlation between the concentration of Cu in surface and bottom water($r = 0.99$) and also concentration of Ni in surface and bottom waters ($r = 0.62$). There exist

significant positive correlation between organic carbon and Cu in sediment (r = 0.5). Particle size analysis of the sediment showed that there was strong negative correlation between the percentage of sand and the concentration of all the studied elements in it. Cd and Cu in surface water showed strong positive correlation (r = 0.93), Cu and Ni in water samples also showed strong positive correlation (r = 0.78).

7.7 Trace metals in seawater and sediments from off Quilon to Manglore (Pre-monsoon season, Cruise 197)

Cruise 197 was in the region from Cochin to Manglore in the pre-monsoon period. Analysis of trace metals in water showed that concentrations of most of the metals studied were higher in surface water than in the bottom water (Table 7.7). Concentration of Cd in surface water ranged from non-detectable level in station 3 to 0.001 ppm in station 4,5 and 6. In the bottom water, the range in concentration of Cd was from 0- 0.008 ppm and the highest concentration was recorded at station 3. The concentration of Cd in water samples studied was well below the critical upper limit value of 0.01 ppm (Lohani, 1981). Nickel in surface water ranged from 0.001 ppm - 0.003 ppm. Ni was recorded from all the stations studied in surface water, but it registered its presence only at the stations 5 and 6 in the bottom water and in all the samples the concentration of Ni was well below the EPA recommended safe level of 0.005 ppm. Concentration of copper ranged from non-detectable level to 0.03 ppm and the highest value was recorded at station 5 while it was non

detectable in all the stations in the bottom waters. Concentration of Cu from station 5 was found to be above the EPA recommended safe level of 0.025 ppm.

Trace metal concentration in sediment samples are given in Table 7. 8. Cadmium in sediment from these six stations ranged from 0.5 ppm – 2.2 ppm and the highest concentration was measured at station 1. Concentration of Pb in sediment varied from 1.2 ppm in station 4 to 12.3 ppm in station 1. Statistical analysis showed that there exists no significant correlation among concentration of metals in surface water and that present in the bottom water. No significant correlation can be drawn between the organic carbon present in sediment samples and the concentration of studied trace elements in the studied samples.

7.8 Trace metals in seawater and sediments from off Quilon to Manglore (Pre monsoon season, Cruise 204)

The cruise was conducted along Kerala coast from Quilon to Manglore during the post-monsoon season. Analysis of trace metals was carried out in samples from four stations only and the results are given in Table 7.9 and 7.10. Concentration of Cd in surface water ranged from non-detectable level to 0.003 ppm. Highest concentration was observed in the station 2. At station 1 and station 4, concentration of Cd in bottom water was 0.002 ppm and in other stations it was non detectable in the bottom waters. Concentration of Cu

in surface water ranged from non-detectable level to 0.002 ppm. The highest concentration was at station 2. In the bottom waters, concentration of Cu ranged between 0.001 ppm to 0.003 ppm, the highest being at station 2. Pb was non detectable in the waters from almost all the stations except at station 2 where its concentration was 0.001 ppm both in surface water and bottom water.

Concentration of the studied metals in sediment was highest in station 1. Concentration of Cd in sediment ranged between 0.5ppm to 1.0 ppm. Concentration of Cu ranged from 0.25 ppm-3.5 ppm. The range of Pb ranged from 0.001 ppm to 0.3 ppm.

While comparing the levels of the studied trace metals in seawater in different cruises, it can be seen that there is temporal variation of these metals in different seasons. Average concentration of Cu, Ni, Cd and Zn in surface and water samples collected during the monsoon months was higher than that observed for the premonsoon and post monsoon periods in the west coast but concentration of Zn in bottom water was the highest in the post monsoon period. Even though there can be regional variations and variation in the source of trace metals, it can be generalized as due to the increased input of effluents by the rivers (Coale and Johnson, 1998). The concentrations of Zn, Cu and Ni in some stations in the present study are found to be above the safe level. Metal pollution in the seas around India has not yet reached dangerous levels. But the potential threat it poses is serious enough to merit dependable

and appropriate monitoring programmes. The occurrence of elevated levels of trace metals especially in the sediments can often be attributed to anthropogenic influences, rather than natural enrichment of the sediment by geological weathering (Jonathan and Ram Mohan, 2003).

7.9 Temporal variation of trace metals in seawater and sediment from off Cochin area

Trace metals recorded in the coastal waters of Cochin are presented in Fig. 7.1- 7.5. The average values for trace metals in premonsoon, monsoon and post monsoon periods are tabulated for each of the 7 stations studied. Concentration of Cu in station 1 ranged from 0.001 ppm- 0.005 ppm. The highest concentration was recorded in the monsoon and post monsoon season. In station 2, the range was from 0.001- 0.0045 ppm and the highest values recorded in the post monsoon followed by the monsoon season where the concentration was 0.004 ppm. In station 3, the concentration of Cu ranged from 0.001 ppm to 0.005 ppm and here also the highest concentration was in the monsoon season. At station 4, the value ranged between 0.001ppm to 0.005 ppm and the highest was observed in the post monsoon period. At station 5, the concentration of Cu was slightly lower (0-0.0025 ppm). At station 6, the rage was from 0- 0.002 ppm and at station 7, the concentration ranged from 0-0.003 ppm. When the average concentration for the first year of sampling is compared with that of the second year, there is slight increase in concentration of Cu in except in station 1 where, there is slight decrease in

concentration. The average concentration of Cu in surface seawater during first year of observation ranged from 0.0001 ppm to 0.001 ppm. Station 1,3,4 and 7 recorded the highest values (0.00395 ppm) and the lowest concentration was observed in station 6. The highest concentration (0.005 ppm) was measured during monsoon season (2001) (May-August) in the sample collected from station 1 and 3 and it was well below the EPA recommended safe level of Cu in sea water, 0.025 ppm.

Statistical analysis (ANOVA) has shown that there was a significant variation in concentration of Cu in water in different seasons ($p < 0.01$), (Appendix IV, Table 1).

In the case of Iron, the average concentration in water for the period was found to be 0.014 ppm. At station 1, the average concentration of Fe for the first year of observation was 0.015 ppm and in the second year it was 0.0158 ppm, in station 2, it was 0.014 ppm and 0.018 ppm, in station 3, the concentration was 0.016 ppm and 0.021 ppm, respectively. In station 4 the average concentration for the second year was almost double of that observed in the first year of study. In station 5, the average concentration for the two years was 0.010 and 0.015 ppm, for station 6, it was 0.013 ppm, 0.012 ppm and for station 7, it was 0.009 ppm and 0.0123 ppm respectively. The highest average concentration was observed at station 3 (0.018 ppm) and the lowest average concentration was in station 7 (0.011 ppm). The highest concentration was observed in monsoon period in almost all stations except in station 4

where the concentration was higher in post monsoon season. Comparing the concentration for the first year of sampling with that of the second year, except in station 6 in all other stations the value was higher in the second year of observation. Statistical analysis of variance showed that there is significant variation in concentration of Fe in water in different seasons ($p< 0.01$), (Appendix IV, Table 2).

In the case of Nickel, the highest concentration was registered in station 1 in monsoon and post monsoon season (0.01 ppm) with an average concentration of 0.005 ppm. Higher concentrations were measured in all stations in the monsoon season except in station 2 and 3 where slightly higher concentrations were observed in the following post monsoon months. When station-wise average was calculated, it ranged from 0.0005 to 0.005 ppm and the lowest was in station 7. In stations 1 and 2, the concentration of Ni was above the EPA recommended safe level of 0.005 ppm. The concentration of Ni in the second year of study was greater than that for the first year. Statistical analysis (ANOVA) has shown that there is significant variation in concentration of Ni in water between different seasons of study ($p< 0.01$), (Appendix IV, Table 3).

Data on concentration of Cu and Fe are scanty especially from Indian coastal waters (Matkar *et al.*, 1981). According to Meenakumari (1988), the average concentration of Cu in the water samples collected at Cochin harbour was 0.0043 ppm and Iron in surface water ranged from 0.021-0.113 ppm. The

present study reveals that the average concentration for Cu in surface for the period of study ranged from 0.0009 ppm to 0.0029 ppm.

Preston *et al.* (1972) found that Ni content varied between 0.0005-0.001 ppm in British coastal waters. According to Chestener and Stoner (1974) the average concentration 0.0054 ppm was recorded in the Indian Ocean. He also measured the lower values in the Sargasso Sea, while higher values were found in the Indian Ocean. The Nickel content of the near shore surface water of world oceans ranged between 0.0005-0.005 ppm with an average of 0.0018 ppm. Meenakumari (1988) found that an average of 0.0022 ppm for premonsoon season, 0.003 ppm for monsoon season and 0.00224 ppm for the post monsoon season. In the present study concentration of Ni in surface water for the first year of observation ranged from 0.0001 to 0.0026 ppm and from 0.001-0.008 ppm for the second year of observation and average for the whole period ranged from 0.0005 to 0.005 ppm.

In the Indian Ocean, 0.0001-0.061 ppm of Fe were recorded by Topping (1969), 0.007-0.0669 ppm by Sen Gupta *et al.* (1978), 0.0085-0.096 ppm by Sanzgiri and Moraes (1979), 0.0062-0.131 ppm by Braganca and Sanzgiri (1980). According to Danielsson (1980), the Iron concentration show a range of 0.00015-0.010 ppm from samples of open ocean Indian Ocean waters. In the present study, concentration of Fe varied from 0.0075-0.016 ppm in the first year and from 0.015-0.02 ppm in the second year of study.

According to the study by Meenakumari (1988) Cd concentration in surface water of Cochin Harbour ranged from 0.00025-0.028 ppm. In the present study the Cd concentration in post monsoon season varied from ND to 0.001ppm in the first year of study, in monsoon season from 0.001-0.012 ppm and in premonsoon season from 0.0005-0.0055 ppm. In the postmonsoon season of 2001, Cd concentration ranged from 0.0005-0.003 ppm in surface water. The highest average concentration of Cd was observed at station 1(0.0034 ppm) which is at a very high range compared to all other oceans. At Mandovi estuary high concentration of labile Cd was observed, which was associated with very high salinity (George *et al.,* 1984). In Bombay, an exceptionally high value of Cd was observed in the polluted coastal waters as to 0.08 ppm (Ganeshan *et al.,* 1984). In the Indian Ocean, an increase of Cd concentration with age of deep water can be observed on a large scale in the high deep-water concentration according to Danielson (1980). At station 1, the average concentration for the first year of study was 0.005 ppm and for the second year it was 0.0017 ppm and the highest value was observed in the post monsoon season. At station 2, the highest concentration was 0.0032 ppm in the monsoon months and the average for the first year was 0.0032 ppm and for the second year it was 0.0029 ppm. At station 3, the concentration of Cd ranged from 0.0027 to 0.0028 ppm, in station 4 from 0.00087 ppm to 0.0017 ppm, at station 5 from 0.0013 ppm to 0.00225 ppm, at station 6 from 0.0021 ppm to 0.0012 ppm and in station 7, it ranged from

0.0006 ppm to 0.00188 ppm respectively for the two years of study. Statistical analysis (ANOVA) has shown that there is significant variation in levels of Cd in water in different seasons ($p<0.01$), (Appendix IV, Table 4).

There are regional differences in the distribution of Cadmium in near shore waters with the highest concentrations being found in the waters around Japan and South Africa (Chester and Stoner, 1974). Relatively higher concentrations of Cd have been reported in coastal waters (0.0042ppm) around the British Isles (Abdulla *et al.,* 1972). The values recorded for South Atlantic and Indian Ocean are similar, and both average to 0.00007 ppm (Danielson, 1980). He found the range for the Indian Ocean as 0.00001-0.00016 ppm. Sanzgiri and Braganca (1981) found the range as 0.00015-0.0019 ppm.

The concentration of lead was the minimum in the coastal waters compared to all other metals studied. The concentration of Pb ranged from ND -0.002 ppm in station 1, from ND -0.001 ppm in station 2, from ND-0.001 ppm in station 3 and from ND – 0.002 ppm in station 4. At station 5 the concentration was ND -0.0025 ppm. Station 6 recorded values ranging from ND-0.001 ppm and in station 7 the range was ND- 0.0005 ppm respectively. The highest concentration was observed in monsoon followed by the post monsoon season. Comparing the data for the two years, the concentrations were higher in the second year of study for all the stations. A significant variation was not observed for Pb in water in different seasons of study

(Appendix IV, Table, 5). According to Orr and Marshal (1969), the values for Pb in seawater was 0.003 ppm and the EPA recommended safe level in seawater is 0.1 ppm. Concentrations of Pb obtained in the present study are very much same as that reported by Meenakumari (1988) where the concentration of Pb in Cochin harbour waters ranged from 0.0001 – 0.0075 ppm.

7.10 Trace metal in sediment in the off Cochin area

The present study revealed a predominance of silt and clay at all stations except in some months. High organic carbon recorded all the stations may be due to marine sedimentation and high rate of delivery from external sources (Shajan, 2001). The shallow silty clay nature of the stations noticed in the present study corroborates to this observation. High inputs of terrigenous materials from effluents and industrial activities could have increased the organic carbon values in the samples that are close to the shoreline. The results of analysis of trace metals in sediments are given in Fig 7. 6- 7. 8

The concentration of Cd in sediment ranged from 7.35 ppm – 17.2 ppm in station 1 where the highest value measured in the post monsoon season in 2002 (17.2 ppm). The average concentration of Cd for the study period at station 1 was 11.78 ppm. At station 2, the concentration ranged from 3.27 ppm-13 ppm lowest in the premonsoon of 2001 and highest being in the post monsoon of year 2002. At station 3, the concentration ranged from 1.85 ppm

– 14.37 ppm. In station 4 , the highest concentration was in post monsoon of 2002 (12.5 ppm) and the lowest in the pre monsoon period (4.5 ppm). Station 5 recorded maximum value of Cd during the post monsoon period (22 ppm) and Cd concentration was the highest in this station. Station 5 marked by the highest organic carbon content (5.7) lowest sand % (25%), highest clay content (35%). Cd concentration in station 6 ranged between 1.97 ppm to 12.5 ppm and the highest concentration was observed in the monsoon months. At station 7, the concentration of Cd ranged from 3.3 ppm to 17 ppm and the highest concentration was recorded in monsoon season. On comparing the concentration of Cd in the initial year of study with that of the second year it showed an increasing trend in all the stations. Analysis of variance showed that there is highly significant variation in copper in sediments in different seasons of study ($p< 0.01$) (Appendix IV, Table 6).

Copper concentration in station 1 ranged from 8.5 ppm in pre monsoon of 2001 to 32 ppm in the post monsoon of year 2002. At station 2, the concentration ranged from 3- 26.5 ppm and the highest value was recorded in post monsoon period. In station 3, the value ranged between 2.7 ppm to 27.6 ppm and the highest was recorded in monsoon season. At station 4, the range was 4.1-24.5 ppm, in station 5 from 4.94 ppm to 37 ppm, highest value being recorded in the post monsoon season. Cu was highest in station 5 in the post monsoon season. In station 6, the concentration ranged between 2.4 ppm to 14 ppm and the highest was in the monsoon season. At station 7, the

concentration ranged from 4.85 ppm to 17.5 ppm. The average concentration for the second year of study was greater than the initial year except in station 7. The average concentration for the entire period was highest in station 1 followed by station 5 where the value was 23.53 ppm and 16.16 ppm respectively. When comparing the concentration seasonally while taking the entire period of study, the highest values were observed in the monsoon season since the concentration of Cu in the post monsoon and pre monsoon season of the initial year of study was comparatively lower. A highly significant variation was observed for concentration of Cu in sediments in different seasons studied ($p< 0.01$) (Appendix IV, Table, 7).

Lead concentration in station 1 ranged from 4.1 ppm in post monsoon of 2000 to 124 ppm in the monsoon of year 2001. At station 2, the concentration ranged from 12.8- 133 ppm and the maximum value was recorded in monsoon period. In station 3 the values ranged between 20.5-ppm to127.6 ppm where the highest was recorded in monsoon season. At station 4 the range was 10.8-132.3 ppm, in station 5 from 17.8 ppm to 122.6 ppm, highest value being recorded in the monsoon season. Pb was highest in station 2 in the monsoon season. In station 6 the concentration ranged between 22.6 ppm to 113 ppm and the highest was in the monsoon season. At station 7, the concentration ranged from 12 ppm to 131 ppm. The average concentration for the initial year of study was greater than the second year except in station 3. The average concentration for the entire period was highest in station 3 followed by station

2 where the value was 72.3 ppm and 58.6 ppm respectively. Analysis of variance has shown that there is significant variation in concentration of Pb in sediments for the different seasons studied ($p< 0.01$) (Appendix IV, Table 8).

The heavy metal distribution in the sediments of the world coastal regions has been elaborately reported (Klein and Goldberg, 1970: Trefrey *et al.,* 1975; Helz and Simex., 1986; Holms, 1986, Subrahmanian and Mohanachandran, 1990: Ramachandran, 1990). Govindasamy *et al.*, 1997, reported concentration of Cu in sediments from the Coromondal coast as 0.99 ppm- 116.51 ppm, and the range in concentration of Cd in his study was ND-19.75 ppm. In the present study at station 5 the concentration of Cd was above this range. Zingde and Desai (1981) reported that in Bombay harbour the Cu concentration was 105 ppm and Cd 10 ppm. Coale and Johnson recorded 6.26 ppm of Cd in the monsoon season in the Coromondal coast. Patel *et al.* (1985) Reported concentration of Cu as 110 ppm and Cd 12 ppm. Daniel (1987) reported that the concentration of Cu in the Madras cost was 25 ppm. In the present study the maximum concentration of Cu is 32 ppm.

In the earlier studies the average concentration of Cu in sediment in the Cochin inner shelf was reported as 0.7 ppm, in the Cochin estuary 7.5 ppm and in the Cochin estuary (North) it was 0.7 ppm. The river Periyar that enters the estuary had a concentration of Cu 2.6 ppm and Muvattupuzha River had 0.6 ppm of Cd (Shajan, 2001). In the present study, the mean concentration of the studied trace metals for different season for the 2 years differed temporally,

and spatially there was no significant variation ($p>0.01$). This may be observed during the study period due to the similarity in the sources of heavy metals in this area (Murray and Murray, 1973). The statistical analysis ANOVA was done between stations and between different seasons and the result shows there is significant variation of Cadmium, Copper and Lead in the different seasons ($p<0.01$).

The metals were significantly higher in the monsoon and post monsoon periods. Such increased level of metals in the sediments have resulted due to monsoonal land run off (Athaley and Gokhale, 1989) and limited availability of heavy metals to the biota as result of the interaction of various physico chemical characters of the sediments. Further. the most obvious mechanism of adsorption of metals from the water column by the resuspended sediments followed by redeposition (Trefrey *et al.,* 1975, Lindberg *et al.,* 1975) might have increased the metal concentration in the surface sediments. Copper concentration was high in the monsoon and post monsoon season. Such variations may be due to the variations in the disposal of material containing Cu compounds, which are potential sources through the land run-off from the river Periyar to the estuary.

The organic carbon in station 1 ranged from 3.34- 6.2 and the highest was recorded at station 2 in the post monsoon season, the highest recorded value of organic carbon was 7.9 in the post monsoon period. The annual average of organic carbon was highest for station 5 followed by station 6 and

7(5.5, 4.94, 4.9) respectively. Percentage of sand in the different stations in the study period was highest in station 1 and lowest in station 5 (32.43% and 25.03%) respectively). The percentage of sand was lower in the post monsoon period and higher in the premonsoon season. At these stations, no significant correlation can be obtained for organic carbon concentration and concentration of heavy metals and also between percentage of silt, clay and sand with that of the concentration of heavy metals.

There are broadly 44 rivers and streams in Kerala. Though tinier in dimension, compared to the major rivers of the country, they drain a surprisingly large quantity of water and sediments into the Arabian Sea. This is due to the heavy rainfall and physical relief of the terrain of Kerala, which slants from the Western Ghats to the plains to finally merge with the Arabian Sea. A distinct characteristic of the rivers in Kerala is that they flow in an almost straight course, further facilitating drainage.

Among the 44 rivers in Kerala 41 are west flowing, and originate mainly from the Western Ghats. They fuse with the Arabian Sea either directly, or through the medium of the backwaters. Some smaller rivers, like the Kumbala, and Bekal, have separate watersheds, and drain into the sea through the channel of the backwaters. Periyar one of the important rivers in Kerala with a length of 244 km long covers a drainage area of 5,398 sq. km. Formed at a height of 1,853m, where a number of rivulets merge together in the Sivagiri Hills; the Periyar flows towards the north and later turns to the northwest, to

finally lose itself in the backwaters at Munambam in Ernakulam District. There are a large number of factories especially, fertilizer factories, oil refineries, rare earth processing factory, and Zn smelters on the banks of Periyar. Besides this, heavy sewage effluents from the Cochin city also add to the high concentration of trace metals in the area studied.

Table 7. 1 Trace metals in water (surface and bottom) from off Gujarat Cruise 181 (ppm)

	Surface				
Stn No	Cu	Pb	Hg	Zn	Cd
1	ND	0.122	0.074	0.140	0.0001
2	ND	ND	0.110	0.060	ND
3	ND	0.132	ND	0.026	ND
4	ND	0.267	ND	0.022	ND
5	ND	0.244	ND	0.004	ND
6	ND	0.343	ND	0.025	ND
	Bottom				
	Cu	Pb	Hg	Zn	Cd
1	ND	0.270	0.070	0.027	ND
2	ND	0.240	0.116	0.025	ND
3	ND	0.440	ND	0.005	ND
4	ND	0.460	ND	0.011	ND
5	ND	0.540	ND	0.002	ND
6	0.013	0.410	ND	0.032	ND

Table 7. 2 Trace metals in sediment from off Gujarat, Cruise 181 (ppm)

Stn. No	Cd	Pb	Cu
1	6.730	122.000	4.000
2	5.700	99.300	5.400
3	5.300	96.300	1.400
4	5.500	105.000	2.200
5	5.960	111.600	1.300
6	6.030	99.000	2.100

Table 7. 3 Trace metals in water from off Quilon to off Gujarat Cruise No.184 (ppm)

Stn. No	Cu	Cd	Zn	Pb	Hg
1	0.017	0.001	0.088	0.460	ND
2	0.032	0.005	0.035	0.420	ND
3	0.033	ND	0.037	0.520	ND
4	0.003	0.004	0.037	0.490	ND
5	0.001	0.007	0.108	0.440	ND
6	ND	ND	0.046	0.390	ND

Table 7. 4 Trace metals in sediment from off Quilon to off Gujarat Cruise No.184 (ppm)

Stn. No	Cu	Cd	Pb
1	1.800	1.060	25.900
2	8.630	2.600	54.000
3	21.360	4.960	97.000
4	2.200	6.100	115.000
5	1.300	2.300	42.000
6	23.060	11.600	99.000

Table 7. 5 Trace metals in water from off Quilon to Mangalore, Cruise No.191(ppm)

Surface

Stn. No	Cd	Ni	Cu	Hg	Zn
1	0.002	0.001	0.005	ND	0.050
2	0.0036	0.001	0.008	ND	0.019
3	0.004	0.010	0.017	ND	0.020
4	0.006	0.002	0.026	ND	0.010
5	ND	0.001	ND	ND	0.030
6	ND	0.001	ND	ND	0.010

Bottom

Stn. No	Cd	Ni	Cu	Hg	Zn
1	0.003	0.001	0.006	ND	0.003
2	0.010	0.001	0.010	ND	0.005
3	0.002	0.003	0.018	0.0001	0.010
4	ND	0.004	0.026	ND	0.005
5	ND	ND	ND	ND	0.010
6	ND	ND	ND	ND	0.005

Table 7. 6 Trace metals in sediment from off Quilon to Mangalore, Cruise No.191(ppm)

Stn. No	Cd	Pb	Cu
1	3.360	10.660	4.800
2	1.230	4.030	2.400
3	1.933	7.060	3.400
4	0.580	2.200	2.500
5	0.210	1.200	1.200
6	0.320	1.250	1.300

Table 7. 7 Trace metals in water from off Cochin to Mangalore, Cruise No.197(ppm)

surface

Stn. No	Cd	Ni	Cu	Hg	Zn
1	0.0004	0.002	0.001	ND	0.050
2	0.0003	0.003	0.005	ND	0.040
3	ND	0.001	0.002	ND	0.002
4	0.001	0.002	0.025	ND	0.005
5	0.001	0.003	0.030	ND	0.010
6	0.001	0.002	ND	ND	0.010

Bottom

Stn. No	Cd	Ni	Cu	Hg	Zn
1	ND	ND	ND	ND	0.010
2	ND	ND	ND	0.0001	0.020
3	0.008	ND	ND	ND	0.010
4	ND	ND	ND	ND	0.010
5	0.001	0.004	ND	ND	0.005
6	ND	0.002	ND	ND	0.005

Table 7. 8 Trace metals in sediment from off Cochin to Mangalore, Cruise No. 197(ppm)

Stn. No	Cd	Pb	Cu
1	2.200	12.300	5.200
2	0.590	5.200	2.400
3	1.100	8.000	3.600
4	1.200	1.200	2.500
5	0.500	2.500	1.780
6	0.500	2.100	2.500

Table 7.9 Trace metals in water from off Quilon to Mangalore, Cruise No. 204 (ppm)

Surface

	Cd	Cu	Pb	Ni	Zn
1	0.001	ND	ND	0.001	0.050
2	0.003	0.002	0.001	0.002	0.020
3	ND	ND	ND	0.001	0.010
4	0.001	ND	ND	0.005	0.060

Bottom

	Cd	Cu	Pb	Ni	Zn
1	0.002	0.001	ND	ND	0.020
2	ND	0.003	0.001	0.001	0.020
3	ND	0.001	ND	0.001	0.010
4	0.002	0.003	ND	0.001	0.010

Table 7. 10 Trace metals in sediment from off Quilon to Mangalore, Cruise No. 204 (ppm)

Stn. No	Cu	Cd	Pb
1	0.500	3.500	15.000
2	0.600	0.850	20.300
3	0.200	0.900	0.001
4	1.000	0.250	0.300

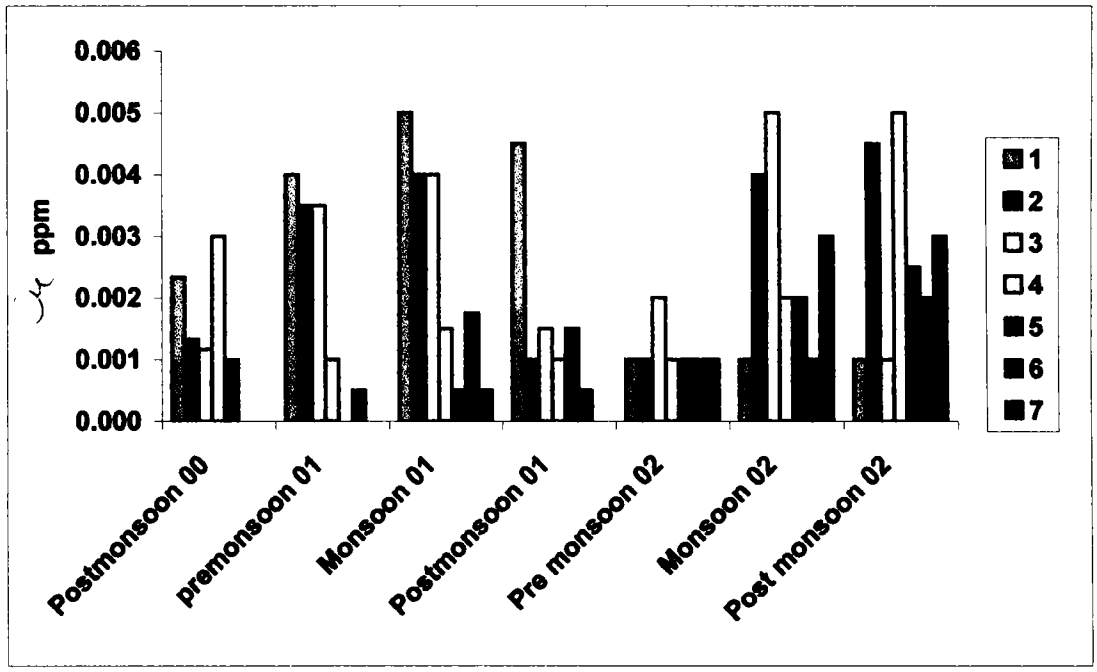


Fig 7.1 Concentration of copper in surface water (ppm) during 2000-2002

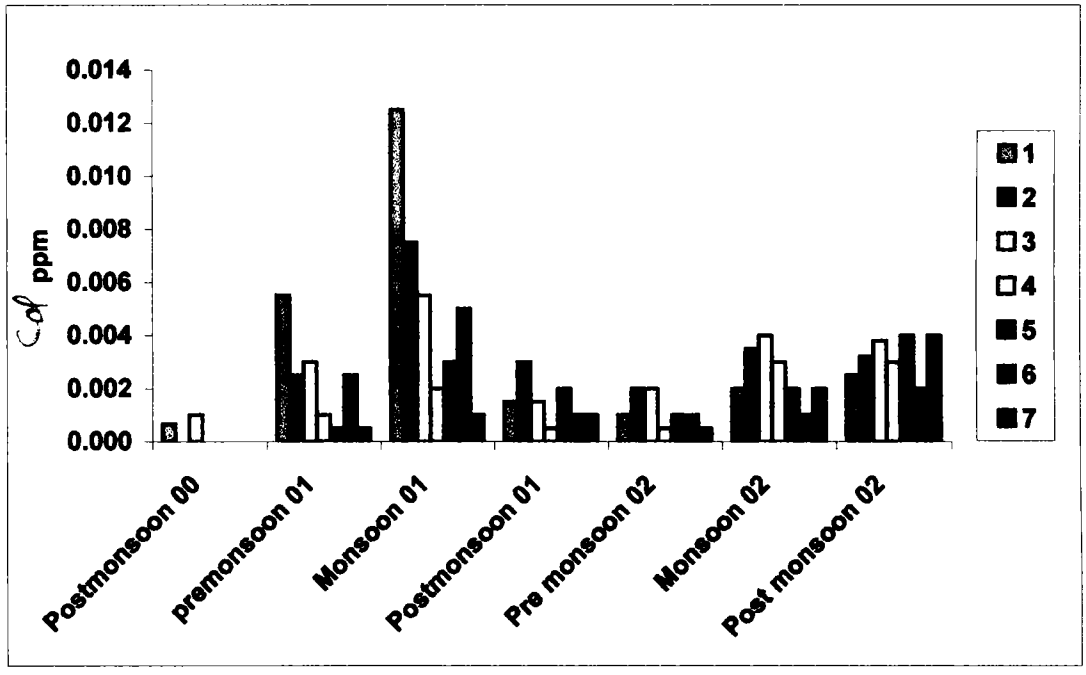


Fig. 7.2 Concentration of cadmium (ppm) in surface water during 2000-2002

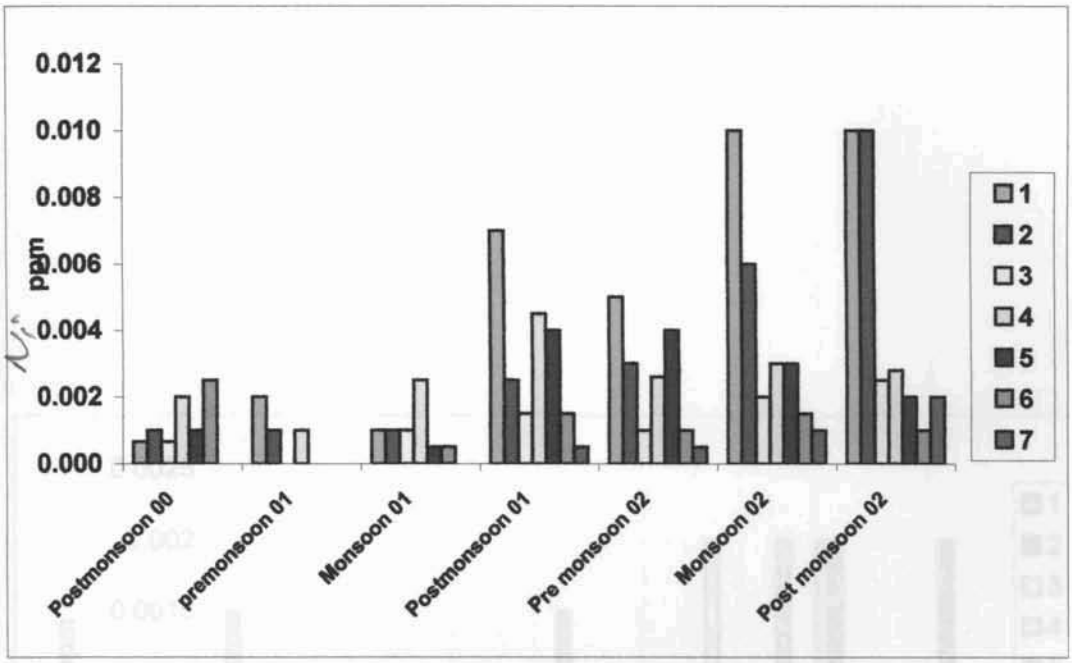


Fig. 7.3 Concentration of nickel in surface water (ppm) from 7 stations in off Cochin during 2000-2002

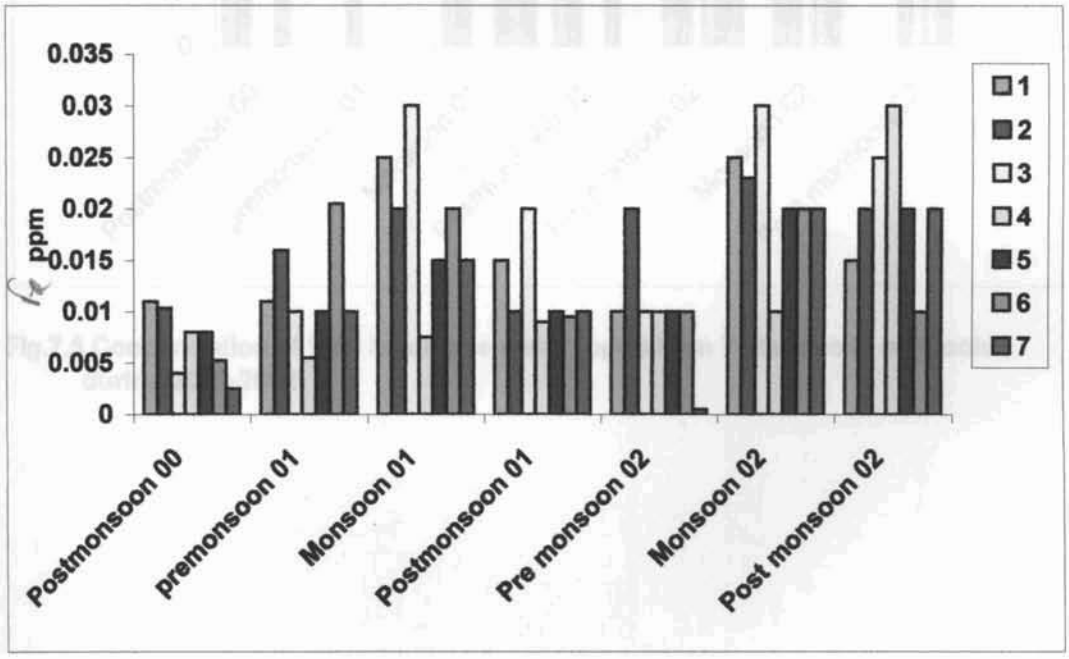


Fig.7. 4 Concentration of Iron in surface water (ppm) from 7 stations in off Cochin during 2000-2002

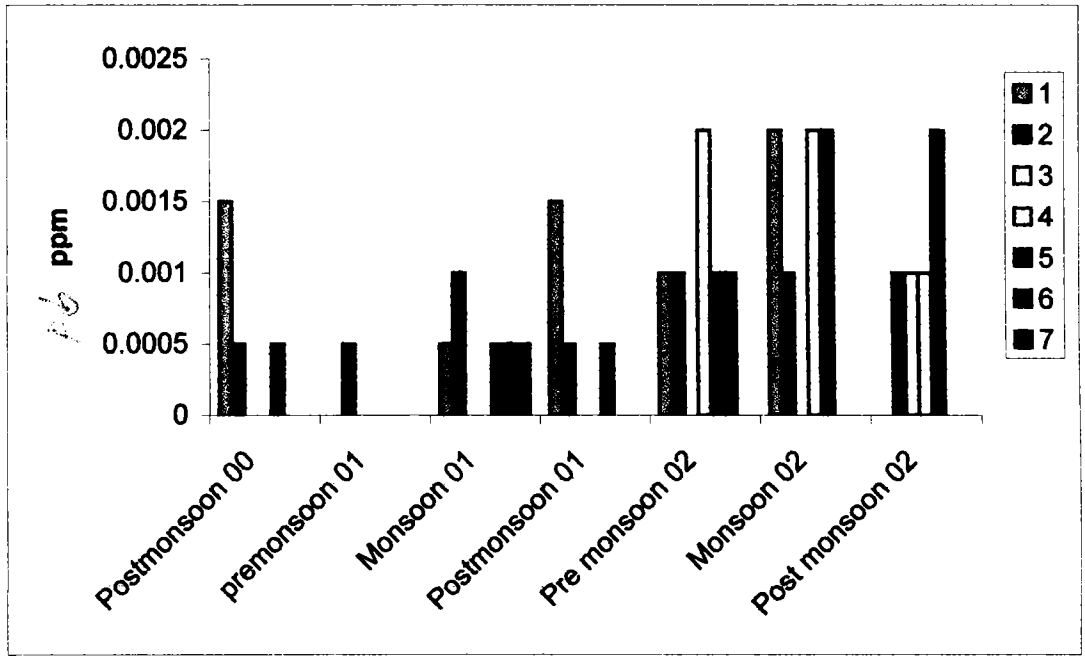


Fig.7.5 Concentration of lead in surface water (ppm) from 7 stations in off Cochin during 2000-2002

APPENDIX III

Table 1 Results of two- way ANOVA on Zn in surface& bottom water from different stations (Cruise 181)

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	0.01688975	5	0.003378	0.270424576	0.911230378	5.050338814
Columns	0.361574083	1	0.361574	28.94611176	0.002989952	6.607876912
Error	0.062456417	5	0.012491			
Total	0.44092025	11				

Table 2 Results of two- way ANOVA on Pb in surface& bottom water from different stations (Cruise 181)

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	0.018572667	5	0.003715	0.264610621	0.914569712	5.050338814
Columns	0.070840333	1	0.07084	5.046422499	0.074610774	6.607876912
Error	0.070188667	5	0.014038			
Total	0.159601667	11				

Table 3 Results of two- way ANOVA on Cd in surface& bottom water from different stations (Cruise 181)

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	0.007983667	5	0.001597	1.683015951	0.290847321	5.050338814
Columns	0.000560333	1	0.00056	0.590612044	0.476892871	6.607876912
Error	0.004743667	5	0.000949			
Total	0.013287667	11				

Appendix IV

Table 1. Results of two- way ANOVA on copper in water (off Cochin) in different seasons

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	2.08229E-05	5	4.1646E-06	5.6309859	0.010032114	3.32583738
Columns	3.8125E-06	2	1.9062E-06	2.5774648	0.125092245	4.10281586
Error	7.39583E-06	10	7.3958E-07			
Total	3.20313E-05	17				

Table 2. Results of two - way ANOVA on iron in water (off Cochin) in different seasons

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	0.000349979	5	6.9996E-05	2.2420789	0.081466606	2.60298805
Columns	0.000705229	5	0.00014105	4.5179244	0.004525844	2.60298805
Error	0.000780479	25	3.1219E-05			
Total	0.001835687	35				

Table 3. Results of two- way ANOVA on nickel in water in different seasons

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	4.59847E-05	5	9.1969E-06	4.4944751	0.004651282	2.60298805
Columns	3.95747E-05	5	7.9149E-06	3.8679717	0.009841638	2.60298805
Error	5.11569E-05	25	2.0463E-06			
Total	0.000136716	35				

Table 4. Results of two- way ANOVA on cadmium in water (off Cochin) in different seasons

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	2.30092E-05	5	4.6018E-06	4.0538834	0.00784873	2.60298805
Columns	3.79792E-05	5	7.5958E-06	6.6913816	0.000440952	2.60298805
Error	2.83792E-05	25	1.1352E-06			
Total	8.93675E-05	35				

Table 5. Results of two way ANOVA on lead in water (off Cochin) in different seasons

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	2.47619E-06	5	4.9524E-07	1.81395349	0.14022215	2.53355381
Columns	2.66667E-06	6	4.4444E-07	1.62790698	0.173901246	2.42052067
Error	8.19048E-06	30	2.7302E-07			
Total	1.33333E-05	41				

Table 6. Results of two way ANOVA on copper in sediments (off Cochin) in different seasons

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	433.8252806	5	86.7650561	2.80143771	0.038383202	2.60298805
Columns	2374.087531	5	474.817506	15.3307302	6.31822E-07	2.60298805
Error	774.2904278	25	30.9716171			
Total	3582.203239	35				

Table 7. Results of two way ANOVA on cadmium in sediments (off Cochin) in different seasons

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	34.76205556	5	6.95241111	1.34518419	0.278212983	2.60298805
Columns	1022.629556	5	204.525911	39.5726055	4.32498E-11	2.60298805
Error	129.2092778	25	5.16837111			
Total	1186.600889	35				

Table 8. Results of two way ANOVA on lead in sediments (off Cochin) in different seasons

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	3127.233333	5	625.446667	1.54396203	0.235390067	2.9012952
Columns	26285.82125	3	8761.94042	21.6295074	1.05553E-05	3.28738281
Error	6076.38	15	405.092			
Total	35489.43458	23				

Chapter 8

TRACE METALS IN FISH

8.1 Introduction

Many outbreaks of food poisoning due to marine products containing excess amounts of toxic metals like mercury; cadmium, lead, etc. have caused increasing concern among scientists and public health authorities about the quantities of these heavy metals in fish and other marine organisms. Marine pollution studies have been reported from Japan (Nitta, 1972) Australia (Gilmour, 1972) Philippines (Lesaca, 1972) and many other parts of the world. In India Ramamurthy, (1979) and Desai *et al.* (1975) have reported levels of mercury in fishes and prawns from various sources. Heavy metal concentrations in some common edible fishes from Bombay and upper east coast have been reported by Khot *et al.* (1985) and Prasad *et al.*(1990). Lakshmanan (1988, 2003) studied the level of Cadmium in seafoods of Kerala coast. Prafulla (2004) studied the heavy metal concentration in cephalopods from the Indian coast. The studies concerning the trace metals in edible fishes from the Indian coast are limited. Imam Khasim *et al.* (1994) analysed the levels of toxic metals in the tissues of some fishes caught during the 56^{th} cruise of FORV Sagar Sampada in the Andaman Sea. Renjith *et al.* (2003) reported the concentration of metals in two species of tuna caught from the Arabian Sea. Radhakrishnan, (1993) studied the concentration of heavy metals in fish and shellfish. In the present study trace metals Cu, Cd and Pb in four species of edible fishes obtained from the west coast of India are studied.

Their tissue levels are compared with that in the surrounding seawater and sediment.

8.2 Materials and Methods

The details of sample collection, sample preparation and determination of metal levels in them by Inductively Coupled Plasma Emission Spectrometer and procedure adopted are described in detail in chapter 2. Statistical analysis was carried out using two- way ANOVA to determine the significant variations if any between different stations and seasons. Correlation analysis was also carried out for comparing the levels of the metals in various trophic levels.

8.3 Results and Discussion

Concentration of heavy metals namely cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn), nickel (Ni) and mercury (Hg) in fish tissues were analysed and the results are presented in Table 8.1-8.10 and Fig. 8.1 – 8.5

8.3.1 Trace metals in fish from off Gujarat area (Pre monsoon season) Cruise No 181.

The results of analysis of trace metals in fishes are given in Table 8.1 and 8. 2. In the three species of fishes analysed, concentration of Cu in the muscle tissue ranged from 0.8 ppm in *Nemipterus japonicus sp.* to 3.3 ppm in *Saurida tumbil.* Gill and liver tissues accumulated more Cu than the muscle

tissue (Fig. 8.1). Concentration of Cd in the muscle tissue ranged from ND to 0.5 ppm, highest was observed in *Epinephelus diacanthus*. Level of lead in muscle tissue ranged from 0.35 ppm in *Epinephelus sp.* to 3.37ppm in *N.japonicus*. Comparing the levels of trace metals in whole tissue of fish from various stations (Fig. 8.2), it has been shown that the levels were higher in station 1. Samples from station 4 and 3 showed lower levels of Cd, Pb and Cu in whole tissue. Copper concentrations in fishes were correlated with that in sediment, and a significant positive correlation existed between the level in *Epinephelus diacanthus* and the level in sediment (r=0.54), and between concentration in sediment and that in *Nemipterus japonicus* (r = 0.91). Concentration of Cd in *Saurida tumbil* showed strong positive correlation with that in the sediment (r= 0.83). Pb in the whole tissue of *Saurida tumbil* showed significant positive correlation with that in the sediment. Concentration of Pb in *Nemipterus japonicus* in the present study also showed significant positive correlation with the concentration in sediment. The concentration of the three metals studied in the whole tissue was highest in the *Saurida tumbil* followed by *Epinephelus diacanthus* and then by *Nemipterus japonicus*.

Copper is an essential element in human nutrition and the daily dietary requirement is 2-3 mg for an adult of 23-50 years (Anon,1980, Gopalan *et al.*, 1989). It has been reported by Mckee and Wolf (1963) that Copper is toxic to man in quantities above 100 mg. However, copper poisoning as a result of

eating copper containing marine organisms is unlikely because their taste at these levels renders them unpalatable (Imam Khasim, 1994). Human taste threshold for copper is about 5-7 ppm (Portman, 1970). The fishes studied here form safe sources of copper in the diet. In all the species the level of copper content was in the following order liver> gills> muscle.

The distribution pattern of Zn among the body parts clearly indicated that liver in the three species form the major site of Zn accumulation. The concentration in muscle varied from 1.3 ppm in *Nemipterus japonicus sp*- 28.5 ppm in *Saurida tumbil*. Zinc concentration in different organs is in the order liver > gill>muscle. In general the edible muscle show relatively low levels of Zn. Zn in the fish samples accumulated in the order *Saurida tumbil* > *Epinephelus diacanthus*> *Nemipterus japonicus*. The high concentration of zinc in the muscle of the fish samples is mainly due to the presence of a large number of fishing vessels and trawlers which use galvanized metal coatings to prevent rusting, that ultimately find it's way into the ambient media through leaching.

Cadmium accumulation showed the order *Epinephelus*> *Saurida tumbil* >*Nemipterus japonicus sp.* Concentration of Cd in the muscle ranged from below detection limit to 0.5 ppm. In the case of Cd also liver showed higher concentration. A study of fish from the Great Barrier Reef in Australia shows

that Cd in liver exceeded 20 mg/kg (Denton and Jones, 1986). High contents of Cd (0.213 and 0.402 ppm) were reported in squid and cuttle fish by Lakshmanan (1998) from west coast of India. Ashajyothy and Vijayalekshmi (1999) reported levels of Cd ranging from 0.06- 0.4 ppm in the edible muscle of fishes from Thane creek. The range in concentration obtained in the present study correlate well with this value. A metal like cadmium is low in juvenile stages but it is accumulated with age. The higher concentration of Cd in liver compared to gill and muscle shows that the main route of uptake of cadmium is through food and water. Numerous sub-acute effects have been reported in both fresh water and marine fishes like decreased growth, morphologic changes in the gut etc. due to Cd toxicity (Moore and Ramamoorthy, 1984). Reports show that chronic exposure to Cd in human beings lead to renal toxicity, such as proteiurea. A tissue residue in excess of 0.285 mg/g usually causes renal dysfunction. The daily allowed dietary allowance for Cd per kg weight for a man is given by FAO/WHO (1975) as 0.95 mg. The permitted tolerance limit for Cd in fish is 0.2-2 ppm (FAO, 1983). In all the species studied from this area, the level of Cd in the edible part is below 2 ppm. This does not pose any threat to human health.

Organic complexes of lead are more toxic to marine fish. Experimental evidence exists for the carcinogenicity of inorganic lead following oral ingestion at high doses in rat (Moore and Ramamoorthy, 1984). In the study by

Lakhsmanan (1994) in cephalopods, the lead content was >1mg/kg. Radhakrishnan (1993) reported level of lead below 7 ppm in deep sea fish collected onboard FORV Sagar Sampada. The values of Pb obtained for lead in the present study correlates well with this.

Hg was detectable in the muscle tissue of *N.japonicus* where the value was 0.21ppm. The earlier reported value for Hg in fishes from the Indian Ocean ranged from 0.005-0.093 ppm (Desai *et al.*, 1975) and from 0.006-0.07 ppm (Radhakrishnan, 1993). The value for Hg obtained for *N.japonicus* in the present study is slightly higher than the earlier reported values by Imam Khasim (1994), which ranged from ND to 0.01 ppm wet weight and by Desai *et al.* (1975), where the concentration of Hg ranged from 0.005 to 0.093 ppm in different varieties of fish and shell fish from different coastal regions of India. But the concentrations of Hg obtained in the present study are below the limits permitted for seafoods. The permitted tolerance limit for Hg in fish is 0.5-1ppm (FAO, 1983). So the metals studied in the fish muscle were well below the permitted levels. Concentration of the studied metals in water, sediment and whole soft tissue from different stations are presented in Fig. 8.3.

8.3.2 Trace metals in fish from off Quilon to off Gujarat area (monsoon season) Cruise No 184

The concentration of trace metals in various fish tissues and whole soft tissue from different stations are presented in Table 8.3, 8.4 and Fig. 8.4 and

8. 5. Even though Cu is an essential element in human nutrition, it is one of the most toxic metals to fishes in higher concentrations. Studies have shown that the LC_{50} for Cu range from 0.02 to 1 mg/l in fresh water. Toxicity is enhanced synergistically by combinations of Cu/Cd/Zn and Cu/Cd/Ni/Zn (Moore *and* James, 1992). Copper residue in fish muscle tissue is generally low. Ashraf and Jaffer (1998) working on 6 species from the Arabian Sea recorded muscle levels of only 0.10-0.51 mg/kg weight. In the three species of fish analysed, concentration of Cu in the muscle tissue ranged from 0.23 ppm in *Epinephelus diacanthus sp.* to 3.5 ppm in *Saurida tumbil.* Gill and liver tissues accumulated more Cu than the muscle tissue. The concentration in liver of *Saurida tumbil* was the highest (88 ppm), followed by that in *Nemipterus japonicus* (35.8 ppm). Cu concentration in the gills was lower than that for the muscle and liver. The recommended daily allowance of Cu is 1mg. Many nations use a standard for the lowest observed adverse effect level in man for Cu as 5.3 mg per day (Federal Register, 1985).

The fishes studied here form safe sources of copper in the diet. In all the species Copper content was in the following order liver > muscle> gills. Zn concentration was higher in liver in the three species. Irrespective of the species caught, generally the liver showed the highest concentration of any given metal. Hellou *et al.* (1995) reported higher concentration of Hg in the liver of cod and explained that it reflects the different rates of metabolism and or elimination by different fish tissues. Higher levels of metals in liver also

indicate that the most of the metals were accumulated in the fishes in a fat-soluble form. Concentration of Zn in muscle varied from 7.5 ppm in *Nemipterus japonicus* to 16.1 ppm in *Saurida tumbil*. Zinc concentration in different organs is in the order liver > gill>muscle. In general the edible, the muscle showed relatively low levels of Zn. Zn in the fish samples accumulated in the order *Saurida tumbil* > *Epinephelus diacanthus*> *Nemipterus japonicus*.

Cadmium accumulation in muscle showed the order *Saurida tumbil* >*Nemipterus japonicus* > *Epinephelus diacanthus*. Concentration of Cd in the muscle ranged from below detection limit to 0.36 ppm. In the case of Cd also liver showed maximum concentration. Metals like cadmium is low in juvenile stages but it are accumulated with age. The size and maturity stage of the fishes influence its accumulation levels. Cd concentration in the muscle tissue is found to increase with the size of the fishes (Latha *et al.*, 2003). Many of the fish samples have attained full maturity during the study period. The higher concentration of Cd in liver compared to gill and muscle shows that the main route of uptake of cadmium is through food and water. The permitted tolerance limit for Cd in fish is 0.2-2 ppm (FAO, 1983). In all the species studied from this area the level of Cd in the edible part is below 2 ppm. This does not pose any threat to human health.

Level of lead in muscle tissue ranged from 1.2 ppm in *Saurida tumbil* to 4.29 ppm in *N.japonicus*. The permitted levels of Pb in fish and fishery products in India are 5 ppm. The edible part of the fishes studied here contains levels well below this. Maximum permitted Hg concentrations in marine organisms for the majority of the Mediterranean countries and in India lie between 0.5-0.7 ppm wet weight (FAO/ WHO, 1975). Highest value of Hg detected in this study was 0.27 ppm for the edible part of the fish. This range was similar to that reported by Kureishy *et al.* (1979). He reported values ranging from 0.09 to 0.21 ppm of Hg (wet weight basis) in marine fishes from the Indian Ocean and it was quite low to reflect any possible contamination. The concentration of Cd in the whole tissue was high in station 3 and station 2 in *Saurida tumbil* (1.2 ppm) and the lowest was at station 4. Stations 2 and 3 are in the off Quilon and off Cochin area. The concentration of Copper was the highest in station 3 (42.5 ppm). A comparison of levels of the Cd, Cu and Pb in seawater, sediments and fish are given in Fig. 8.6. A significant correlation could not be made between the levels in fish and those in its environments. Different ecological and biological factors control concentration of trace metals in fishes. In the area studied there is notable influence from the Ashtamudy Lake and Attingal river (8° 42' N; lat 76° 09' E long.) which carry the sewage and industrial effluents from Kollam city and it might contribute to the heavy metal load in seawater.

8.3.3 Trace metals in fish from off Quilon to Off Manglore (monsoon season) Cruise No 191

The results of analysis of trace metals in various fish tissues and whole tissues from different stations are given in Table 8.5, 8.6 and Fig. 8.7 and 8.8. Concentration of Cu in muscle tissue of *Nemipterus japonicus* was 5.5 ppm, *Epinephelus sp* was, and 8.5 ppm and *S. tumbil* was 30 ppm. Copper concentration was slightly higher than that reported earlier by Radhakrishnan (1993). The copper content in the liver varied widely. Liver contained the highest concentration in all the three species (20- 152 ppm). Concentration of Zn in the muscle tissue of *S. tumbil* was also high (52 ppm) and the corresponding concentration in liver was 320 ppm. The order of accumulation of Cu and Zn in the tissues were liver > gill > muscle. The highest concentration of Cd in edible muscle was in *E. diacanthus* (0.8 ppm). Concentration of Pb in the muscle varied from 1.2- 2.2 ppm. Highest concentration of Hg was observed in *N. japonicus* (0.01ppm). Concentration of Cd in the whole soft tissue ranged from 0.5 in *Epinephelus diacanthus* to 1.2 ppm in *Saurida tumbil*. Higher concentrations were observed in samples from off Manglore and off Quilon area. Concentration of Pb and Cu in whole soft tissue was greater in stations near off Cochin. Similar observations of higher concentration of Pb and Cu in Cephalopods from off Cochin area have been reported by Prafulla (2002). Concentrations of Pb in whole tissue varied from 1- 3.2 ppm and concentration of Cd in whole tissue ranged from 0.5- 1.2 ppm.

Concentration of the studied metals in seawater, sediments and fishes from the area are represented in Fig. 8.9. Compared to the levels in water and in sediment the levels in fish tissues were higher.

8.3.4 Trace metals in fish from off Cochin to off Manglore (Pre monsoon season) Cruise No 197

The results of analysis of trace metals in various fish tissues and whole soft tissues from different stations are given in Table 8.7, 8.8 and Fig. 8.10 and 8.11. Concentration of Cu in muscle tissue of *Nemipterus japonicus* was 3.2ppm, in *Epinephelus diacanthus* it was 1 ppm and in *S.tumbil* the concentration was 5.8 ppm. Copper concentration was slightly higher than that reported earlier by Radhakrishnan (1993). Liver contained the highest concentration in all the three species. In liver the concentration was 55 ppm in Saurida tumbil, 48 ppm in *Nemipterus japonicus* and 76 ppm in *Epinephelus diacanthus*. The corresponding concentrations in the gill were 12.5 ppm, 10.3 and 33.1ppm respectively. In the edible muscle Cd was the highest in *Epinephelus diacanthus* and the concentration was 0.8 ppm. In *Saurida tumbil* the concentration of Cd was 0.45 ppm and in *Nemipterus japonicus* it was 0.1 ppm. Concentration of Pb in the muscle was also high and the highest concentration was in *Saurida tumbil* (3.5 ppm) and the lowest in *Nemipterus japonicus* (1.2 ppm). Hg was present only in the muscle tissue of *Saurida tumbil* (0.002ppm)

At station 5 in off Manglore area, the concentration of Cd in the whole tissue of the fishes was higher. Concentration of Cu in the whole tissue was higher in station 3 in the off Cochin area. Accumulation of all the studied elements in whole tissue was in the order *Saurida tumbil* > *Nemipterus japonicus* > *Epinephelus diacanthus* except in some stations and the tissue wise distribution of trace metals was in the order liver> gill> muscle. The relative concentration of trace metals in seawater, sediment and fish are given in Fig. 8. 12

8.3.5 Trace metals in fish from off Quilon to off Manglore (post monsoon season) Cruise No 204

Trace metal concentration in fish tissues and the whole soft tissue are given in Fig. 8.13 and Table 8.9, 8.10. Concentration of Cu in muscle tissue of *Nemipterus japonicus* was 3.5 ppm, in *Epinephelus sp.* it was not detectable and in *Saurida tumbil* the concentration was 17.6 ppm. The copper content in the liver varied widely. Liver contained the highest concentration in all the three species followed by gills. In liver, the concentration was 20.2 ppm in Saurida tumbil, 35.5 ppm in *Nemipterus japonicus* and 12.5 ppm in *Epinephelus diacanthus*. The corresponding concentrations in the gill were 17.4 ppm, 12.5 ppm and 10 ppm respectively. Cd in the muscle tissue was observed only in *Saurida tumbil* (0.8 ppm). In the liver, the concentration was 2.2 ppm in *Saurida tumbil*, 5.2 ppm in *Epinephelus diacanthus* and 0.8 ppm in *Nemipterus japonicus sp.* Concentration of Pb ranged from 1- 1.5 ppm in the

muscle tissue of the three species studied. In liver, the concentration of Pb was 1.1 ppm, 2.2 ppm and 1.5 ppm in *Saurida tumbil, Epinephelus diacanthus, and Nemipterus japonicus* respectively. Zn concentration varied from 12.5 ppm in *Saurida tumbil* to 1.3 ppm in the muscle tissue of *Epinephelus diacanthus*. Ni was non detectable in *Epinephelus diacanthus* and its concentration was 3.3 ppm in *Saurida tumbil*.

At station 1, the concentration of Cd in the whole tissue of the fishes were higher. Concentration of Cu in the whole tissue was also higher in station 1. Accumulation of all the studied elements in whole tissue was in the order *Saurida tumbil* > *Nemipterus japonicus* > *Epinephelus diacanthus* except in some stations. The levels of the studied metals in seawater, sediments and fishes are given in Fig. 8.14. At stations 1 and 2 the levels of the metals studied were higher in fish tissues than that in the seawater and sediments from the same area.

8.4 Trace metals (Cadmium, Copper and Lead) in fish collected from the Cochin Coast

The trace metal distributions in the three species of fishes in the various seasons of study are given in Fig. 8.15-8.20.

8.4.1 Cadmium

Cadmium content in the whole tissue of the *Nemipterus japonicus* was <3 ppm in all the seasons (Fig.8.15). The average concentration of Cd in the

study period in the whole tissue of *Epinephelus diacanthus* was 0.693 ppm, in Sciaenids it was 1.009 ppm and in *Nemipterus japonicus* it was 0.773 ppm. The highest concentration of Cd in the whole tissue was observed in Sciaenids in the post monsoon season (2.2 ppm). The average concentration of Cd in the edible muscle in *Epinephelus diacanthus* was 0.24 ppm, in Sciaenids it recorded 0.22 ppm and in *Nemipterus japonicus* the concentration registered 0.21 ppm (Fig 8.16). When the level in the first year of study was compared with that of the second year, there was a gradual increase in concentration for the second year. A significant variation was observed in the concentration of Cd in the edible muscle and whole soft tissue of three species of fishes studied ($p< 0.05$) (Appendix V, Table 1a and 1b). Cd was higher in whole soft tissue in the pre monsoon season and higher levels in edible muscle were observed in monsoon and post monsoon season. Similar observations were made Prafulla (2002) in *Loligo duvauceli.* The permitted tolerance limit for Cd in fish is 0.2-2 ppm (FAO, 1983). In all the species studied from this area the level of Cd in the edible part is below 2 ppm. This does not pose any threat to human health.

The concentration of Cd in the muscle tissue of the fishes in the present study agrees with that done by Radhakrishnan (1993). He reported levels 0.17 ppm- 1.86 ppm Cd in edible muscle of various marine fishes. Imam Khasim (1994) reported 0.25 ppm of Cd in *Epinephelus diacanthus* and 0.20ppm in

Nemipterus japonicus. Statistical analysis of Variance (ANOVA) was carried out and the results showed that there is significant variation in the concentration of Cd in the whole tissue and in the edible muscle in the fishes studied ($p< 0.01$) (Appendix IV, table 1 a & 1b) in different seasons.

8.4.2 Copper

Elevated levels of Cu were seen in the whole tissue of fishes through out the study period (Fig. 8.17). The mean copper content in the whole tissue of *Epinephelus diacanthus* was 8.9 ppm, in Sciaenids it was 5.4 ppm and in *Nemipterus japonicus* it was 9.36 ppm. The levels were higher in the post monsoon seasons in all the fishes studied, a maximum of 15.3 ppm was observed for *Epinephelus diacanthus,* 8.63 ppm in Sciaenids and 16.12 ppm *Nemipterus japonicus* sp. In the muscle tissue (Fig. 8.18) of *Epinephelus diacanthus*, concentration of Cu varied from 2.3 ppm – 5.2 ppm, in *Nemipterus japonicus* the edible muscle contained levels ranging from 1 ppm- 4.2 ppm of Cu. In Sciaenids the concentration of Cu in edible muscle ranged from 1.2 ppm to 5.1 ppm. Maheswary *et al.* (1997) reported Cu in muscle tissue of fishes from coastal waters of Cochin, which ranged from Non detectable levels to 4.63 ppm. The results of the present study compared well with that reported by the referred author. A significant variation was observed in the concentration of Cu in fish muscle for various seasons ($p<0.05$). Higher values of Cu were observed in post monsoon season. Higher ability to accumulate Cu in whole soft tissue by *V. cyprinoids*, *M. casta* and *P. viridis* during post

monsoon season was observed by Lakshmanan (1982) and Prafulla (2002). The concentration of Cu in muscle tissue of edible fishes in the present study is slightly higher than that reported by Radhakrishnan (1993) which ranged from 0.5-3.30 ppm and by Imam Khasim (1994) which ranged from 0.84 ppm in *Nemipterus sp* to 4.25 ppm in *Leognathus sp.* But the levels of Cu in edible parts of the fishes in the present study are well below the permitted levels of Cu in fish and fishery products in India, (10 ppm)(FAO, 1983). Analysis of Variance showed that there is significant variation in the concentration of Cu in the edible muscle tissue in different seasons ($p < 0.05$), (Appendix IV Table 2a &b).

8.4.3 Lead

Concentration of Pb in the edible muscle tissue of *Epinephelus diacanthus* ranged from 1.2-2.3 ppm, in Sciaenids it was 2.3 ppm –5.1 ppm, and in *Nemipterus japonicus* the level was 1.9 ppm –5 ppm (Fig. 8.20)

In the whole tissue of *Epinephelus diacanthus* concentration of Pb ranged from 2 ppm – 9.1 ppm, in Sciaenids the level ranged from 3 ppm – 5.8 ppm, and in *Nemipterus japonicus* the range was from 2 ppm – 6.5 ppm (Fig.19). The permitted levels of Pb in fish and fishery products in India are 5 ppm. In *Nemipterus japonicus and* Sciaenids during the monsoon season the level of Pb reached 5 ppm. The edible part of the other fishes studied here contains levels well below this. Statistical analysis of variance showed that

there was no significant variation in the concentration of lead in the fish tissue in different seasons (Appendix IV, Table 3a & b).

It is evident from the study that the concentration of the studied elements showed highest values in fish, sediment and water in the monsoon and post monsoon seasons. According to Philips (1980) the factors that are responsible for seasonal change of metals in the biota are pollutant delivery, organism physiology and water quality like temperature and salinity (Prafulla, 2002). Seasonal variation was observed in trace metal concentration in water and sediment and the higher concentrations were recorded during the monsoon and post monsoon period were salinity and pH were lower in water and pollutant input from rivers were higher. But a significant correlation could not be drawn between the levels of the metals in water sediment with that in fishes in the various seasons of study. It has been shown (Philips, 1980) that the variations in microelement composition of commercial fishes, although significant, are smaller than could have been expected from the variability of the chemical composition of the environment, food types and ecology of the fish studied. In many cases no significant differences could be observed between the contents of the individual metals in marine fish, diadromous fish and fresh water fish. Variability in metal concentrations in fish could be as a function of their sexual maturity (Oomen,1977). A greater number of mature fishes were obtained in August to January, reproductive cycle (as reproduction

is accompanied by many biochemical changes in the tissues) causing changes in the affinity of lipids, proteins and carbohydrates in fish tissues to the metals.

It is immediately apparent that the average metal concentration in inland sea fish is higher than in oceanic species. Thus for instance the average concentration of Cd in the fishes obtained from off Gujarat and off Manglore are lower than that obtained from the near shore samples from Off Cochin area.

The recorded range in the edible muscle of the different species of fishes from the different locations studied indicated that the levels had exceeded the permissible level prescribed for consumption in some samples mainly from the near shore locations especially in the off Cochin area where in other samples the levels were below he threshold limit designated for human consumption. The results indicated that wide variations in the levels of metals between species. Compared to muscle the concentration in the gill and liver was higher. The comparatively lower concentrations in fish muscle were reported by Kureishy *et al.* (1983) and Harding and Goyette (1989). Though the input of anthropogenic pollutants into the system has not affected the levels of metals in edible muscle in an alarming extent, this baseline data can be used for regular ecological monitoring considering the industrial growth along the studied area.

Table 8.1 Heavy metals (ppm wet weight) in various tissues of fishes collected from off Gujarat (Cruise 181)

	Muscle				
Species	**Cu**	**Zn**	**Cd**	**Pb**	**Hg**
Saurida tumbil	3.3	28.5	0.08	1.45	ND
Nemipterus japonicus	1.5	1.3	ND	3.37	0.21
Epinephelus diacanthus	0.8	2.5	0.5	0.35	ND
	Liver				
Saurida tumbil	110	235	0.75	5.8	ND
Nemipterus japonicus	20.5	98.3	0.2	0.1	ND
Epinephelus diacanthus	70.6	210.5	0.95	0.5	ND
	Gill				
Saurida tumbil	8.5	100.5	0.05	0.1	ND
Nemipterus japonicus	9.5	57.8	0.3	0.1	ND
Epinephelus diacanthus	3.5	85.5	0.1	0.3	ND

Table 8.2 Heavy metals (ppm wet weight) in whole tissue of fishes from the study area off Gujarat (Cruise 181)

Stn.1	**Cd**	**Pb**	**Cu**
Saurida tumbil	1.1	5.8	88
Nemipterus japonicus	0.8	4.8	21.3
Epinephelus diacanthus	0.9	0.5	78.3
Stn. 2			
Saurida tumbil	0.8	5	35.5
Nemipterus japonicus	0.9	3.5	21
Epinephelus diacanthus	0.8	1.1	77
Stn. 3			
Saurida tumbil	0.5	4.2	48.9
Nemipterus japonicus	0.6	3.3	22
Epinephelus diacanthus	0.9	2	65
Stn. 4			
Saurida tumbil	0.9	5.2	22
Nemipterus japonicus	0.86	4	18.2
Epinephelus diacanthus	0.78	2.3	15.2

Table 8.3 Heavy metals (ppm wet weight) in various tissuesof fishes collected from Quilon-Gujarat (Cruise 184)

	Muscle				
Species	**Cu**	**Zn**	**Cd**	**Pb**	**Hg**
Saurida tumbil	3.5	16.1	0.36	1.2	ND
Nemipterus japonicus	2.2	7.5	0.2	4.29	0.27
Epinephelus diacanthus	0.23	10.09	ND	3.31	ND
	Liver				
Saurida tumbil	88	214	0.5	1.8	0.1
Nemipterus japonicus	35.8	125	0.25	5.2	0.5
Epinephelus diacanthus	5.4	134	0.5	4.5	ND
	Gill				
Saurida tumbil	2.5	95.5	ND	0.8	0.2
Nemipterus japonicus	0.3	78	0.2	5.15	ND
Epinephelus diacanthus	ND	66.6	0.1	3.2	0.008

Table 8.4 Heavy metals (ppm wet weight) in whole tissues of fishes collected from Quilon-Gujarat(Cruise 184)

Stn.1	**Cd**	**Pb**	**Cu**
Saurida tumbil	0.5	1.5	52.5
Nemipterus japonicus	0.2	4.6	25
Epinephelus diacanthus	0.6	3	7.5
Stn. 2			
Saurida tumbil	0.8	1.9	22
Nemipterus japonicus	0.4	5.1	25
Epinephelus diacanthus	0.9	2.1	5.2
Stn. 3			
Saurida tumbil	1.2	1.5	42.5
Nemipterus japonicus	0.8	6.2	12
Epinephelus diacanthus	0.9	4.6	19.5
Stn. 4			
Saurida tumbil	0.5	2.5	18
Nemipterus japonicus	0.8	8.5	12.5
Epinephelus diacanthus	0.79	4.6	10.2
Stn. 5			
Saurida tumbil	0.6	1.8	9.5
Nemipterus japonicus	0.7	4.3	12.5
Epinephelus diacanthus	0.5	4.2	14

Table 8.5 Heavy metal concentration (ppm wet weight) in various tissues of fishes collected from Quilon-Mangalore (Cruise 191)

	Muscle				
Species	**Cu**	**Zn**	**Cd**	**Pb**	**Hg**
Saurida tumbil	30	52	0.6	2.1	0.026
Nemipterus japonicus	5.5	16	0.5	2.2	0.01
Epinephelus diacanthus	8.5	16.1	0.8	1.2	ND
	Liver				
Saurida tumbil	152	320	1.2	3.2	ND
Nemipterus japonicus	20.3	160	1	2.5	0.02
Epinephelus diacanthus	36	175	1	2.1	ND
	Gill				
Saurida tumbil	40	56	0.65	2.7	ND
Nemipterus japonicus	8.2	17	0.56	2	ND
Epinephelus diacanthus	8.8	18.9	0.6	1.3	ND

Table 8.6- Heavy metals (ppm wet weight) in whole tissues of fishes collected from Quilon-Mangalore (Cruise 191)

Stn.1	**Cd**	**Pb**	**Cu**
Saurida tumbil	1	2.5	88.5
Nemipterus japonicus	0.8	2	25.5
Epinephelus diacanthus	0.5	1.7	12.5
Stn. 2			
Saurida tumbil	0.9	2.2	120
Nemipterus japonicus	0.5	1.8	150
Epinephelus diacanthus	0.7	1	52
Stn. 3			
Saurida tumbil	0.9	3.1	132
Nemipterus japonicus	0.8	2.1	85
Epinephelus diacanthus	0.5	2.5	27
Stn. 4			
Saurida tumbil	1.2	3.2	48
Nemipterus japonicus	0.6	1.1	45
Epinephelus diacanthus	0.9	2.1	62
Stn. 5			
Saurida tumbil	1	2.5	47
Nemipterus japonicus	0.9	2	19
Epinephelus diacanthus	0.87	1.6	28

Table 8.7 Heavy metals (ppm wet weight) in various tissuesof fishes collected from Cochin to Manglore (Cruise 197)

	Muscle				
Species	**Cu**	**Zn**	**Cd**	**Pb**	**Hg**
Saurida tumbil	5.8	14.5	0.45	3.5	0.002
Nemipterus japonicus	3.2	27	0.1	1.2	ND
Epinephelus diacanthus	1.1	13.4	0.8	2.7	ND
	Liver				
Saurida tumbil	55	14.8	0.5	4.9	0.005
Nemipterus japonicus	48	28.06	0.58	5.8	0.002
Epinephelus diacanthus	76	33	1.2	12.3	0.01
	Gill				
Saurida tumbil	12.5	12.5	0.4	4.7	ND
Nemipterus japonicus	10.3	12.5	0.13	6.8	0.01
Epinephelus diacanthus	33.1	32.8	0.37	6.1	ND

Table 8.8 Heavy metals (ppm wet weight) in whole tissues of fishes collected from Cochin to Manglore(Cruise 197)

Stn.1	**Cd**	**Pb**	**Cu**
Saurida tumbil	0.7	5.2	65
Nemipterus japonicus	0.8	8	32.5
Epinephelus diacanthus	0.45	2.2	45.5
Stn. 2			
Saurida tumbil	0.5	1.5	58
Nemipterus japonicus	0.4	4.5	47.5
Epinephelus diacanthus	0.8	6.3	56
Stn. 3			
Saurida tumbil	0.8	3.1	123
Nemipterus japonicus	0.8	2.1	84
Epinephelus diacanthus	0.6	2.5	56
Stn. 4			
Saurida tumbil	0.6	5	30.5
Nemipterus japonicus	0.42	2.1	22
Epinephelus diacanthus	0.5	3	28
Stn. 5			
Saurida tumbil	1.1	3.2	32
Nemipterus japonicus	0.8	2.8	15.5
Epinephelus diacanthus	0.8	3.6	26

Table 8.9 Heavy metals (ppm wet weight) in various tissues in fishes collected from Quilon-Mangalore (Cruise 204)

	Muscle				
Species	**Cu**	**Cd**	**Ni**	**Pb**	**Zn**
Saurida tumbil	17.6	0.8	3.33	ND	12.5
Epinephelus diacanthus	ND	ND	ND	ND	1.3
Nemipterus japonicus	3.5	ND	1.59	ND	6.85
	Liver				
Saurida tumbil	20.2	2.2	3.5	1.1	52
Epinephelus diacanthus	35.5	5.2	5.8	2.2	75.9
Nemipterus japonicus	12.5	0.8	2.3	1.5	84
	Gill				
Saurida tumbil	17.4	2.1	3.3	0.8	33
Epinephelus diacanthus	12.5	3.3	0.5	0.5	25
Nemipterus japonicus	10	1	0.8	ND	44

Table 8.10- Heavy metals (ppm wet weight) in whole tissues of fishes collected from (Cruise 204) Quilon to Manglore

stn. 1	**Cd**	**Cu**	**Pb**
Saurida tumbil	1.48	17.6	ND
Epinephelus diacanthus	1.62	14.6	ND
stn. 2			
Saurida tumbil	1.6	12.2	5.4
Epinephelus diacanthus	ND	ND	ND
stn. 3			
Saurida tumbil	ND	ND	ND
Epinephelus diacanthus	0.2	ND	ND
stn. 4			
Saurida tumbil	ND	ND	ND
Epinephelus diacanthus	ND	11.5	ND
stn. 5			
Saurida tumbil	ND	ND	ND
Epinephelus diacanthus	ND	0.687	ND

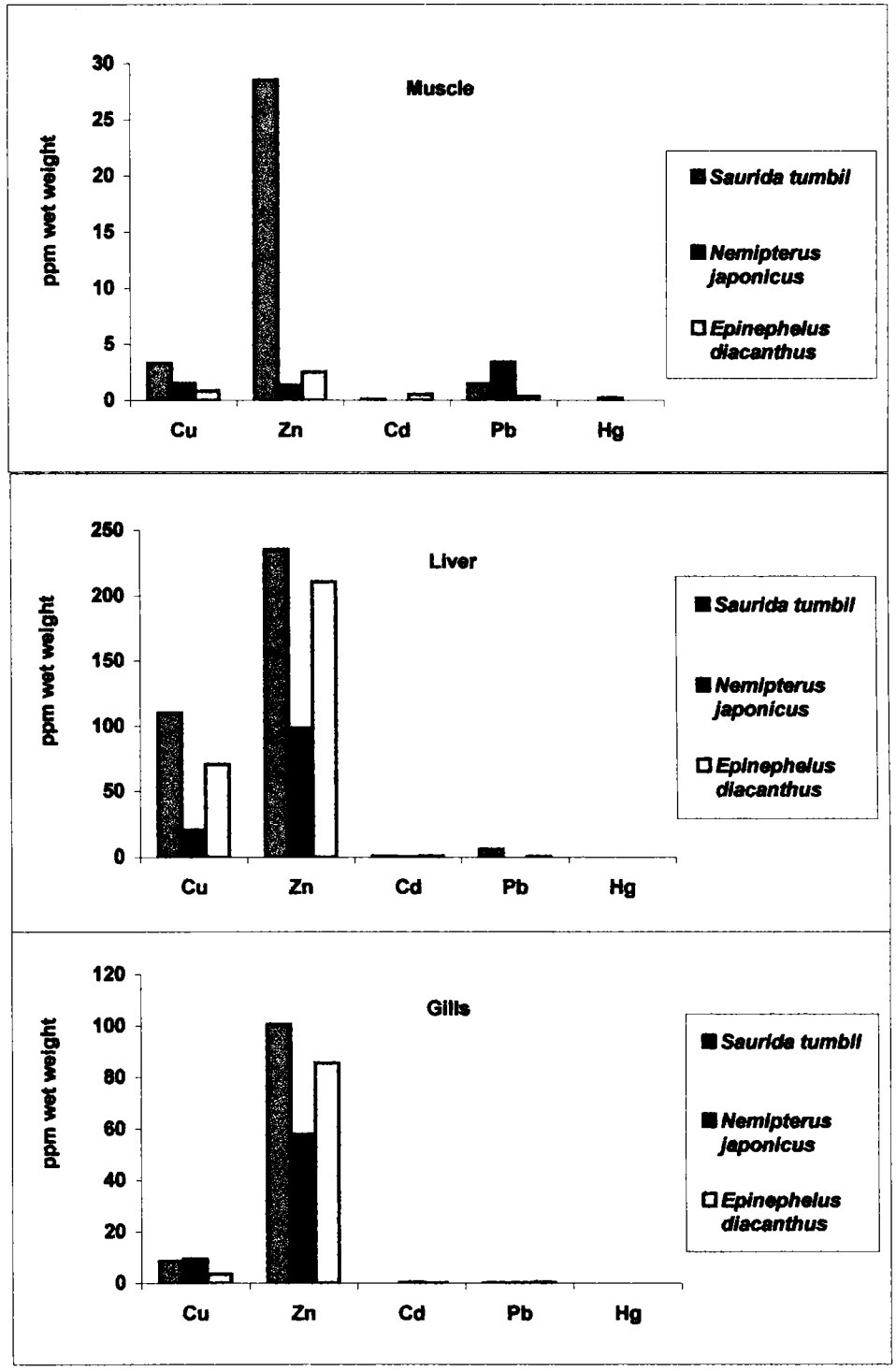


Fig. 8.1 Heavy metals (ppm wet weight) in various tissues of fishes collected from off Gujarat (Cruise 181)

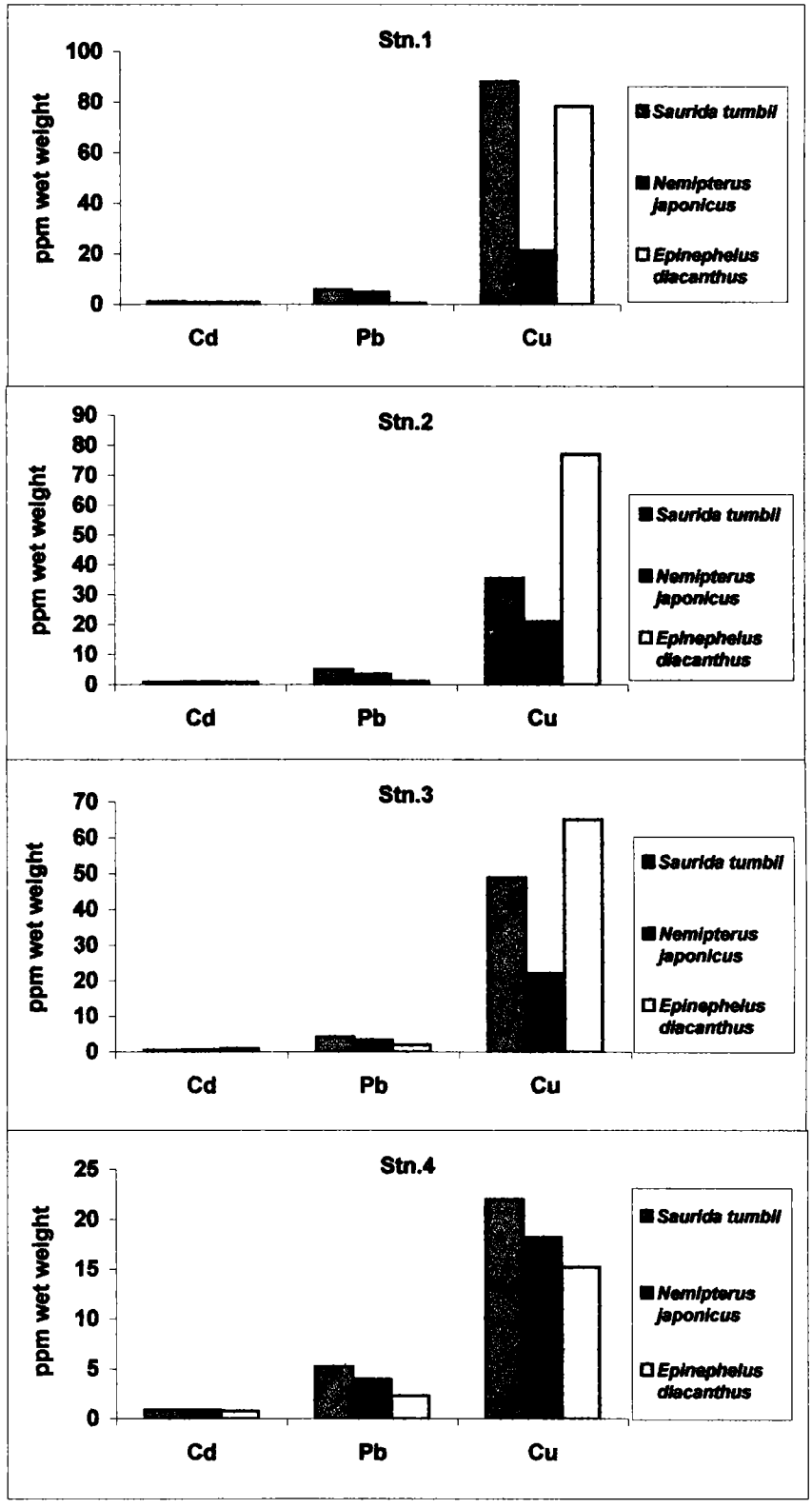


Fig. 8.2 Heavy metals (ppm wet weight) in whole tissue of fishes from the study area off Gujarat (Cruise 181)

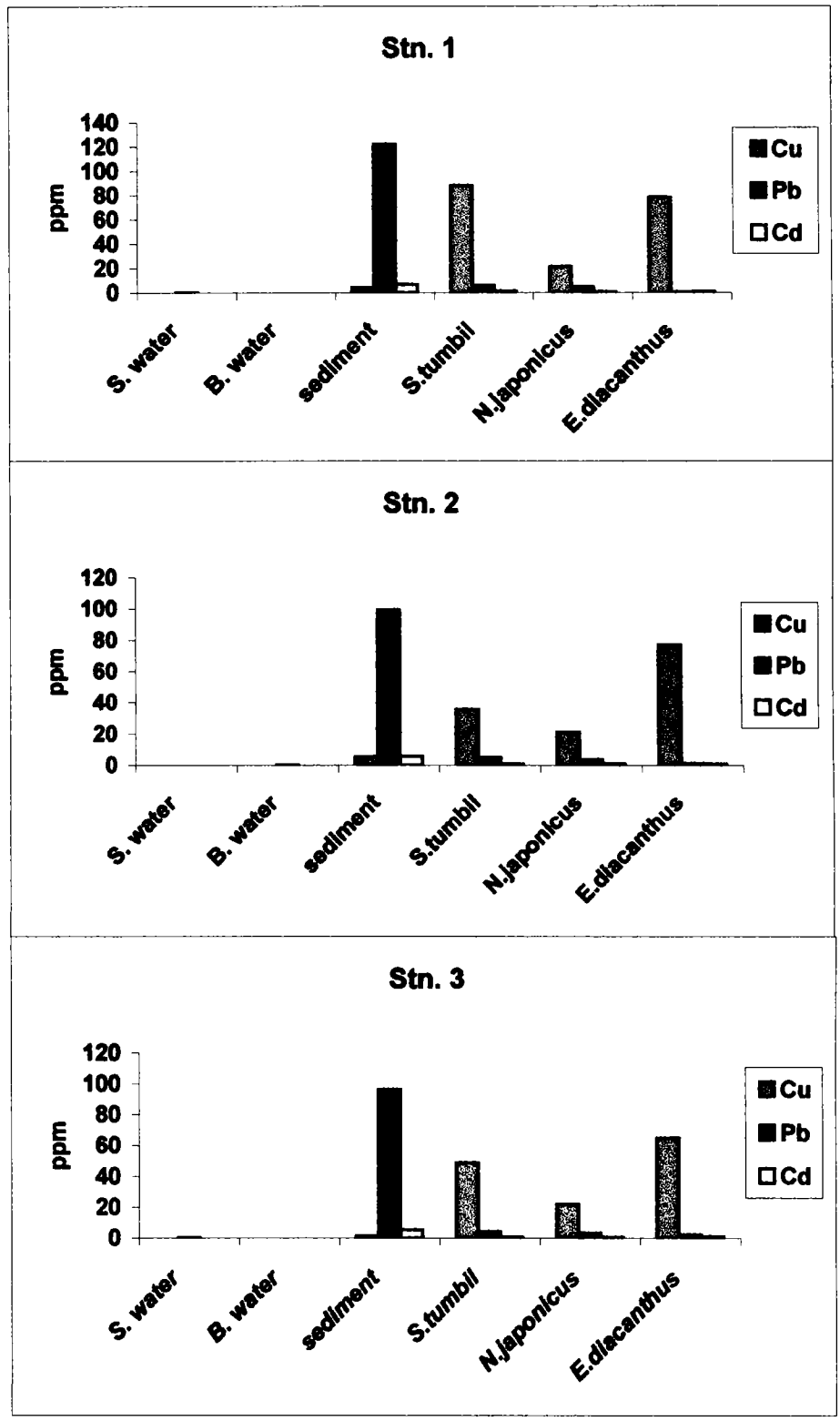


Fig. 8.3 Trace metal concentration in water, sediment and fish from stations in off Gujarat (Cruise 181)

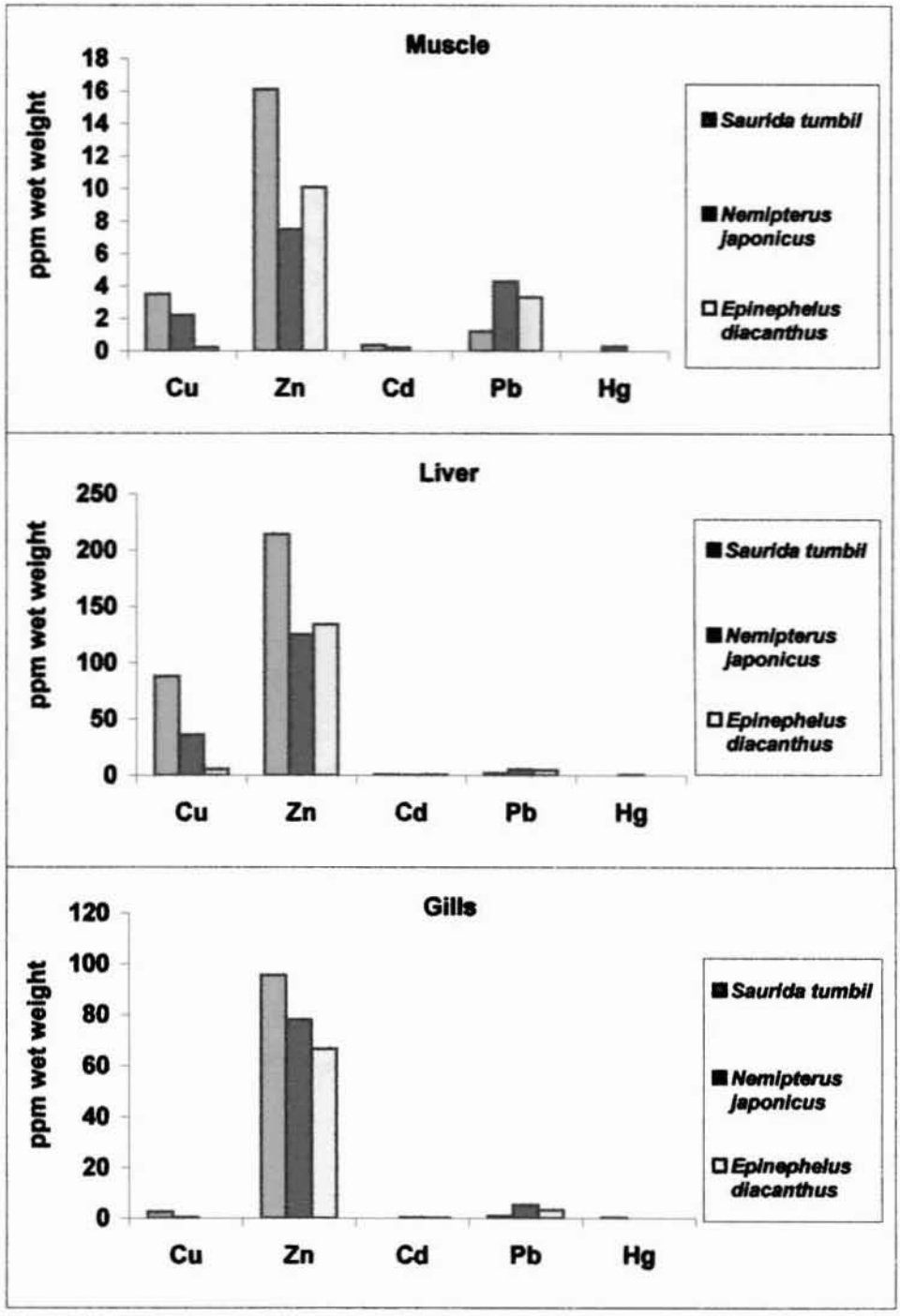


Fig. 8.4 Heavy metals (ppm wet weight) in various tissuesof fishes collected from Quilon-Gujarat (Cruise 184)

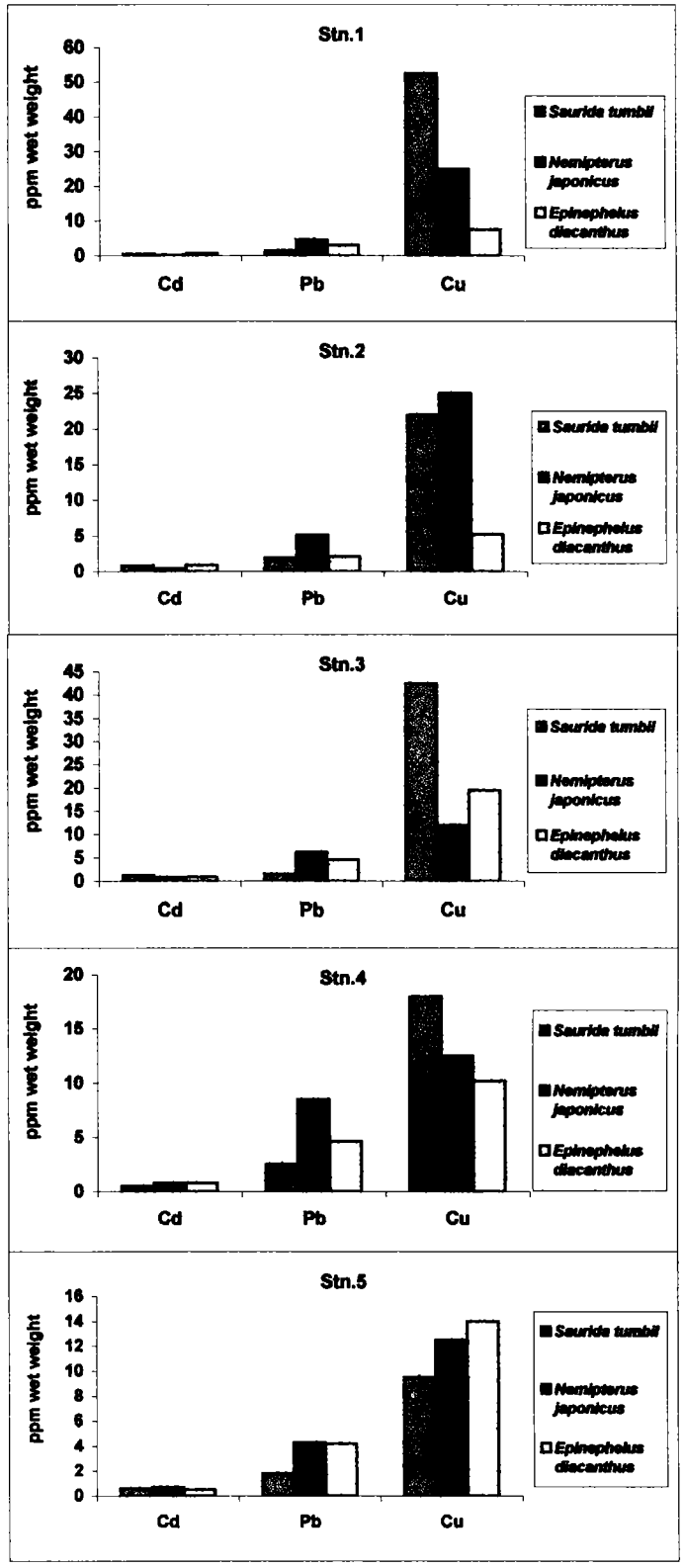


Fig. 8.5 Heavy metals (ppm wet weight) in whole tissues of fishes collected from Quilon-Gujarat (Cruise 184)

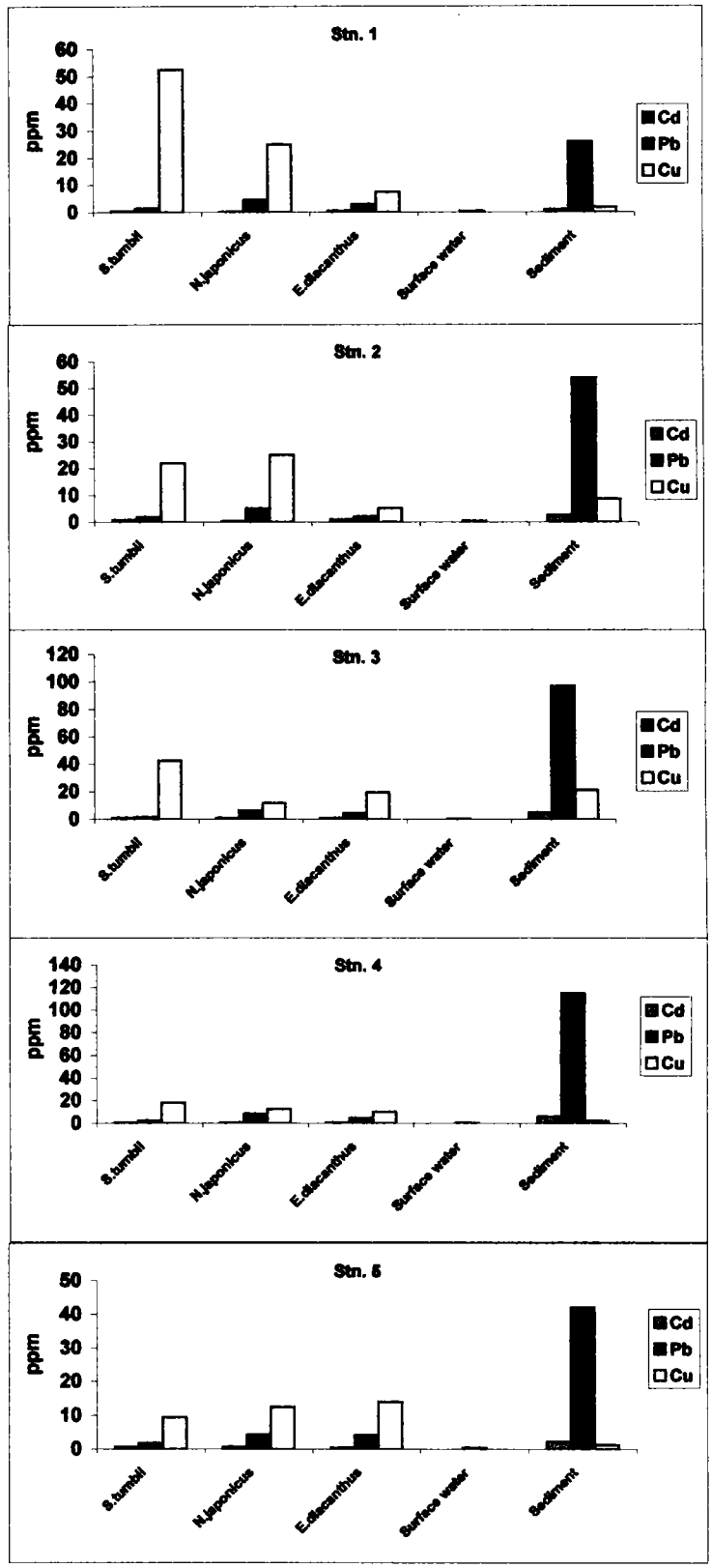


Fig. 8.6 Trace metal concentration in water, sediment and fish from stations in Quilon to off Gujarat (Cruise 184)

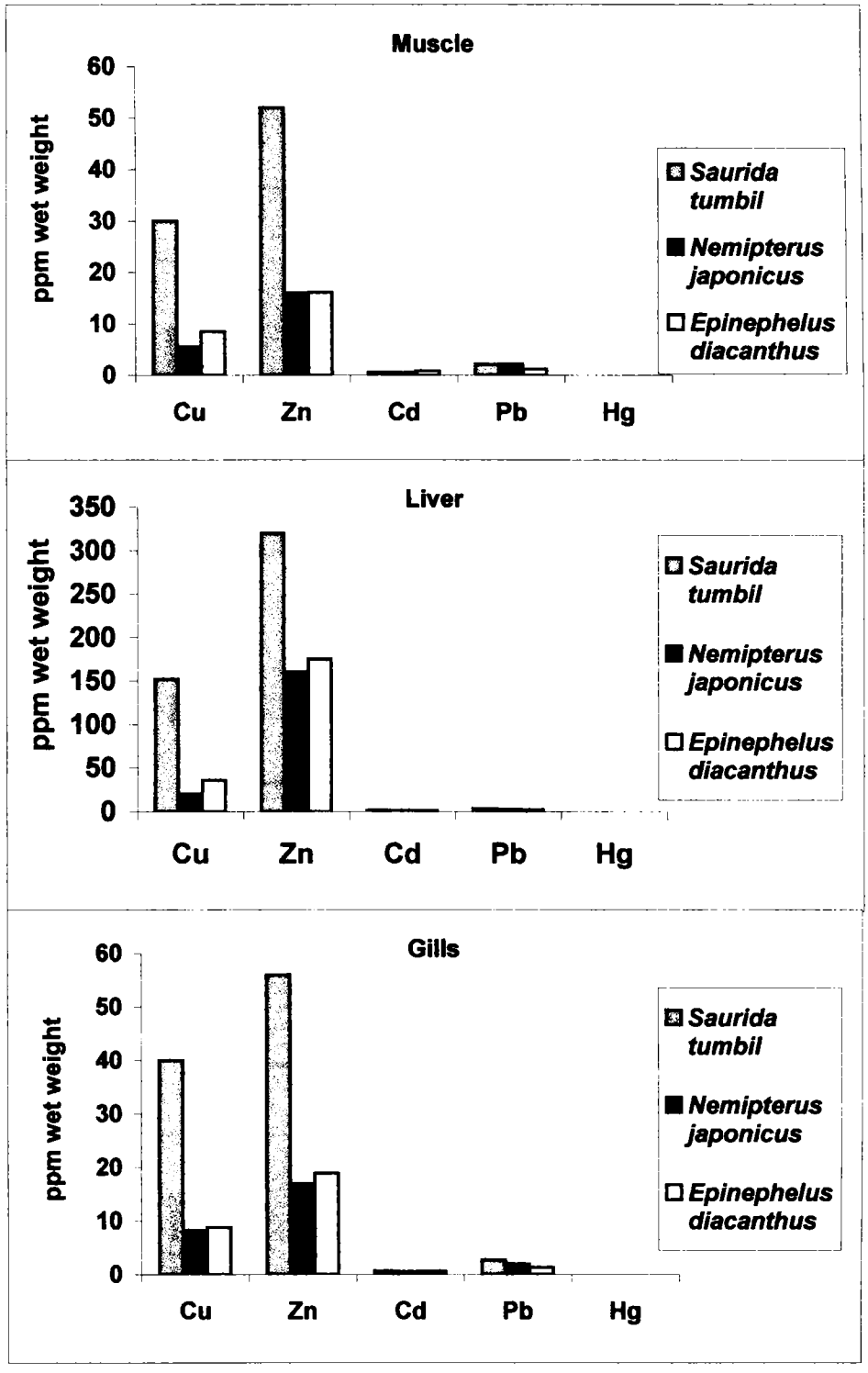


Fig. 8.7 Heavy metal concentration (ppm wet weight) in various tissues of fishes collected from Quilon-Mangalore (Cruise 191)

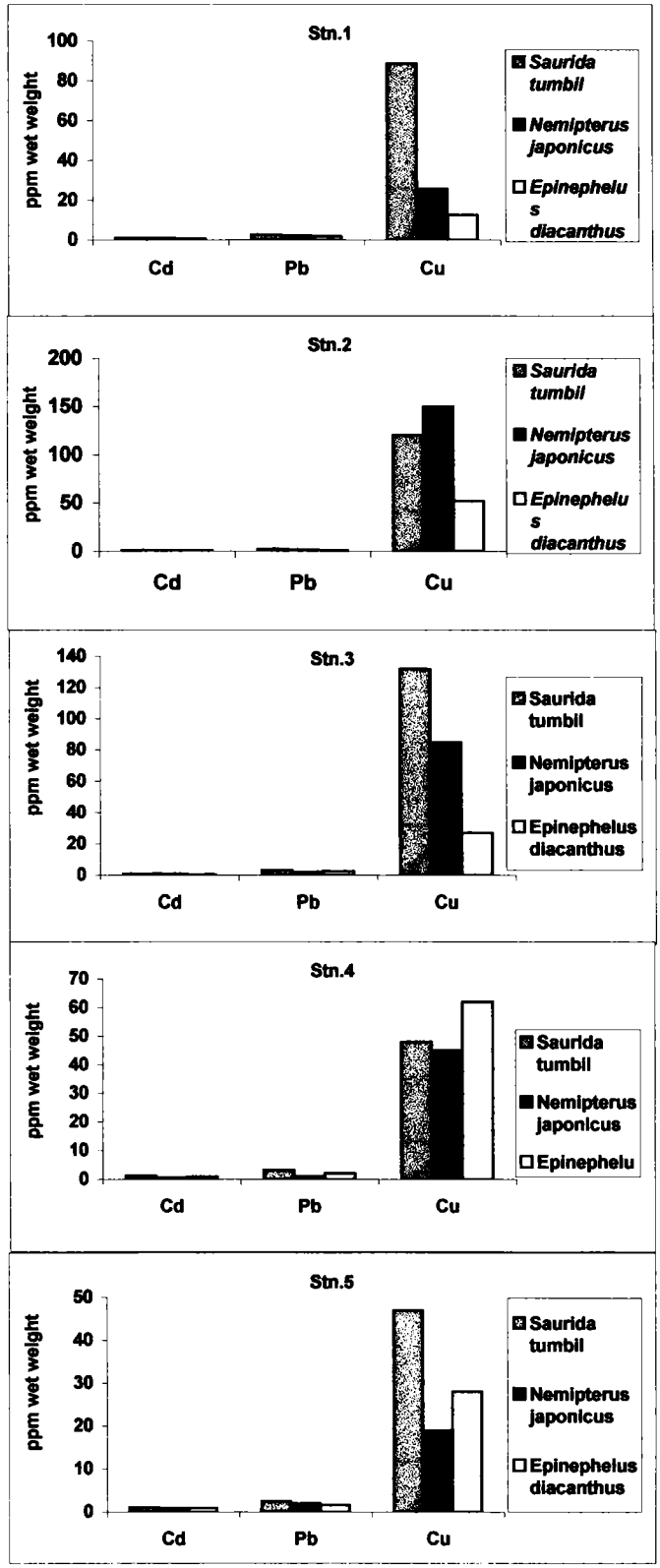


Fig. 8.8 Heavy metals (ppm wet weight) in whole tissues of fishes collected from Quilon-Mangalore (Cruise 191)

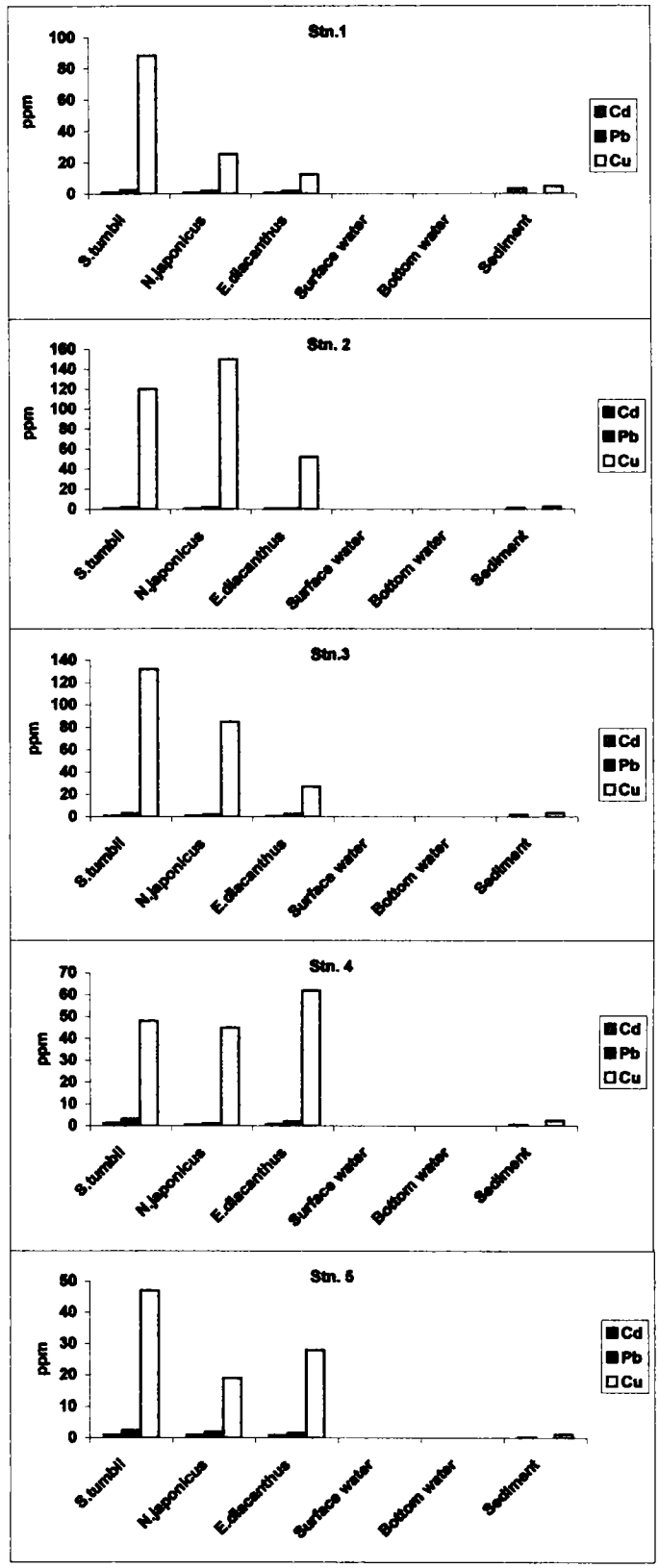


Fig. 8. 9 Trace metal concentration in water, sediment and fish from stations in off Quilon to off Mangalore (Cruise 191)

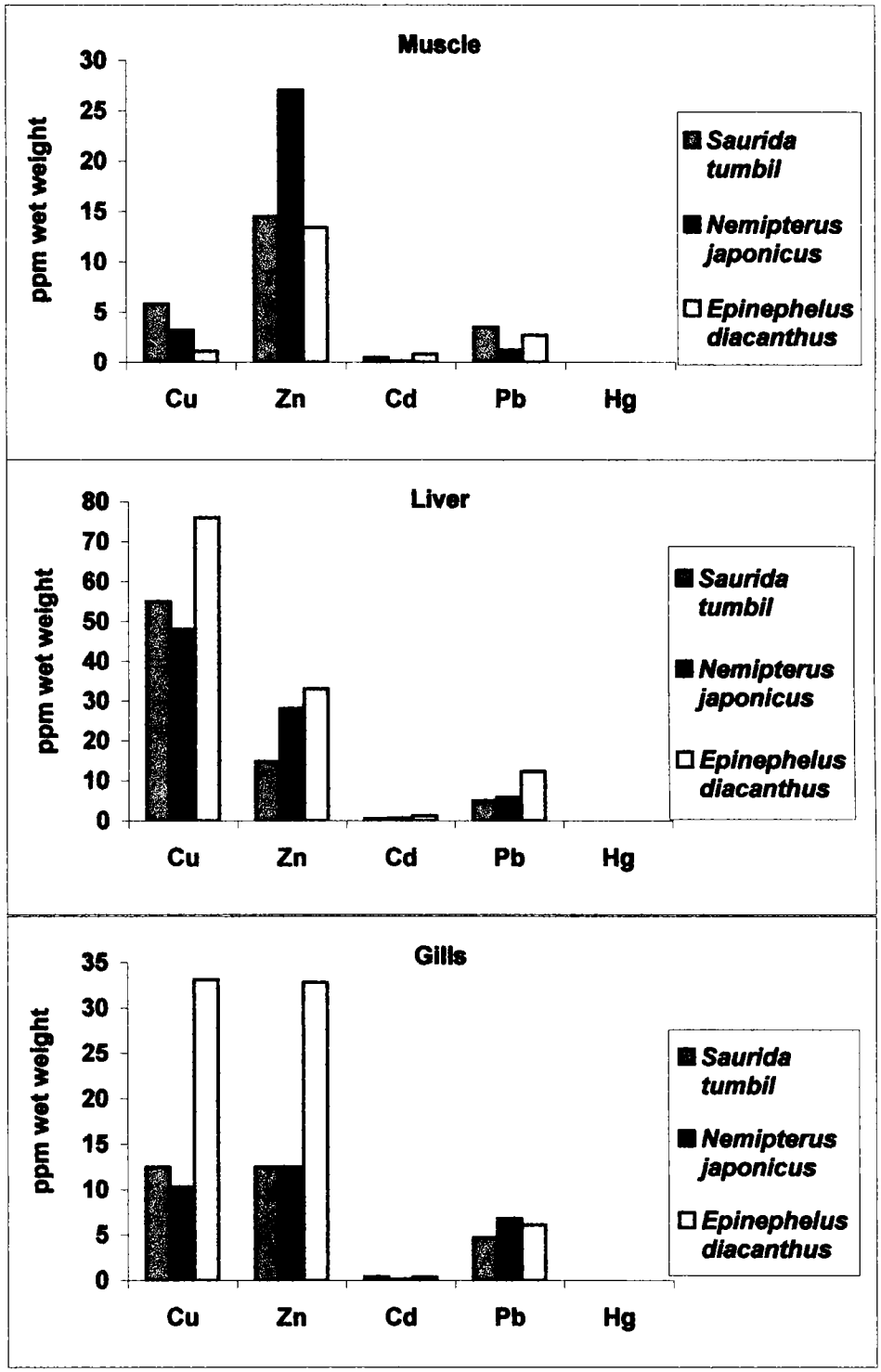


Fig. 8.10 Heavy metals (ppm wet weight) in various tissues of fishes collected from Cochin to Manglore (Cruise 197)

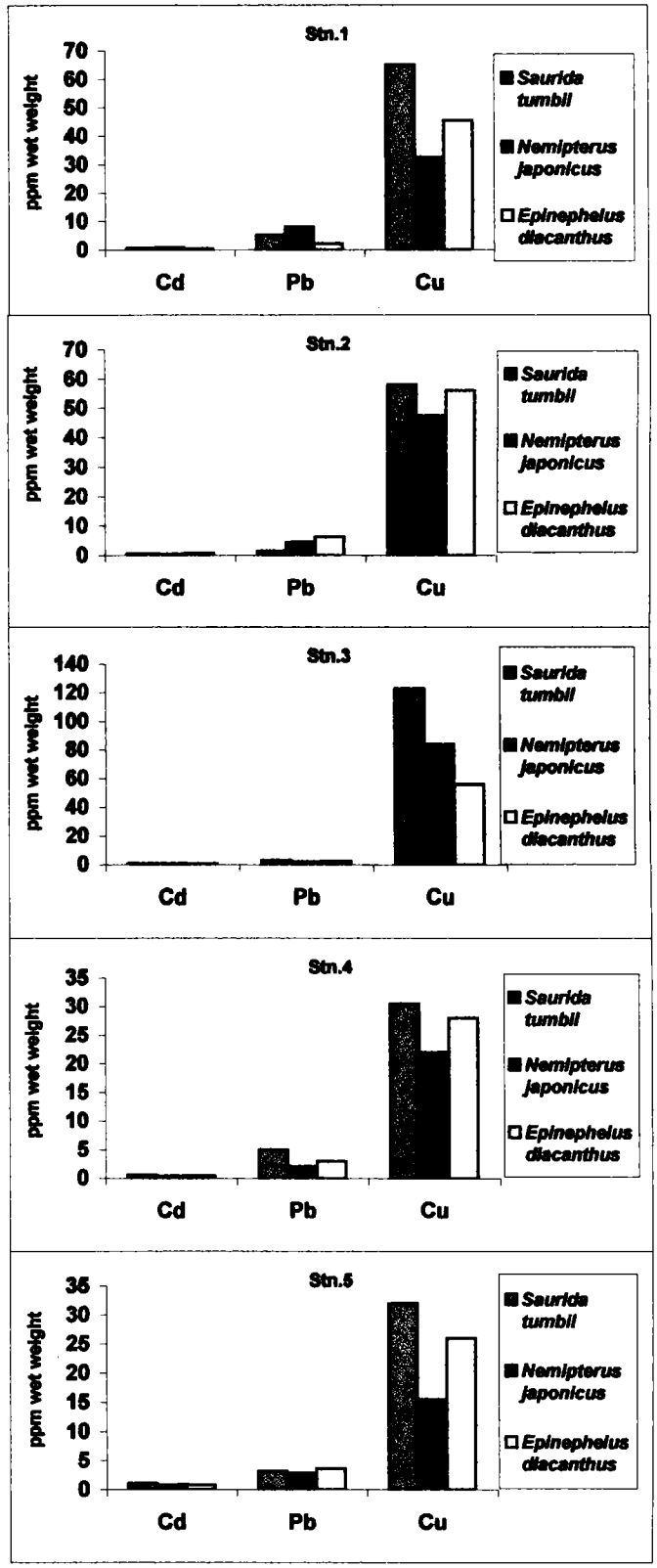


Fig.8.11 Heavy metals (ppm wet weight) in whole tissues of fishes collected from Cochin to Manglore (Cruise 197)

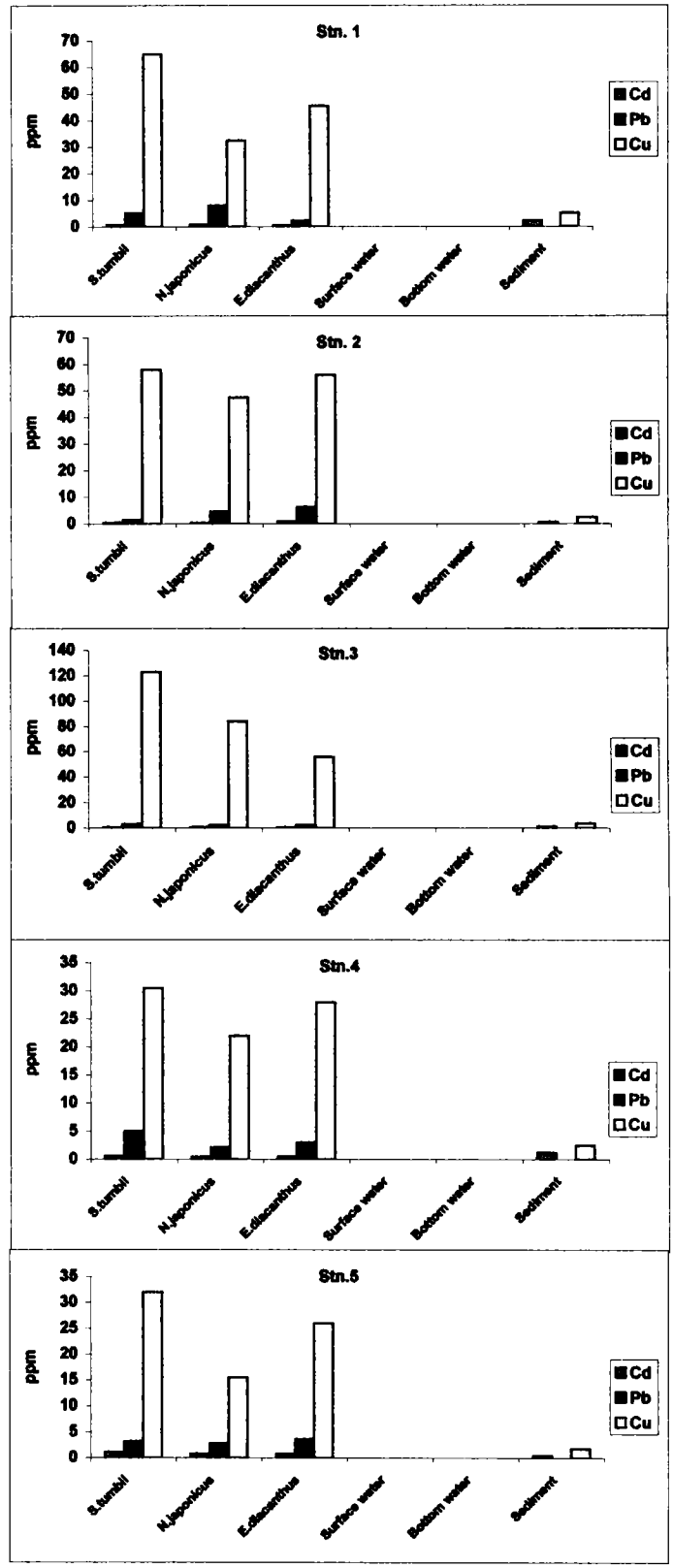


Fig. 8.12 Trace metal concentration in water, sediment and fish from stations in off Cochin to off Mangalore (197)

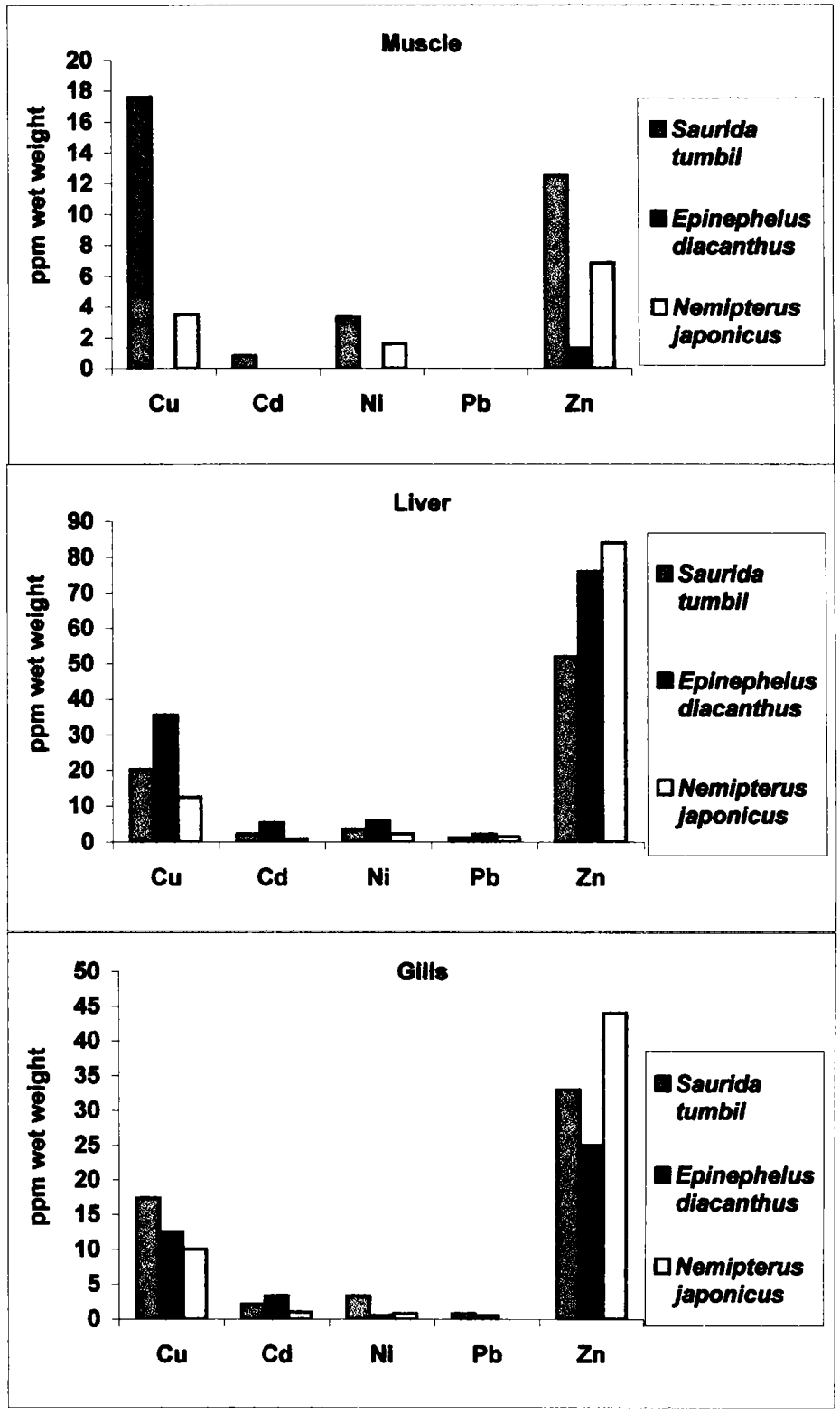


Fig. 8.13 Heavy metals (ppm wet weight) in various tissues in fishes collected from Quilon-Mangalore (Cruise 204)

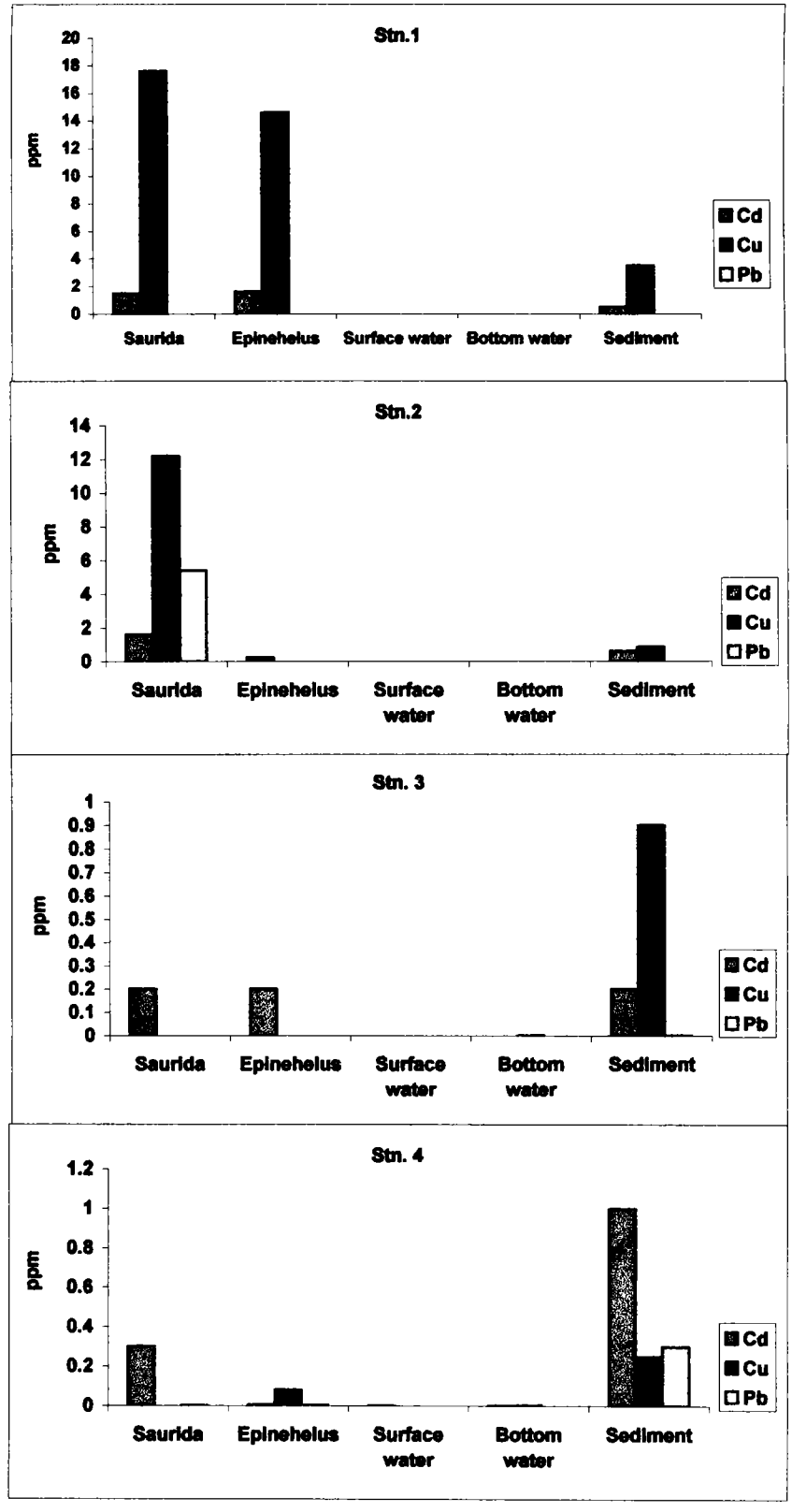


Fig. 8.14 Trace metal concentration in water, sediment and fish from stations in off Quilon to off Mangalore

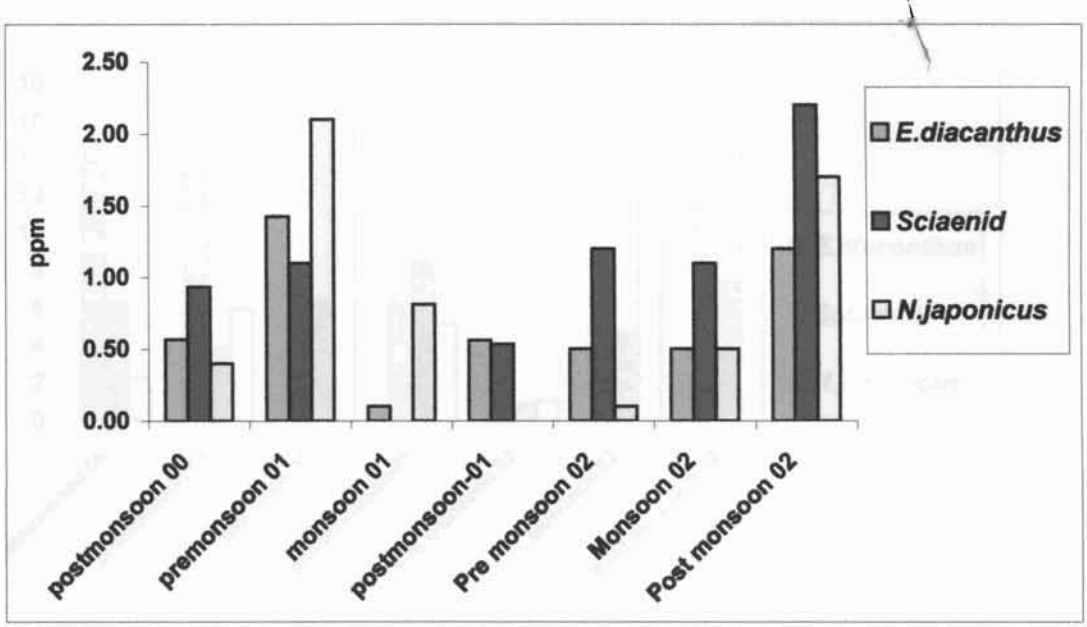


Fig.8.15 Concentration of cadmium in whole tissue of fishes (ppm wet weight) from off Cochin

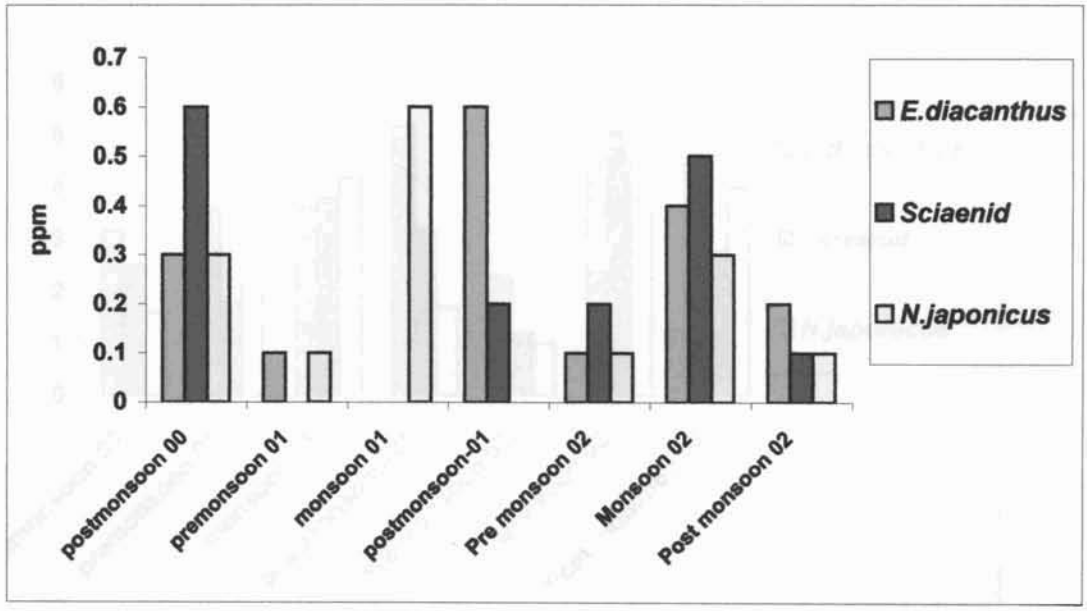


Fig. 8.16 Concentration of cadmium in muscle tissue of fishes (ppm wet weight) from off Cochin

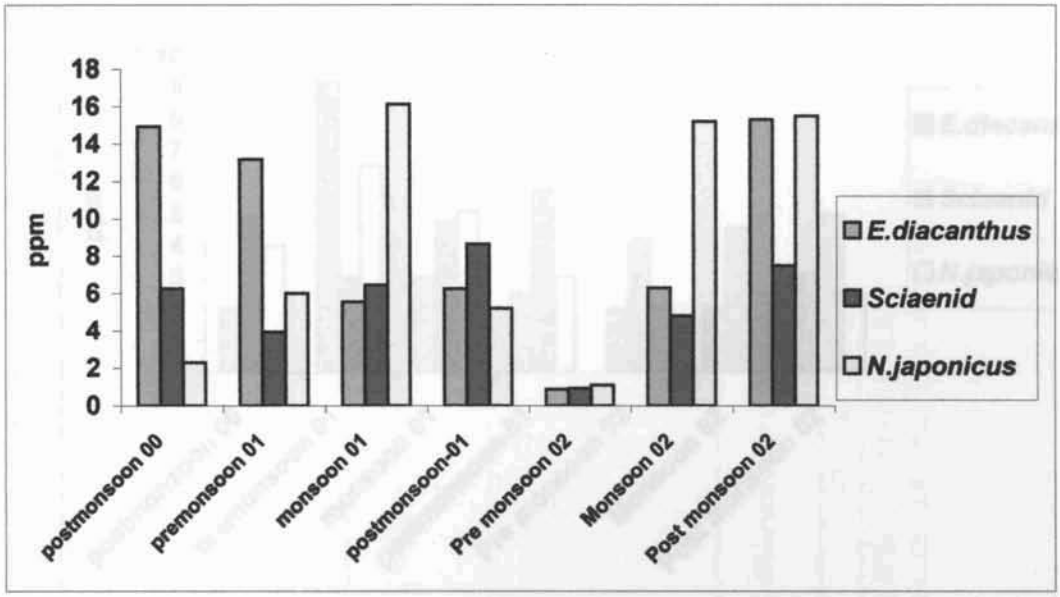


Fig. 8.17 Concentration of copper in whole tissue of fishes(ppm wet weight) from off Cochin

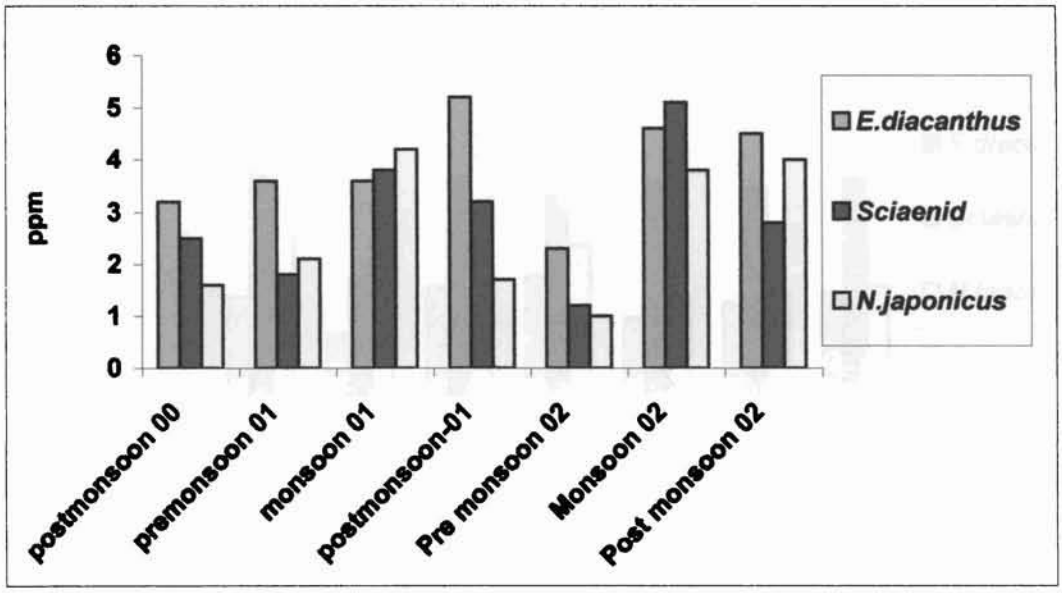


Fig. 8.18 Concentration of copper in fish muscle (ppm wet weight) from off Cochin

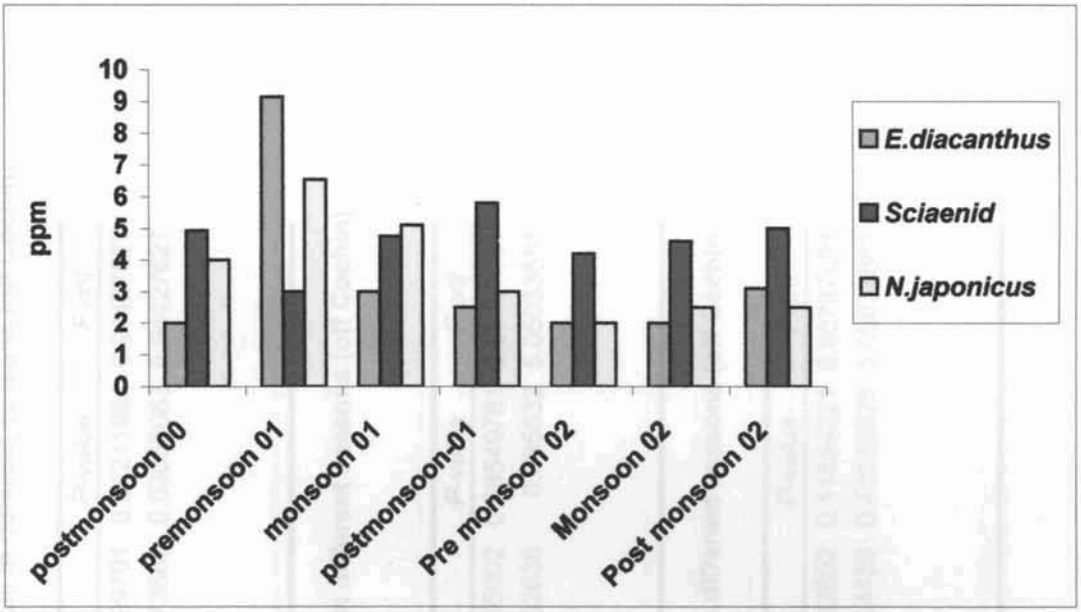


Fig. 8.19 Concentration of lead in whole tissue of fishes (ppm wet weight) from off Cochin

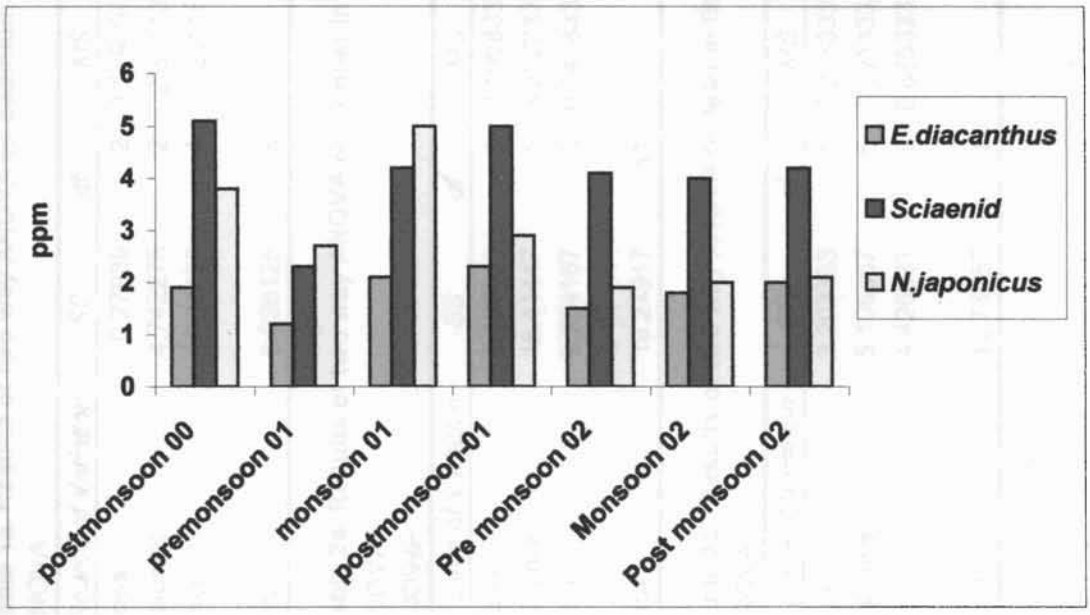


Fig. 8.20 Concentration of lead in fish muscle (ppm wet weight) from off Cochin

Appendix V

Table 1a. Results of two way ANOVA on cadmium in fish muscle in different seasons (off Cochin)

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	0.27939	2	0.13969475	0.556299701	0.61211984	6.94427627
Columns	4.742278	2	2.3711392	9.442473667	0.03055063	6.94427627
Error	1.004457	4	0.2511142			
Total	6.026125	8				

Table 2a. Results of two way ANOVA on copper in fish muscle in different seasons (off Cochin)

ANOVA

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	0.100833	1	0.10083333	0.184395002	0.68549781	6.60787691
Columns	16.41417	5	3.28283333	6.003352636	0.035632	5.05033881
Error	2.734167	5	0.54683333			
Total	19.24917	11				

Table 3a. Results of two way ANOVA on lead in fish muscle in different seasons (off Cochin)

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	3.203333	1	3.20333333	3.618222892	0.11554221	6.60787691
Columns	5.106667	5	1.02133333	1.153614458	0.43960825	5.05033881
Error	4.426667	5	0.88533333			
Total	12.73667	11				

Table 1b. Results of two way ANOVA on cadmium in whole soft tissue in different seasons (off Cochin)

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	0.179213272	2	0.0896066	0.3768205	0.69538025	4.102815865
Columns	7.977952623	5	1.5955905	6.7098953	0.00544876	3.325837383
Error	2.377966358	10	0.2377966			
Total	10.53513225	17				

Table 2b. Results of two way ANOVA on copper in fish mscle in different seasons (off Cochin)

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	60.26123706	1	60.261237	3.7349037	0.11112085	6.607876912
Columns	170.7125	5	34.1425	2.1161024	0.21509385	5.050338814
Error	80.67307946	5	16.134616			
Total	311.6468165	11				

Table 3 b Results of two way ANOVA on Lead in fish muscle in different seasons (off Cochin)

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	0.858675	1	0.858675	0.3127584	0.60011492	6.607876912
Columns	15.59459167	5	3.1189183	1.1360152	0.44605874	5.050338814
Error	13.72745	5	2.74549			
Total	30.1807167	11				

Chapter 9

SUMMARY AND RECOMMENDATIONS

Summary and Recommendations

Reports show that there is increased incidence of human cancers in recent times and the major risk elements are the environmental factors like polluted air, water and food. Polycyclic Aromatic Hydrocarbons and other toxic compounds from industrial effluents are noted for their high potency for skin, lung, bladder, and gastrointestinal cancers. Increased industrialization, and population growth led to greater production of wastes. Deposition of such harmful industrial byproducts, wastes and contaminants into the ocean poses serious problems to the environment. Any exposure of the food fishes to the toxic contaminants in the environment will lead to their subsequent bioaccumulation in them. This in turn is transferred to human beings through the food chain.

The Arabian Sea is a major oil tanker route to the South East Asia and beyond. In addition to accidental spillage, Oil tankers after unloading the oil in the ports often wash their storage tanks and pump their washings into coastal waters. These coupled with off shore oil explorations in many countries in the area made Indian seas very vulnerable to oil pollution.

Although pollution from toxic metals and pesticides are well studied, reports on pollution by Polycyclic Aromatic Hydrocarbons (PAHs), which are established potential carcinogens, is scanty. An attempt is made here to

study the salient aspects of the problem within the scope of a large study on the pollution profile of our coastal seas. The water, sediments and selected four species of fishes available round the year, are studied for the purpose.

The study also covers the pollution of our coastal waters with metals like Hg, Pb, Cd, Cu, Zn and Ni. The seasonal changes in the concentration of these metals along the coast with special emphasise on the waters off Cochin was also studied as a part of this study. Pesticides and PAHs have received attention due to their carcinogenic effects. The metals studied here are known to cause various other diseases/ disorders in consumers if taken in excess. For example, Cd and Ni can cause mental degeneration and infertility. Ni and Cd can leach from metal recycled pots and pans, inducing high blood pressure and heart attacks. An excess of Cu in the body can lead to arthritis, insanity and scrizophrenia.

The main objectives of the study were:

1. To collect base line data on the concentration of PAHs in seawater and sediment from the west coast of India.
2. To study the concentration of PAHs in four species of fishes from the west coast.
3. To study the comparative levels of PAHs in fish and in the aquatic environment of the west coast of India
4. To study the influence of sediment characteristics on the concentration of PAH in sediment.

5. To study changes in PAH concentration in water, sediment and fish
6. To provide a baseline concentration of trace metals in water, sediment and fish from the west coast of India
7. To study the seasonal change in content of selected trace metals in water, sediment and fish from the west coast of India.

The results of the present study are organized under 9 chapters. In the first introductory chapter, the rationale of the study and the present scenario in our waters are highlighted.

In chapter 2 an exhaustive review on similar studies conducted both nationally as well as internationally ~~are also~~ reviewed.

In Chapter 3 details of all the materials and methods employed for the present study are described. Samples were collected from west coast of India onboard FORV "Sagar Sampada" and the Fishing Vessel, MFB "Matsyakumari" (Central Institute of Fisheries Technology). Samples were collected during the Cruises namely, 181, 184, 191, 197 and 204 of FORV (Fisheries Oceanographic Research Vessel) Sagar Sampada under the Department of Ocean Development, Govt. of India during the period February 2000 to October 2002. The operational area covered lat 8^0 N -21 ^{0} N and long 69 ^{0} – 75 ^{0} E. Monthly collections of the water, sediment and fish samples were made between the years 2000-2002 from off Cochin area from MFB "Matsyakumari". The sampling in the off Cochin area was done at a depth of 20-25m. The operational area covered latitude 9^0 54' 28"N to 10^0 02 58N" and

Longitude 76^0 05' 58"E to76^0 12' 47"E. Standard methods of AOAC (1990) and Grasshoff *et al.* (1976), Strickland and Parson (1972) were adopted for analysis of trace metals and the method of Lizia Guzella (1994) for the analysis of PAH.

The results on physico chemical parameters in the seawater are presented in chapter 4. The parameters such as dissolved oxygen, temperature, salinity, pH and nutrients in water were analyzed following standard procedures. Organic matter and sediment pattern in the mud collected from sea bottom were also analyzed. It is found that there is an increase in salinity from south to north. The salinity of surface water samples during the monsoon season (May- August) is found to be lower (33.38-34.5 ‰ in may and 33.03-34.25 ‰ in August) when compared to that of the other 2 seasons when the salinity was 35.7-35.98 ‰ in February and 34.8-35.5 ‰ in October. The surface dissolved Oxygen ranged from 2.01 ml/l-4.89 ml/l. At stations of depth below 100 m, the range was between 2.3-3.7 ml/l. At higher depths D.O as low as 0.1 ml/l. Macronutrients like nitrite- N, phosphorous and total Nitrogen were relatively lower in surface waters than in the bottom waters. Analysis of physico chemical parameters of the water samples from the off Cochin area showed the following results: Salinity in different stations ranged from 21.86 ‰ 34.05 ‰. Highly significant variation was observed in salinity in different studied seasons ($p<0.01$). High salinity was observed in the pre monsoon months and a drop in salinity in the monsoon. A slight increase in

salinity was seen for the second year of study in most of the stations. The pH was comparatively lower during the monsoon season. Low pH was usually observed during the period when salinity values were lower. DO in the surface water in the studied stations ranged from 3.5 ml/l to 7.9 ml/l. Lower values were observed in monsoon and higher values in post monsoon season. Statistical Analysis showed a significant variation in phosphorous in different seasons studied, and the concentration ranged from 0.03 ppm – 0.25 ppm. Nitrite was found in traces in all the seven stations.

In chapter 5, Polycyclic Aromatic Hydrocarbons in water and sediment were analysed. Generally, outside coastal areas very low concentrations of PAHs were found in the Arabian Sea. In seawater the predominant PAHs were two and three ring compounds. Concentration of PAHs was higher in seawater near the sea floor than in the surface water. The elevated concentrations in the bottom water may be attributed to contribution of resuspended sediment particles. The marine sediments from the off shore areas were silty clay in nature having high amount of organic matter. PAHs in the different sediments showed wide variations depending on the kind of sediment. In most of the stations a linear relationship was obtained between the organic carbon content and PAH content in sediments. In sediments, the high molecular weight and more lipophilic and more hydrophobic PAHs predominated probably due to their higher persistence. The experimental results indicated that the higher molecular weight aromatics seem to be preferentially adsorbed by particulate

matter and incorporated in the sediment. The results from different seasons have also been compared. The concentration of PAHs in sediment in the pre - monsoon season was higher. This might be attributed to seasonal change in degradation intensity. During this seasons of high planktonic growth and productivity, high amount of detrital material is produced that might effectively scavenge PAHs and transfer them to sea floor. A plankton bloom was observed during this season in the study area.

In chapter 6 PAHs in fish samples are presented. PAHs may exert toxic effects on organisms at tissue concentrations of only a few µg/ g for fish (Klaasen, 1996). The PAH concentrations in edible fish muscle studied here are coming within the range of values reported by Takatsuki *et al.* (1985) for zones defined as unpolluted elsewhere (2- 592 µg/g dry weight).

The safe level of Benzo (a) pyrene for human consumption is given as 4 ng/g dry weight (for consumption of 50 g fish per week), 1 ng/g for the consumption of 200 gm fish per week. None of the samples studied here contained levels above this. Significant correlation was obtained for concentration of PAHs in fish and sediment levels in all seasons except in monsoon. In monsoon season due to the wave action and heavy rainfall PAHs might have dispersed into the surrounding areas.

It is evident from the study that PAHs of lower molecular weight are generally present at higher concentrations in fish tissues. Such patterns of accumulation are characteristics of PAH generated by petrogenic pollution

(Dou Abul *et al.*, 1987). Naphthalene was one of the most prevalent compounds. Chrysene and Benzo (a) pyrene were also present in the fish muscle studied here as were fluoranthene, pyrene and benzo (a) anthracene. The absence of higher molecular weight components like dibenzo (a, h) anthracene, benzo (g, h,I) perylene in the fish analysed here may be attributed to their rapid depuration or biotransformation in fish. The results of analysis of PAH in fishes from the off Cochin area showed that the concentration of PAH was more in the pre monsoon period. The concentration of higher molecular weight compounds was more in these samples than that from the off shore study areas. This indicated the fact that the source of contamination could be oil pollution along with other petrogenic source in the near shore area. The highest concentration of naphthalene was found in *Epinephelus sp* and the concentration was 8706 ng/g. Statistical analysis of correlation showed that the levels on PAHs in sediment and that in fish were highly correlated ($p<0.01$).

When compared to the guideline values protective against the majority of adverse effect, the level of the PAHs in present samples can be considered chronic. For Naphthalene the US Sediment Quality Criteria (SQC) values, Chronic/Acute is 500/10500 ng/g, for phenanthrene it is 2400/14000 ng/g, for Benzo (a) anthracene it is 1600/55000 ng/g, for Chrysene it is 1200/115000 ng/g.

In chapter 7 trace metals in seawater and sediment from the west coast are dealt with. Metals analysed in water were, Cu, Zn, Cd, Ni and Hg and the

metals analysed in the sediment were Cd, Pb and Cu. Results show that the highest recorded value of Zn in water in the present study from off Gujarat region is higher than the Environmental Protection Agency recommended safe level for Zn in sea water (0.1 ppm) (Anon, 1991) both in surface and bottom water (Average in surface water is 0.04 ppm and in bottom water is 0.39 ppm). Concentration of Cu was above the EPA recommended safe level in some stations near the off Mangalore area during cruise No. 184 in the monsoon season. Levels of Ni and Cu were above the recommended safe level in some stations in off Quilon area during cruise No. 191 in the monsoon season. The concentration of Cu in water in the present study from off Cochin to off Mangalore area during cruise No 197 in the pre-monsoon season was also found to be higher than the EPA recommended safe levels. These stations in the study area are marked by the influence by the discharge from the rivers and are near to major industrial outfalls. There is a major amount of sediment being delivered from the rivers into the ocean. This accounts for an increased concentration of all the trace metals found in the region near this area.

While comparing the levels of the studied trace metals in seawater in different cruises, it can be seen that there is temporal variation of these metals in the marine environment. Average concentration of copper, cadmium and lead in water in the monsoon period is higher than that observed for the premonsoon period in the west coast. Even though there can be regional variations, variation in the source of trace metals it can be generalized as due

to the increased input of effluents by the rivers (Coale and Johnson, 1998). Concentration of the metals studied in the sediment was higher in the post monsoon season when compared with the pre monsoon periods.

Temporal variation of trace metals in seawater in the off Cochin area is also dealt with in this chapter. Data on concentration of Cu and Fe are scarce especially from Indian coastal waters (Matkar *et al.,* 1981). Concentration for Cu in surface water for the period of study ranged from 0.0009 ppm to 0.0029 ppm which correlated well with what has been reported by other authors (Meenakumari, 1988) The present study revealed that the average concentration of Ni in surface water for the first year of observation ranged from 0.0001 to 0.0026 ppm and from 0.001-0.008 ppm for the second year of observation and average for the whole period ranged from 0.0005-0.005 ppm. In the present study, concentration of Fe varied from 0.0075-0.016 ppm in the first year and from 0.015-0.02 ppm in the second year of study. The concentration of lead was the minimum in the coastal waters compared to all other metals studied. Concentrations of metals in seawater were more mostly during monsoon followed by post monsoon season and less during premonsoon season.

The present study revealed a predominance of silt and clay at all stations in the off Cochin area. High organic carbon values for all the stations may be due to marine sedimentation and high rate of delivery from external sources. In the present study, the mean concentration of the studied trace

metals for different season for the 2 years differed temporally, but spatially there was no significant variation. This may be observed during the study period due to the similarity in the sources of heavy metals in this area (Murray and Murray, 1973). The statistical analysis ANOVA was done between stations and between different seasons and the result shows there is significant variation of Cadmium, Copper and Lead in sediment in the different seasons ($P<0.01$). The metals were significantly higher in the monsoon and post monsoon periods. Such increased level of metals in the sediments have resulted due to monsoonal land run-off (Athaley and Gokhale, 1989) and limited availability of heavy metals to the biota as result of the interaction of various physico chemical characters of the sediments (Eldford and Heporth, 1975). Further the most obvious mechanism of adsorption of metals from the water column by the resuspended sediments followed by redeposition (Trefrey *et al.*, 1975, Lindberg *et al.*, 1975) might have increased the metal concentration in the surface sediments.

In chapter 8, the concentration of Cu, Cd and Pb in the edible muscle and whole soft tissue of three species of fish viz, *Epinephelus diacanthus*, *Nemipterus japonicus* and *scianidae* sp. From the west coast are being dealt with. It is apparent that the average metal concentration in inland sea fish is higher than in oceanic species. Thus for instance the average concentration of Cd in the fishes obtained from off Gujarat and off Mangalore are lower than that obtained from the near shore samples from Off Cochin area. The

recorded range of the studied trace metals in the edible muscle of the different species of fishes from the different locations studied indicated that the levels had not exceeded the permissible level prescribed for consumption.

The results indicated that wide variations in the levels of metals between different species. Compared to muscle, the concentration of the studied metals in the gill and liver was higher.

Chapter 9 embodies the summary and recommendations.

Though the input of anthropogenic pollutants into the system has not affected the levels of metals in edible muscle in an alarming extent, this baseline data can be used for regular ecological monitoring considering the industrial growth along the studied area.

This study has provided comprehensive information available to date for PAHs in seawater, sediment and fishes from the west coast of India especially from the Quilon to Mangalore region. Detectable levels of Polycyclic Aromatic Hydrocarbons in seawater are essentially limited to coastal and estuarine areas. Among the PAHs lower molecular weight components predominated in the samples suggesting the petrogenic source for the PAHs. Their concentration in the sediments from some stations in the off Cochin areas were high and found to pose a threat of acute toxicity and many of the other samples analysed have potential for chronic toxicity on aquatic organisms.

Recommendations

- Given the elevated concentrations of Polycyclic Aromatic Hydrocarbons found at some locations in this pilot study, long term monitoring of PAH in the Arabian Sea especially in major port areas and areas of higher industrial activity and large conurbations is recommended.
- Cargo ships and oil tankers visiting Indian ports may cause oil pollution in harbour waters by operational or accidental discharge. Such spills are highly dangerous and the owners of the ships must be made liable to pay compensation for clean up. It is possible to identify the exact source of pollution by matching samples of residues in the suspected tanker and the oil in harbour waters using IR spectrometry.
- The harmful effects of these known contaminants on the environment, and subsequently on man could be significant, therefore be further investigated.
- At present, no quantitative information is available as to whether accumulated PAHs in fish organs pose a risk to humans. Data on human exposure to PAHs including the determination of levels causing adverse effects other than cancers should be obtained.
- Preliminary study conducted on the east coast (not presented here) had shown that elevated levels of PAHs were found in the sediments along the Madras and Tuticorin coast. These indicate to the necessicity of regular monitoring in the east coast also.

- Emphasise should be given for analyzing and detecting the role of trace metals in causing various adverse effects in human beings other than cancers.
- Studies on isolation, identification and culturing of halophilic strains of bacteria, which can degrade petroleum hydrocarbons, must be conducted to explore the possibility of using them for clean up of PAH residues in the oceanic waters.
- Places near atomic power plants may be carefully monitored for radioactivity in seawater to ensure safety (Bombay, Koodamkulam, Chennai, Tuticorin, etc.).

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