ASSESSMENT OF HEAVY METALS IN THE ENVIRONMENTAL COMPARTMENTS OF THE CENTRAL AND NORTHERN COAST OF KERALA, INDIA

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by

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Declaration

I hereby declare that the thesis entitled **"Assessment of Heavy Metals in the Environmental Compartments of the Central and Northern Coast of Kerala, India"** is an authentic record of the research work carried out by me under the supervision and guidance of Dr. P.P. Ouseph, Scientist-F, Head, Chemical Sciences Division, Centre for Earth Science Studies, Thiruvananthapuram in partial fulfillment of the requirement for the Ph. D. degree of Cochin University of Science and Technology under the faculty of Environmental Studies and no part of it has previously been used as the basis for the award of any degree, diploma, associateship, fellowship or any other similar title or recognition in any other university.

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CERTIFICATE

This is to certify that the thesis entitled **"Assessment of Heavy Metals in the Environmental Compartments of the Central and Northern Coast of Kerala, India"** is an authentic record of the research work carried out by **Mr. Udayakumar P (Register No. 3405)** under my supervision and guidance for partial fulfillment of the requirements for the Ph. D. degree of Cochin University of Science and Technology under the faculty of Environmental studies and no part thereof has been previously presented for the award of any degree, diploma or associateship in any other university.

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Preface

The nearshore marine ecosystem is a dynamic environment impacted by many activities, especially the coastal waters and sediments contiguous to major urban areas. Although heavy metals are natural constituents of the marine environment, inputs are considered to be conservative pollutants and are potentially toxic, accumulate in the sediment, are bioconcentrated by organisms and may cause health problems to humans via the food chain. A variety of metals in trace amounts are essential for biological processes in all organisms, but excessive levels can be detrimental by acting as enzyme inhibitors. Discharge of industrial wastewater, agriculture runoff and untreated sewage pose a particularly serious threat to the coastal environment of Kerala, but there is a dearth of studies in documenting the contaminant metals. This study aimed principally to assess such contamination by examining the results of heavy metal (Cu, Pb, Cr, Ni, Zn, Cd and Hg) analysis in seawater, sediment and benthic biota from a survey of five transects along the central and northern coast of Kerala in 2008 covering a 10.0 km stretch of near shore environment in each transect. Trophic transfer of metal contaminants from aquatic invertebrates to its predators was also assessed, by employing a suitable benthic food chain model in order to understand which all metals are undergoing biotransference (transfer of metals from a food source to consumer).

The study of present contamination levels will be useful for potential environmental remediation and ecosystem restoration at contaminated sites and provides a scientific basis for standards and protective measures for the coastal waters and sediments. The usefulness of biomonitor proposed in this study would allow identification of different bioavailable metals as well as provide an assessment of the magnitude of metal contamination in the coastal marine milieu. The increments in concentration of certain metals between the predator and prey discerned through benthic food chain can be interpreted as evidence of biotransference.

This thesis is arranged in nine Chapters. At the end of the thesis, selected research papers (published) referred in the thesis are listed out. The list of publications published (10 in number) and under review (3 in numbers) including presentations/proceedings in symposia/conferences (3 in numbers) have been listed in the beginning.

First Chapter deals with general introduction about coastal ecosystem and heavy metal pollution, a brief review of literature about various aspects of the research problem and also deals with the aim and scope of the present study.

The second Chapter deals with general features of the study area. It also contains the details of the sampling and analytical methodology employed for determining various environmental samples.

The results of hydrography, seasonal and spatial variability in the nutrient distribution, stoichiometry, and phytoplankton biomass in the coastal waters of study area are presented in third Chapter.

The spatial and temporal variability in the distribution of dissolved metals *viz*. Cu, Pb, Cr, Ni, Zn, Cd and Hg along the central and northern coast of Kerala are discussed in the fourth Chapter.

The fifth Chapter discusses the spatial and temporal distribution of heavy metals *viz*. Cu, Pb, Cr, Ni, Zn, Cd and Hg in the sediments of central and northern coast of Kerala. The pollution status of study area was assessed by comparing the results with the sediment quality criteria guidelines.

In the sixth Chapter, the temporal and spatial variability in the accumulation of heavy metals, *viz*. Cu, Pb, Cr, Ni, Zn, Cd and Hg in the polychaete *G. longipinnis*, and its host sediment and its usefulness as biological indicator of heavy metal pollution along the central and northern coast of Kerala are discussed.

The seventh Chapter describes and discusses the concentration levels of heavy metals, *viz*. Cu, Pb, Cr, Ni, Zn, Cd and Hg in the organs of benthic fish

Cynoglossus macrostomus, risk assessment to humans and its usefulness as a biological indicator along the central and northern coast of Kerala.

The eighth Chapter details the link existing for heavy metal concentrations in flatfish with those of polychaetes and sediment metal concentration through food and feeding.

The ninth Chapter summarizes the results and conclusions from the study and suggests recommendations for increased understanding of metal dynamics for potential environmental remediation and ecosystem restoration of the Kerala coast. The relevant literature cited in the text is listed in the reference section at the end of the thesis.

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List of Publications of the Author

International and National peer reviewed Journals

[1] **Udayakumar P**, Chandran P, Jean Jose J, Prasanthan V, Deepak M P and Narendra Babu K (2011). Heavy Metals in the polychaete *Glycera longipinnis* from the Southwest of India. ***Chemistry and Ecology***, Vol.27 (4): pp 327-336. (DOI:10.1080/02757540.2011.579963).

[2] **Udayakumar P**, Ouseph P P, Jean Jose J, Rajesh B R, Chandran A and Narendra Babu K (2011). Seasonal dynamics of dissolved heavy metals in surface coastal waters of southwest India. ***Bulletin of Environmental Contamination and Toxicology***, Vol.87: pp 662– 668. ((DOI: 10.1007/s00128-011-0402-0).

[3] Baba M, Jean Jose J, **Udayakumar P** and Narendra Babu K (2011). Unusual foaming along Thiruvananthapuram Coast. ***Current Science***, 100(8): pp 1121.

[4] Jean Jose J **,Udayakumar P**, Deepak M P, Rajesh B R, Narendra Babu K and Chandran A (2011). Assemblages of the Marine Polychaete genus *Glycera* (Phyllodocida: Glyceridae) along the Kerala coast, India as an indicator of organic enrichment. ***Nature, Environment and Pollution Technology***, 10 (3): pp 395-398.

[5] Prasanthan V, **Udayakumar P**, Sarath Kumar and Ouseph P P (2011). Influence of abiotic environmental factors in the abundance and distribution of *Vibrio sps*. along the southern coast of Kerala,India. ***Indian Journal of Geo Marine Sciences***, 40(4): pp 587 -592.

[6] Jean Jose J, **Udayakumar P**, Chandran A, Narendra Babu K and Sudhanandh V S. (2011). Zooplankton Diversity in Vallarpadam, India. Influence of Hydrochemistry, Season and Semi Diel Cycle. ***Asian Journal of Water, Environment and Pollution***, 8(1), pp. 103 -108.

[7] Jean Jose J, **Udayakumar P**, Ajimon V J, Shibu R, Narendra Babu K and Baiju R S (2010). "Hierarchical Analysis of Zooplankton Assemblages over Semidiel Pattern in the Lagoon of Kavaratti Atoll, Lakshadweep Archipelago, India. ***Current Research Journal of Biological Sciences***, 2(4): pp 294-298.

[8] **Udayakumar P**, Abhilash P P and Ouseph P P (2009). "Assessment of Water Quality Using Principal Component Analysis- A Case Study of the Mangalore Coastal Region, India". ***Journal of Environmental Science & Engineering***, 51(3): pp 179-186.

[9] Ouseph P P, Prasanthan V, Abhilash P P and **Udayakumar P** (2009)."Occurrence and distribution of some enteric bacteria along the coast of Kerala". ***Indian Journal of Marine Sciences***, 38(1), pp 97-103.

[10] **Udayakumar P**, Ajimon V. J., Jean Jose J and Narendra Babu K (2009).

[11] Hydrochemical studies in Kavaratti Lagoon Waters, Lakshadweep Archipelago. ***Eco-chronicle***, **4** (3): pp 171 - 178.

[12] **Udayakumar P,** Chandran A**,** Jean Jose J, Rajesh B R, Prasanthan V, Baiju R S, Baijulal B and Narendra Babu K (2012). Nutrient – characteristics, stoichiometry and response stimulus of phytoplankton biomass in the southwest coastal waters of India. ***Aquatic Ecosystem Health and Management*** (under review).

[13] **Udayakumar P,** Ouseph P P**,** Chandran A**,** Jean Jose J and Anoop Krishnan K (2012). Trophic link of heavy metals in a benthic food chain – A case study from the southwest coast of India. ***Chemosphere*** (under review).

[14] **Udayakumar P,** Ouseph P P**,** Chandran A**,** Jean Jose J, K Narendra Babu and K Anoop Krishnan (2012). Seasonal dynamics of heavy metals contamination in the surficial sediments along the southwest coast of India. ***Marine Pollution Bulletin*** (under review).

[15] **Udayakumar P,** Ouseph P P**,** Chandran A**,** Jean Jose J and K Anoop Krishnan (2012). Heavy metals level in flatfish (Malabar tongue sole; *Cynoglossus macrostomus*) and its usefulness as bioindicator for heavy metal pollution along the SW coast of India. ***Environmental Forensics*** (under review).

National proceedings/presentations

[1] Shibu R, Jean Jose J, **Udayakumar P**, Ajimon V J and Narendra Babu K (2009). Biological productivity of Kavaratti Lagoon- Macrophytes versus Microalgae. National Conference on Coastal Processes, Resources and Management, CESS, Thiruvananthapuram: pp. 311-315.

[2] Jean Jose J, Vishnu S Raj, **Udayakumar P**, Baiju R S and Narendra Babu K (2011). Extraction of marine microalgal chlorophyll pigment using soxhlet apparatus for estimation – a convenient and effortless approach. 23rd Kerala Science Congress 29 -31, January 2011, India.

[3] Noufal K N, **Udayakumar P**, Faisal A K, Baiju R S and Anoop Krishnan K (2012). Identification of spatiotemporal physico- chemical pattern in coastal waters of Kochi and Mangalore, southwest coast of India. National Seminar on Frontiers in Chemistry, University of Kerala, Thiruvananthapuram: 25-27 April 2012, pp.23.

Acronyms and Abbreviations

BOD	Biochemical Oxygen Demand
Cd	Cadmium
CF	Concentration Factor
Cr	Chromium
CRV	Coastal Research Vessel
Cu	Copper
DO	Dissolved Oxygen
et al.	et alii (Latin word meaning 'and others')
etc.	et cetera (Latin word meaning 'and other similar things; and so on')
GF/F	Glass Fibre/Filter
Hg	Mercury
ICPOES	Inductively Coupled Plasma Optical Emission Spectroscopy
I_{geo}	Geoaccumulation Index
M	Monsoon Season
MLD	Million Litres per Day
MSI	Metal Selectivity Index
NH_3-N	Ammonia-Nitrogen
Ni	Nickel
NO_2- N	Nitrite-Nitrogen
NO_3-N	Nitrate- Nitrogen
Org-M	Organic Matter
Pb	Lead
PCA	Principal Component Analysis
PLI	Pollution Load Index
PM	Pre Monsoon Season
PO_4- P	Phosphate- Phosphorus
POM	Post Monsoon Season
PP	Primary Productivity
ppb	Parts Per Billion
psu	Practical Salinity Unit
Si $(0H)_4$ - Si	Silicate – Silicon
SSC	Suspended Sediment Concentration
TF	Transference/Biotransference Factor
TN	Total Nitrogen
TP	Total Phosphorus
TSI	Tissue Selectivity Index
Zn	Zinc
µg g^{-1}	Microgram per gram
µg l-1	Microgram per litre
µmol l^{-1}	Micro moles per litre

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Chapter **1**

INTRODUCTION

1.1	**General Introduction**
1.2	**Sources of Metals and its Toxicity**
1.3	**Marine Pollution: International and National Scenario**
1.4	**Coastal Pollution in Kerala**
1.5	**Review of Literature**
1.6	**Aim and Scope of the Present Study**

1.1 General Introduction

The Coastal zone is an area that has been defined as the junction between two major biomes where the land meets the Ocean. It has been regarded as an area of intense hydraulic, depositional, chemical and biological activity, since many processes in both environments are intensified at this boundary. The coastal Ocean accounts for only 7% of the total oceanic area, but it plays a very important role in biogeochemical cycles. It not only exchanges energy and matter with the open ocean, but terrestrial inputs of materials such as fresh water, sediments, dissolved or particulate nutrients and organic matter by surface runoff and groundwater flow have to pass through it (Gattuso *et al*., 1998; Gattuso and Smith, 2007). The processing of these materials in shallow waters is markedly different from that in the open Ocean. The contributions of the former to biogeochemical fluxes is disproportionately large, and approximately comprise 15% of oceanic primary production, 80% of organic burial, 50 % of calcium carbonate deposition, 90% of sedimentary mineralization, and 75 – 90% of oceanic sink of suspended material carried by rivers (Naqvi and Unnikrisnan, 2010). The socioeconomic importance of coastal Ocean is reflected by the facts that it provides 90% of the world fish catch, and its overall economic value is estimated to be greater than 40% of the world's ecosystem services and natural capital (Ryther, 1969; Gattuso and Smith, 2007). Finally, as much as 40% of the world's population lives within 100 km of the coastlines and this makes contamination of coastal waterways virtually ubiquitous.The contaminants of major concern are sewage, nutrients, metallic compounds, persistent organic pollutants, petroleum hydrocarbons and substances disrupting endocrine functions (GESAMP, 1982; 2001). In the coastal system, these contaminants, in the long run, aquatic microorganism's breakdown organic compounds to carbon dioxide and water as end products. But inorganics, especially heavy metals are continuously accumulating in marine environments because of its non biodegradable nature, except for a minor portion that may be taken away along with marine food and other products. The term heavy metal is widely defined and includes those metals

whose specific gravity is approximately 5 or higher (Lapedes, 1974; Venugopal and Luckey, 1975; Lesaca, 1977). In general, the expression 'Heavy Metals' is used where there are connotations of toxicity. Heavy metals occur naturally in the marine environment. In addition, these heavy metals enter the aquatic systems by direct discharges via industrial and urban effluents, surface run off and indirectly from atmospheric fallout (Ansari *et al.*, 2004). The common feature of these metals is that they are all relatively toxic even at fairly low concentrations and are readily concentrated by aquatic organisms, and plants. The significance of heavy metal contamination is further aggravated by the fact that they are generally water-soluble, non-degradable, vigorous oxidizing agents and are strongly bonded to many biochemicals inhibiting their functions. Certain metals are essential to normal growth and development of organisms, but some are toxic. An element can be regarded as essential only (i) if the organism can neither grow nor complete its life cycle in the absence of the element, (ii) if the element cannot be replaced by any other element, and (iii) if the element exerts a direct influence on organism and its metabolism. Similarly, an element can be regarded as toxic if that element injures growth or metabolism of an organism when supplied above a certain concentration (Bowen, 1979). In fact, all metals are toxic at high concentrations but some are highly toxic even at lower concentrations. Elements like copper, mercury, lead, cadmium, zinc and chromium are very toxic. Except copper and zinc, others are non essential and toxic (Ansari *et al*., 2004). Because certain metals are required in life processes, most organisms have a capability of concentrating them. Capability is enhanced by some feeding and metabolic processes which can lead to enormously high concentrations. Invertebrates appear to have a particularly high capability for concentrating metals along with other foreign materials found in their environment which they ingest inadvertently during foraging (Waring *et al*., 2006). Fishes apparently can accumulate metals either directly from sea water or indirectly through food chain. Because of the ability of many metals to form complexes with organic substances, they have a tendency to be fixed in the tissue and not to be excreted. In other words, they have a large biological half-time. This is perhaps one of the major harm that metals pose with respect to their effects on aquatic organisms. A major concern regarding the elevated levels of heavy metals in

coastal habitats and the organism that live within them is the potential for these heavy metals to be accumulated and magnified within the food chain (Philips and Rainbow, 1988), particularly commercial fishes and cause harm to humans (Bryan *et al*., 1980). This concern is because heavy metals are persistent, induce changes that can be irreversible and cause permanent damage to living organisms. Many catastrophic events of human health significance due to heavy metal pollution have occurred in the past. The well documented examples being Hg, Cd and Cu poisoning (Goldberg, 1992). Contaminations by these toxic elements have had, made tragic consequences for both local human societies (eg. mercury at Minamata and Cadmium induced ' Itai-Itai' disease both in Japan) and ecosystem (eg. copper in Macquarie Harbour, Australia and tributyltin in coastal waters off Brittanny, France) (Luoma and Rainbow, 2008). The study of heavy metals in marine environment, and their impact on aquatic organism received increased attention after the aforementioned detrimental events. If concentrations of heavy metals are not high enough to kill the fish, but are high enough to destroy the organisms on which the fish feeds, there will be substantial damage to fishery. Toxicity of a metal is dependent upon residence time of metals concerned and the chemical characteristics of the surrounding medium. Generally, most metals have a long residence time and hence exert their toxic effect over a long time. The effects of heavy metals on aquatic organisms can be divided into (a) direct effects and (b) indirect effects. The latter is effected through the effect on food chain organisms and ecological stress. The direct effects are seen in behavior, migration, physiology, metabolism, reproduction, development and growth of aquatic animals (Blaxter and Tjabbes, 1992). Thus heavy metal toxicity in aquatic organisms in association with the long residence time within food chains and the potential risk of human exposure makes it necessary to monitor the levels of these contaminants in marine milieu.

1.2 Sources of Metals and its Toxicity

In general, it is possible to distinguish between five different sources from which the metal pollution of the environment originates: (i) geologic weathering, (ii) industrial processing of ores and metals, (iii) the use of

metal and metal components, (iv) leaching of metals from garbage and solid waste dumps, and (v) animal and human excretions which contain heavy metals (Forstner and Williams, 1981). The dominant pathway for which the heavy metals enter into coastal environment are through rivers and land run off, but for a few metals such as Hg, As, and Pb airborne transport is an important route. The important anthropogenic sources of metals like Cr, Mn, Co, Ni, Cu, Zn, Pb, Cd, Hg and As to coastal and inshore waters are from industrial processing of ores and metals, ferrous and non ferrous metal industries including metal plating, industries producing both organic and inorganic chemicals, use of metal and metal components, leaching of metals from solid wastes and offshore dumping of domestic sewage, sludge and industrial wastes (Owens *et al*., 1997). The Table 1.1 shows the wide application of metals in diverse productions of commodities of modern society and as such they can become a common environmental pollutant.

Table 1.1: Industrial and agricultural sources for heavy metals in the environment

Use	Metal
Batteries and other electrical	Cd, Hg, Zn, Mn, Ni
Pigments and paints	Ti, Cd, Hg, Pb, Zn, Mn, Sn, Cr, Al, As, Cu, Fe
Alloys and solders	Cd, As, Pb, Zn, Mn, Sn, Ni, Cu
Biocides	As, Hg, Pb, Cu, Sn, Zn, Mn
Catalysts	Ni, Hg, Pb, Cu, Sn
Glass	As, Sn, Mn
Fertilizers	Cd, Hg, Pb, Al, As, Cr, Cu, Mn, Ni, Zn
Plastics	Cd, Sn, Pb
Textiles	Cr, Fe, Al
Refineries	Ni, V, Pb, Fe, Mn, Zn
Fuel	Ni, Hg, Cu, Fe, Pb, Cd

Source: Committee for Inland Fisheries of Africa (1991)

The term heavy metal may have various general or more specific meanings. According to one definition, the heavy metals are a group of elements between copper and lead on the periodic table of the elements; having atomic weights between 63.546 and 200.590 and specific gravities greater than 4.0. Under this definition the seven metals to be analyzed in this study copper (Cu), lead (Pb), chromium (Cr), nickel (Ni), zinc (Zn), cadmium (Cd) and mercury (Hg) are all within the confines of the classification for heavy metals.

1.2.1 Copper (Cu)

Copper is an essential micro-nutrient required in the growth of both plants and animals. It is widely distributed in nature especially in sulfide, arsenide, chloride and carbonate deposits. Presently Cu is widely used in many industrial, agricultural, and domestic purposes. Because of its widespread use, Cu is one of the most common environmental pollutants. It has been shown that anthropogenic inputs are the major sources of Cu contamination (Nriagu, 1979). Copper is indeed essential, but in high doses can cause anaemia, liver and kidney damage, and stomach and intestinal irritation in humans and mortality of marine biota. While interaction of copper with the environment is complex, research showed that most copper introduced into the environment is, or rapidly becomes, stable and results in a form which does not pose a risk to the environment. In fact, unlike some man-made materials, copper is not magnified in the body nor bio-accumulated in the food chain.

1.2.2 Lead (Pb)

Lead has been mined since ancient times and has been processed in many ways, e.g. for water pipes, containers and, as acetate, even for sweetening wine ("lead sugar"). World production amounts to millions of tons and is used in the manufacture of accumulators, solders, pigments, cables and anti-rust agents (red lead/lead oxide) and, a considerable amount still, into anti-knock petrol. The main sources of lead pollution in the environment are industrial production processes and their emissions, road traffic with leaded petrol, the smoke and dust emissions of coal and gas-fired power stations, the laying of lead sheets by

roofers as well as the use of paints and anti-rust agents. Environmental exposure to low levels of Pb has been associated with a wide range of metabolic disorders and neuropsychological deficits, especially in children (Nriagu, 1988; Silvany- Neto *et al*., 1989) and adverse effects in aquatic biota (Wong *et al*., 1978).

1.2.3 Chromium (Cr)

Chromium is the 21st most abundant element in Earth's crust with an average concentration of 100 ppm. Chromium exhibits a wide range of oxidation states. The most common oxidation states of chromium are +2, +3, and +6, with +3 being the most stable. Chromite ($FeCr_2O_3$) with a chromic oxide content of 68% is the only commercially important ore mineral. It is used in the production of ferrous alloys, refractory bricks, and in manufacturing of other Cr chemicals. The major contributions to airborne Cr are from ferrochrome production and from the handling and production of refractory bricks, coal combustion, and chrome steel production. The principal Cr contamination sources of natural waters are effluent discharges from metal-finishing processes, leather tanning, textile dyeing, and laundry chemical industries (Moore and Ramamoorthy, 1984; Nriagu and Nieboer, 1988). Chromium (VI) is one of the most toxic water pollutant and is comparatively more toxic than trivalent compounds. Chromium and its compounds are known to cause cancer of the lungs, nasal cavity and paranasals sinus and are suspected of causing cancer of the stomach and larynx in humans. In marine biota smaller species and early life stages are affected by Cr toxicity (Holdway, 1988).

1.2.4 Nickel (Ni)

Nickel, is a toxic element, ranking 24th among other elements on the earth crust and with 6% occurrence in the center crust (Pane *et al*., 2003). The levels of Ni in industrial wastewater discharges are higher than the average in places of low industrial density (Agency for Toxic Substances and Disease Registry, 2005). Nickel is a compound that occurs in the environment only at very low levels and is essential in small doses but it can be dangerous when the maximum tolerable amounts are exceeded. This can cause various kinds of

cancer on different sites within the bodies of humans, mainly of those that live near refineries. The most common application of nickel is an ingredient of steel and other metal products. Nickel is released into the air by power plants and trash incinerators and will settle to the ground or fall down after reactions with precipitation. It usually takes a long time for nickel to be removed from air. Nickel can also end up in surface water when it is a part of wastewater streams. The larger part of all nickel compounds that are released to the environment will adsorb to sediment or soil particles and become immobile as a result. In acidic ground however, nickel becomes more mobile and will often rinse out to the groundwater. Microrganisms can also suffer from growth decline due to the presence of nickel, but they usually develop resistance to nickel after a while. Nickel is not known to accumulate in plants or animals and as a result nickel has not been found to biomagnify up the food chain. For animals nickel is an essential foodstuff in small amounts. The toxic effect of Ni involves damages to DNA and impairs the reproductive function, principally when the organisms are exposed to high doses (Patriarca *et al*., 2000).

1.2.5 Zinc (Zn)

Zinc occurs naturally in air, water and soil, but zinc concentrations are rising unnaturally, due to addition of zinc through human activities. Mostly zinc is added during industrial activities, such as mining, coal and waste combustion and steel processing. Zinc is a trace element that is essential for human health. Zinc-shortages can cause birth defects.

1.2.6 Cadmium (Cd)

Cadmium (Cd) is a relatively rare earth element that is almost uniformly distributed in the earth's crust with an average concentration of 0.15 -0.20 ppm. Cadmium is probably the most biotoxic element and is regarded as a priority pollutant. It is widely used in various industrial products and processes including electroplating, pigments, plastic stabilization, batteries, and metallic alloys. Cadmium is also present as an impurity in several products, including phosphate fertilizers, detergents and refined petroleum products. Because of its

wide variety of uses, anthropogenic inputs into the marine environment are considered the principal source of Cd contamination. It is therefore expected that human activities in the coastal areas may result in relatively high concentration of Cd. Cadmium is very bio persistent but has few toxicological properties and once absorbed by an organism, remains resident for many years. Cadmium is concentrated particularly in the kidneys, the liver, the blood forming organs and the lungs. The harmful effects are kidney damage (necrotic protein precipitation) and metabolic anomalies caused by enzyme inhibitions. It is now established that the ltai-itai sickness in Japan (with bone damage) is a result of the regular consumption of highly contaminated rice with cadmium.

1.2.7 Mercury (Hg)

Mercury is a natural metallic element that occurs in many forms. Natural sources of mercury include weathering of rocks and minerals, forest fires, volcanoes, undersea vents, and hot springs. Man has used mercuric oxide (HgO) and cinnabar (HgS) as a pigment or a cosmetic since prehistoric times (Saha, 1972). Presently, Hg is extensively used in chloralkali plants, electrical products and processes, paints, instruments, dental preparations and catalysts. Mammals with toxic levels of mercury exhibit abnormal behavior, eating disorders, loss of balance, lack of coordination, and paralysis of legs (Environment Canada, 2005). The toxicity of Hg in the marine environment started with the case of Minamata disease in Japan where in the 1950s several people died or became terminally sick after consuming fish and shellfish containing relatively high concentrations of methyl mercury (Kurland, 1960).

1.3 Marine Pollution: International and National Scenario

Marine pollution occurs when harmful, or potentially harmful effects, result from the entry of chemicals, particles, industrial, agricultural and residential waste, noise, or the spread of invasive organisms into the Ocean. Most sources of marine pollution are land based. The pollution often comes from nonpoint sources such as agricultural runoff and windblown debris and dust. The vulnerability of coastal zone to human abuse, enhances the possibility

of several near shore areas including well-flushed regions, enclosed and semi enclosed region such as the Baltic, Mediterranean and North sea's getting increasingly polluted, eventually spreading the damage even to the open ocean in the long run (Sericano *et al*., 1995). The major factor driving coastal ocean degradation is the growth in human population that increasingly occupies the coastal space often modifying natural habitats, including mangrove forests, coral reefs, salt marshes and sea grass beds. Rapid depletion of mangrove areas at the rate of 5000 hectare per year due to their use in wood chip industry east Malaysia and conversion of 3200 hectare of mangrove forests to farms are the examples of habitat destruction (Sen Gupta *et al*., 1990).

The pollution of coastal waters in India is mainly due to the disposal of sewage, industrial wastes and agriculture run off. There are other minor sources such as aquaculture, ship breaking yards and disposal of wastes from fishing trawlers and small ships. These wastes are disposed into the coastal waters either directly or they reach through the rivers and other water bodies. Out of these sewage forms a major pollutant. There are 498 towns and cities in India in which seven cities have a population of more than one million. The estimated sewage generated from domestic sources is about 7000 million liters per day (MLD). Treatment capacity mostly for primary treatment is available for 1655 MLD and therefore, the remaining sewage is disposed in untreated conditions into creeks, estuaries and directly into the sea (ICMAM, 2010). Increase in suspended particulate matter (SPM), quarrying of corals, destructive fishing methods and pollution have lead to the degradation of coral reef which sustains diverse ecosystem in Andaman-Nicobar, Lakshadweep Islands and Gulf of Mannar. Development in terms of commercial and domestic activities as an outcome of international tourism has affected the pristine condition of marine waters. These developments are also found to affect traditional fisheries, interfere with marine life and eliminate near shore habitats. Coastal belts of Goa, Maharashtra, Karnataka, Kerala and Tamil Nadu offer many such instances of tourism related habitat degradation.

The development activities of ports and harbour usually results in the localized degradation of the environment. The flushing or water exchange in these regions is generally restricted. As a result contaminants like oily wastes, cargo escapement and sewage released from shipboard tend to accumulate in port basin. The development of ports in India has attracted industries and human settlements. As an outcome of this, all major ports in India like Mumbai, Kochi, Chennai and Visakhapatnam invariably receives large amount of untreated domestic and industrial wastes leading to the deterioration of the environmental quality, which has reached to an alarming proportion in some cases (Zingde, 1989). The contaminants can enter the coastal waters through a variety of pathways, such as direct release through outfalls, rivers, estuaries, creeks and bays. In addition to the above pathways, other sources include agricultural runoff including agrochemicals, sediment as a result of coastal erosion, deforestation and desertification in the hinterland. One of the major pollutants that contaminate the coastal waters of major cities is the solid wastes including garbage. The dumped garbage's especially in low lying areas and leachates, particularly during monsoon, enter nearby marine waters. About 5000 tons per day of garbage, 2500 tons per day of debris and 500 tons per day of industrial waste is generated in Mumbai; which finally ends up in marine water. Pollutant from such solid wastes include microorganisms, inorganic substances, oxidisable organic matter, nutrients, heavy metals, synthetic organic compounds, non-degradable matter, petroleum related compounds, particulate matter and heat.

The coastal population of India generate 11.10×10^9 m^3 of sewage annually leading to wide spread contamination of inshore and nearshore coastal areas particularly around coastal cities and towns. Thane, Mahim, Versova creeks and Ulhas estuary in Mumbai receives an estimated 2.3×10^5 m^3 per day of industrial and untreated effluents. These water bodies are characterized by abnormally high and tide dependant levels of PO_4^{3-}, NO_3^- - N and NH_4^+-N, variable DO often falling to zero at low tides in some instances and abnormally high population of pathogens. A large number of inshore waters bodies along

the west as well as the east coasts of India suffer from varying degree of environmental degradation. Notable examples are Veraval and Porbandar harbours, Mindola, Purna, Par, Ambika, Auranga, Damanganga, Ulhas and Ashtamudi estuaries, interior Kochi backwaters along the west coast, Paradeep,Visakhapatnam, Chennai ports, interior Hoogli and Rushikulya estuaries along the east coast (Zingde, 1989). Nutrient enhancement or loads brought in by a number of rivers which predominantly drain agricultural and forest areas in their hinterland into coastal waters can lead to eutrophication in extreme cases. This has serious implications particularly for fishery since subsurface water mass in the Arabian Sea is deficient in DO and an increase in organic matter can potentially decrease the thickness of the DO rich surface layer. The Baltic and Adriatic seas are notable example of such conditions (Goldberg, 1995). The increased fertility of coastal waters due to nutrient enrichment has resulted in changes in the structure of planktonic and benthic communities often with substantial ecological and economic consequences. Eutrophication leads to phytoplankton blooms which may have highly toxic poisons that can cause death to marine organisms and even humans. Cases of algal blooms leading to human death as in the case of Amnesic shellfish poisoning (ASP) in Prince Edward Island in 1987 and Neurotoxin shellfish poisoning (NSP) in New Zealand have been well documented. Events of exotic algal blooms particularly called red tide are known to occur in the Arabian Sea and to a lesser extent in the Bay of Bengal (Devassy, 1987).

India is one of the industrialized countries in the world. The industrial towns/cities such as Jamnagar, Surat, Mumbai, Thane, Mangalore, Kochi, Tuticorin, Cuddalore, Pondicherry, Vishakapatnam, Paradip, Haldia, Howrah and Kolkata are located near the coast. Major sources of industrial chemical discharges are from paper and pulp mills, sugar factories, distilleries, iron and steel works, dye industries, petroleum refineries, petrochemical industries, fertilizer factories, leather tanning and pharmaceutical establishment. These industries were found to generate 1078 MLD of waste water and are discharged to the coastal waters (ICMAM, 2010). The untreated effluents of these

industries are often complex and on a localized scale it can cause immense damage to the ecology. Another group of chemical contaminants of serious concern are those of synthetic organic compounds that can accumulate to relatively high concentrations in areas of restricted water exchange. These persistent halogenated hydrocarbons do not adversely affect the lower organisms in the sea; they are hazardous to predators which accumulate residue in fatty tissues as observed among the populations of marine mammals and birds of the Baltic and Wadden sea regions (Goldberg, 1995). The restrictions imposed on the manufacture and use of several organochlorine compounds has reflected in the decreased trends of concentration in the marine environment as well as biota. The decrease in the concentration of chlorinated hydrocarbons in oysters from the northern Gulf of Mexico and Naples bay (south Florida) has been reported (Sericano *et al*., 1995). Roughly, 25000 tons of chlorinated pesticides are used annually in India and about 50 tons of DDT is transported to the Arabian Sea and Bay of Bengal every year through river discharge (Shailaja and Nair, 1997). The present trend of decreased use of chlorinated pesticides in India may however result in decrease in their concentrations in the components of marine environment in future. Another group of contaminants which are of global concern are heavy metals because of their toxicity, persistence and bioaccumulation. The metals of concern are Pb, Cd, Hg and to a lesser extent Cr, Ni, Cu, Zn and As. Their levels in the coastal sediment is generally as a result of lithogenic contribution though some localized inshore areas shows elevated concentration over the years due to industrial and domestic effluents. Examples of region showing some toxic heavy metals are Mahim creek, Ulhas estuary and Vishakhapatnam harbor (Satyanarayana *et al*., 1994).

1.4 Coastal Pollution in Kerala

Kerala, with a narrow contiguous area extending along the coast (570 km), is dependent on coastal resources than any other state in the country. About 30% of the population lives in the coastal areas, resulting in very high density of > 2000 persons per sq.km. The main driving forces of coastal pollution are pollution owing to population followed by discharge of industrial

effluents, indiscriminate use of agricultural chemicals damaging the quality of river water and adding to marine pollution, oil pollution and air pollution. According to Kerala State Pollution Control Board (KSPCB), in Kerala about 3000 medium and large scale and about 2000 small scale industries are discharging effluent directly into saline and fresh water bodies. About 104536 m^3 of treated effluents per day is being discharged into the backwaters or sea in the coastal zone of the state. The extensive use of fertilizers, pesticides and fungicides results in undesirable residues causing considerable damage to the quality of water in rivers ultimately adding to the marine pollution problems and seriously affecting human beings as well as aquatic life. The operation of large scale oil tankers and other activities connected to handling of oil add to the problem of marine oil pollution by way of oil spills and use of motorized boats. A number of industries situated on the banks of rivers and backwaters continuously discharging their effluents into the wetland system. These effluents contain a large number of toxic ingredients such as acids, alkalies, heavy metals, suspended solids and a number of other chemicals. Among various industrial pollutants, heavy metals require special considerations due to their non degradable nature.

1.5 Review of Literature

1.5.1 Metals in Seawater

Literature providing information on the levels of metals in the different marine compartments along the West and East coast of India are confined only to a few localized regions. Sankaranarayanan and Reddy (1973) studied the distribution of dissolved Cu in the inshore waters around Goa coast. They attributed increased land discharge from natural and artificial sources for the increase in dissolved Cu in the inshore waters. Rao and Satyanarayana (1974) studied the distribution of trace metals (Fe, Cu, Mn and Co) in coastal waters off Vishakapatnam and in different regions in the Bay of Bengal. They observed higher values of Fe, Cu, Mn and Co in August-November (monsoon) and attributed it to the contribution from rivers and storm water channels draining the areas of mineral deposits located at north of Vishakapatnam.

Concentrations of Fe, Cu and Mn in surface waters of different regions of the Bay of Bengal revealed only slight variation during March-April, and showed an increasing trend away from south to north direction from the Nicobar area. Zingde *et al*., (1979) reported the concentration levels of As, Cu, Zn and Mn in marine flora and fauna of the coastal and estuarine waters around off Goa. A high level of dissolved Mn was discerned in the water and attributed the iron-manganese ore bearing land mass and mining operation for the increase. Duinker and Nolting (1977) have measured the dissolved and particulate trace metals in the southern Bight and the Rhine estuary in order to study the relative importance of precipitation and sedimentation processes as compared to mobilization processes in the estuary, and their impact on trace metal levels in the Southern Bight. Singbal *et al*., (1978) reported a range of 26 to 130 ng l^{-1} and an average of 77 ng l^{-1} concentration of dissolved Hg in the sea water collected at nine stations from the Arabian Sea. Sanzgiri and Moraes (1979) reported the distribution of trace metals like Fe, Cu, Mn, Zn, Co and Ni in both dissolved and particulate forms at five stations in the Laccadive Sea. The concentration levels were found to be within the range reported for the other areas of the world Oceans. Increased concentration of dissolved metals in the Cochin estuary, Ulhas estuary and Mahim creek due to localized anthropogenic inputs has been documented (Kulkarni and Desai, 1980; Sabnis, 1984; Bhosale and Sahu, 1991; Ouseph, 1992). Sanzgiri and Braganca (1981) determined the concentration levels of dissolved and particulate trace metals (Cu, Cd, Zn, Pb, Fe, Mn, Co and Ni) from the Andaman Sea. The results showed that Cu, Zn and Pb are more effectively removed onto particulate matter than Co, Ni and Mn.

The concentration of metals in seawater, marine biota and selected fishes in the Indian seas were extensively reviewed by Qasim and Sen Gupta (1988), Sen Gupta and Qasim (1985). They concluded that the levels of metal pollution in the Indian seas have not reached an alarming limit. Distribution patterns of Zn, Mn, Cu, Fe, Co, Ni, Cd, Cr, Pb and Sn in water, sediment and its possible impact on the harbour ecosystem, benthic species in Bombay harbor have been investigated by Patel *et al*., (1985). The concentration levels of these metals

were within the range of nearshore and oceanic waters and were far below to adversely affect the life and quality of benthic communities. The distinctly high concentration of Hg due to the effluent release from chlor alkali industry in Ulhas estuary, Thane creek –Mumbai Harbour (Zingde and Desai, 1981; Bhosale and Sahu, 1991), Rishikulya estuary (Sahu and Panda, 1987; Shaw *et al*., 1988; Sahu *et al*., 2002) and nearshore waters of Karwar (Krishna Kumar and Pillai, 1990) have been documented. Trace metal association in the water column of southern San Francisco bay, California was studied by Kuwabara *et al*., (1989). Schaule and Patterson (1981) determined Pb concentration in 34 surface and deep-water samples collected in the northeast pacific between Hawaii and California and concluded that Pb concentration are about 10 fold higher in surface and thermocline waters than in deep waters. Studies on the depth wise distribution of heavy metals in the North Indian Ocean by Sanzgiri *et al*., (1981) recorded dissolved Cd concentration in the surface waters and intermediate waters with an overall average of 0.15 ng l^{-1} and 0.34 ng l^{-1} respectively. The levels of selected dissolved metals like Cu, Co, Cu, Fe, Pb, Ni and Zn from five offshore stations of the Indian oceans was studied by Danielson (1980). Concentrations of dissolved Cu, Zn and Cd have been measured in the Dutch and Belgian coastal and offshore regions of the North Sea by Duinker and Nolting (1982). The average concentration reported for Cu, Zn and Cd were 0.20 -0.30 µg l^{-1}, 0.30 - 0.43 µg l^{-1} and 0.02-0.03 µg l^{-1} respectively.

Monitoring of Fe, Mn, Cr, Ni, Cu, Pb and Cd levels in sea water was conducted by Hall and Yen (1986) in the vicinity of a industrial site located along the western coastline of the Island of Trinidad with the objective of acquisition of baseline information prior to the commencement of industrial activity. The location located close to a number of already existing industries showed the highest average for all metals except Cd; while at all other stations the average concentration for all metals except Cd were generally similar. The concentration of Cd, Co, Cu, Fe, and Ni were found to agree with other open Ocean regions while Pb and Zn were found to be high. Windom (1999)

assessed the processes occurring in the low (0–5) salinity region and the role of biological processes in the transport and fate of trace metals in a coastal lagoonal system. Based on the results, in Patos Lagoon three zones were identified, within each of which certain processes dominate the fate and transfer of materials. Govindasamy and Azariah (1999) reported the dissolved heavy metals and associated hydrographic nutrient data in the coastal water of the Coromandel Coast, Bay of Bengal. They reported enrichment of heavy metal contamination due to Cu, Zn, Ni, Co, Cd and Hg in the Coromandel Coast, when compared to other marine environments of the Indian Coast. The distribution of mercury along the west coast of India was studied by Kaladharan *et al*., (1999). The distribution showed a conspicuous pattern showing low levels ranging upto 0.058 $\mu g\ l^{-1}$ during premonsoon and monsoon seasons and an increase of 100% during the post monsoon season.

Fatoki and Mathabatha (2001) investigated the distribution of heavy metals Zn, Cd, Cu, Fe, Mn and Pb in sediment and sea water from the East London and Port Elizabeth harbours. The results are indicative of the contribution of heavy metal pollution from storm water drains and streams which carry run off from industrial, urban and residential sources.

Nutrient and metal distribution in the Gulf of Astakos, Greece was studied by Eleftheriadou and Skoullos (2003) in view of the need for sustainable development of the region. Seasonal fluctuations were recorded in both nutrient and metal concentrations in the region. Ansari *et al*., (2004) addressed a review regarding the basic concepts, sources, speciation, mode of action, levels, analytical measurement, bioavailability, bioaccumulation, biological role and toxicity of heavy metals in the marine environment.

The concentrations of heavy metals Zn, Cu, Mn, Pb, Ni and Cd were measured by Accornero *et al*., (2004) in surface coastal waters of the southern Adriatic Sea. Concentrations exhibited relatively low values, lower (or similar) than those observed in other Italian coastal areas and generally much lower than at other sites of the coastal Mediterranean. The distribution of heavy metals in

abiotic phases (dissolved and particulate) and biotic fauna were analysed and studied by Shilla *et al*., (2008) in the Scheldt estuary. Results showed that the contribution from the dissolved phase was more significant compared to the particulate phase and the bioaccumulated heavy metals in the tissue were above the acceptable limits, implying critical estuarine pollution.

Aloupi *et al*., (2007) carried out survey along the Mediterranean coastline to provide recent information in selected susceptible marine environments along the Mediterranean coastline. The results revealed small quantity of untreated sewerage affecting the water quality as revealed by the higher mesotrophic character of the water and presence of low level metals.

Satpathy *et al*., (2008) monitored the seasonal variation in mercury (Hg) concentration in the coastal waters of Kalpakkam. The Hg level (dissolved + acid leachable) ranged from 3 to 50 ppb for surface and 1.5 to 47.9 ppb for bottom-water samples, yielding an annual average concentration of 20.42 ± 11.44 and 23.11 ± 13.06 ppb for surface and bottom waters respectively. The observed values are significantly lower (30 times) than the earlier reported values from this coast.

Trace metals in the coastal waters and organisms of the austral Chilean channels and fjords was investigated by Ahumada *et al*., (2008). The results revealed bioaccumulation in the order Cu > Pb > Zn > Cd. Ashokkumar *et al*., (2009) carried out studies on the heavy metals level in the Mullipallam creek of Muthupettai Mangrove, southeast coast of India and the levels followed the order Fe > Mn > Zn > Cd > Hg.

The physico-chemical and biological characteristics of water and sediments in the coastal region from Mangalore Harbour to Suratkal , southwest coast of India indicated larger variations due to anthropogenic inputs (Shirodkar *et al*., 2009). The observed contamination of coastal waters indicated anthropogenic inputs of Cd and phenol from industrial effluent sources at Kulai and Suratkal, ammonia from wastewater discharges off Kulai and harbour, PHC and Hg from boat traffic and harbour activities of New Mangalore Harbour.

Zinc, copper and lead levels in the aquatic phase and underlying surface sediments from the coastal zone of the West Bengal, were recorded by Chakraborty *et al*., (2009). Results elucidated a sharp exchange of selected metals between the aquatic phase and sediment in the system.

Rajamohan *et al*., (2010) analysed for distribution of heavy metals *viz* Fe, Cu, Cd, and Hg in the coastal water of southeast India. The samples were collected from the vicinity of Madras Atomic Power Stations. Study inferred that heavy metal concentration in the vicinity of the power station is comparable to unpolluted pelagic waters of the Bay.

1.5.2 Metals in Marine Sediment

The textural compositions of the central –southwest coast of India with low percentage of clay in the outer shelf and high percentage in the inner shelf have been reported (Nair and Murthy, 1968; Nair, 1976; Rao *et al*., 1983). The distribution pattern of Cu in the sediments of the western continental shelf of India has been studied by Rao and Satyanarayana (1974). The influence of metropolis waste, which is discharged through various points to the harbour environment of Mumbai coast have been reported (Naidu and Shringapure, 1975; Zingde *et al*., 1979; Zingde *et al*., 1989; Ramaiah *et al*., 1992; Ramaiah and Nair, 1993; Ramaiah and Nair, 1997; Ramaiah and Nair, 1998; Swami *et al*., 2000; Zingde and Govindan, 2000). Total Mercury in water, sediments and animals along the Indian coast was documented (Sanzgiry *et al*., 1988). The geochemical investigations on surficial sediment samples of the Mangalore-Cochin shelf and upper slope were made by Paropkari (1990) to understand the distribution, sources and processes by which various major and trace elements are incorporated into the sediments. Several workers reported distribution of organic carbon in the surficial sediments and sediment cores collected along the western margin of India and related variations due to changes in water masses, productivity and intensity of monsoons both at regional and global scales (Sarkar *et al*., 1990; Babu *et al*., 1999; Naidu and Shankar, 1999; Thamban *et al*., 2001; Agnihotri *et al*., 2003; Pattan *et al*., 2003).

The concentration of heavy metals in surficial sediments were studied to evaluate the pollution staus of the North sea, Suez Gulf, Mediterranean sea , southern Caspian coast and Maderia island shelf sediments (Everaarts and Fischer, 1992; El Nemr *et al*., 2006; El Nemr *et al*., 2007; Parizanganeh *et al*., 2007; Anabela *et al*., 2007). Textural and trace elemental distribution in sediments of the Beypore estuary, SW coast of India and its adjoining innershelf was studied by Nair and Ramachandran (2002); and indicated the effect of industrial effluents on their incorporation in sediments. The importance of heavy metal bioavailability on the bioconcentration in aquatic biota was examined by Mountouris *et al*., (2002) employing statistical analysis. Results showed satisfactory correlations, only when factors that affect bioavailability, such as metal oxides concentration and organic carbon content in the sediment, are taken into account.

Balachandran *et al*., (2003) analysed the textural and geochemical fraction such as Fe, Co, Cr, Cu, Mn, Ni, Pb and Zn on a seasonal basis in the coastal sediments of central southwest coast of India. The geochemical processes revealed increased metal due to monsoonal supply in the coastal waters and effective masking of these metals by incorporation into clay and organic association which follows immediately after the monsoon. The geochemical condition of surface sediments in a tropical estuary and adjoining shelf region of the Central southwest coast of India was presented for their elemental interactions using statistical methods (Balachandran *et al*., 2005).

Detailed surveys of intertidal sediments have been performed along the north and south shores of the Inner Clyde estuary, by Hursthouse *et al*., (2003). Surface sediment data reveal significant spatial variation in Cr content and an association with major sediment characteristics and location within the estuary. Sediment grain size and organic carbon (OC) data collected over the past 50 years, from Todos Santos Bay were interpreted by Smith *et al*., (2008). Results inferred sediment OC composition is apparently controlled by energy-related sorting and deposition, oxidation of much of the original terrigenous organic carbon, and replacement of some terrigenous organic carbon by marine organic

carbon. Abdallah and Abdallah (2008) determined concentrations of Cd, Cu, Co, Zn, Mn and Fe in biota and sediment samples collected from the Eastern Harbour and El-Mex Bay in the Mediterranean Sea, Egypt and observed a high variability in the metal levels among the studied biota and between the investigated sites.

Concentration levels of Cr, Ni, Zn, Pb and Cu in relation to those of the nutrients – total phosphates, exchangeable nitrates, total organic carbon, etc. have been investigated in the sediments of Nagapattinam beach after the 2004 tsunami (Sujatha *et al*., 2008). Amin *et al*., (2009) determined the concentration of Cd, Cu, Pb, Zn, Ni and Fe in the surface sediments of Dumai coastal region and classified it as a moderately polluted coastal environment. Galanopoulous *et al*., (2009) determined ten elements Cd, Pb, W, Zn, Mn, As, Se, Cr, and Cu, organic carbon in the surficial sediments of Keratsini harbor, Saronikos Gulf, Greece. The contamination of the sediments was assessed on the basis of geoaccumulation index and to corresponding sediment quality guidelines (SQGs) effects range low/effects range median. The results revealed highly elevated Cd, Pb, W, Zn, As, Se, Cr, Cu, and organic carbon values due to the contribution of the Central Athens sewage outfall.

Spatial distribution of metal concentration in the surface sediment samples collected from marine locations carrying different coastal ecosystems such as mangroves, sea grasses, dead coral and sandy beaches of the Andaman Islands, India was studied by Nobi *et al*., (2010). The results in general showed that metal concentration was less in this ecosystem when compared with similar ecosystems of mainland of India.

Surficial and Core samples collected from the sedimentary microenvironments of Lakshadweep Archipelago were analyzed by Gopinath *et al*., (2010) for their trace metal contents. Group linkage clustering technique was used for drawing dendrograms to show the similarity among them. Surface sediments of the lagoons of Lome Togo, were analyzed for mercury, methylmercury, and trace elements by Kissao (2011). Concentrations were

found to be greater than typical for natural lagoon sediments and confirmed the possibility of input of waste discharges into the lagoon.

1.5.3 Metals in Marine Biota

Baseline study of the level of concentration of mercury in the food fishes of Bay of Bengal, Arabian Sea and Indian Ocean was done by Ramamurthy (1979). The results reveals that mercury levels in 18 groups of fish and other sea food had the mean average values ranged from 5 - 65 µg/kg. Levels of the mercury concentration in some known food fish of the Indian Ocean, Bay of Bengal and Arabian Sea were compared with similar species found in the Mediterranean, Atlantic and Pacific Ocean. A statistical study of environmental factors controlling concentration of heavy metals in the burrowing bivalve *Scrobicularia plana* and the polychaete *Nereis diversicolor* was carried out by Luoma and Bryan (1982). An unexplained increase in concentration of Cu in the tissues of bivalve was noted. Kureishy *et al*., (1983) analysed for Hg,Cd and Pb in several fishes representing different trophic levels in the Andaman Sea. The Cd levels in liver of almost all fishes showed increased concentration while Hg was low in all the tissues. Benthic invertebrates as cosmopolitan biomonitors have been studied extensively (Philips, 1976; Orren *et al*., 1980; Martincic *et al*., 1986; Rainbow and Philips, 1993; Shuklin and Kavun, 1995; Rainbow, 1995; Saiz-Salinas *et al*., 1996; Cantillo, 1998; Amin *et al*., 2009). The calcareous skeletons of sea urchins can concentrate metallic elements from sea water by up to several thousand times and two species *Paracentotus lividus* and *Arabacia lixula* were reported with high capacity of heavy metals in Portman Bay, Spain (Auernheimer and Chinchon, 1997). The edible species *Paracentotus lividus* was proposed as a bioindicator for heavy metals (Mustafa and Collins, 1995). The toxicity test on the gastropod *Morula granulata* from the east coast of India indicated low tolerance to heavy metals such as Cu, Cd, Zn and hence not suitable as bioindicator for these metals was documented (Uma Devi, 1997). The relationship between sediment trace metals (Ag, Cd, Cr, Cu, Ni, Pb, Zn) and bioaccumulation in tissue of macrobenthos was described from 1975-1985 on the San Pedroshelf, California by Maurer *et al*., (1997).

Krishnamurti and Vijayalakshmi (1999) estimated levels of Cu, Zn, Cd, Pb and Ni in different tissues of 10 species from Thane and Bassein creeks. The trend in accumulation indicated that irrespective of species Cu and Zn contributed 42-58% to the total metals accumulated. A post Gulf sea water pollution assessment program was carried out in the liver, skin and muscle tissues of the localized *Lethrinus lentjan* fish species (Yousuf *et al*., 2000). The study concludes that the marine fish from the Arabian Gulf are comparatively clean and do not constitute a risk for human health. Concentration of trace metals like Hg, Cd, Pb, Cu, Zn, Fe, Mn, Cr, Co and Ni were determined in the squids, *Loligo duvauceli*, and *Doryteuthis Siboge* collected from Mangalore, Cochin and Quilon, the three major fish landing centres in the west coast of India (Prafulla *et al*., 2001). Geographical variations in metal levels were observed in these species. Krishna Kumari *et al*., (2006) analysed some trace metals in the short neck clam *Paphia malabarica* from Mandovi estuary, Goa. Cadmium accumulation was highest in the mantle and adductor muscle, Pb in foot, Cu in digestive gland and gonad, and Zn and Fe, in gills. Geeta *et al*., (2006) studied heavy metal accumulation in Green mussels representing different size groups and habitats from the inshore waters of Karnataka (southwest coast of India) to analyze the tissue concentrations of Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn. Tissue concentrations of Cr, Cu, Fe, and Pb were significantly higher in smaller mussels than in the larger size group. Significantly higher concentrations of Cr, Cu, Fe, Mn, and Ni were observed in mussels sampled from intertidal beds when compared to mussels from the subtidal beds.

Waring *et al*., (2006) measured whole tissue trace metal concentrations of ten metals in eight common coastal Australian polychaete species collected from uncontaminated locations. Principal components analysis of trace metal signatures revealed that the habitat, i.e. exposed coast sand or rock, estuarine sand or estuarine mud substrate in which a polychaete species was found, had a significant influence on the bioaccumulation of six trace metals (Mn, Cu, Zn, Ag, Cd and Pb). Alquezar and Markich (2006) examined the metal concentrations and nutritional value (protein and lipid content) of sediment

infauna consumed by the estuarine smooth toadfish (*Tetractenos glaber*) at sites with varying metal contamination in the Sydney Harbour, southeastern Australia, and the resulting influence on toadfish size and their tissue metal concentrations statistically. Fishes collected from five different locations from the Calicut region, India were analysed for the levels of organochlorine pesticides (OCPs) and heavy metal residues in order to elucidate the status of these chemical contaminants in fish and shellfish meant for human consumption (Sankar *et al*., 2006). Burgera *et al*., (2007) examined the levels of arsenic, cadmium, chromium, lead, manganese, mercury, and selenium in the kidney, liver, and muscle of great sculpin and flathead sole from Adak Island in the Aleutian Islands, Alaska. There were significant differences in the levels of heavy metals as a function of tissue for both fish species; the liver of sculpin and sole generally had the highest levels of most metals, except for arsenic, lead, and selenium. Levels of arsenic, lead, and mercury may pose a risk to predators that consume them, and arsenic and mercury may pose a risk to human consumers. Magalhaes *et al*., (2007) related fish biological and ecological characteristics to total and organic mercury concentrations to determine whether accumulation is influenced by trophic level, Hg concentration in the diet, and vertical distribution. Enhanced mercury bioaccumulation in relation to depth appears to be determined primarily by concentrations in food and ultimately by water chemistry.

Accumulation of heavy metals like Hg, Pb, Cd in fishes and crabs to a considerable extend in the Gulf of Cambay,India occurring due to rigorous anthropogenic activities has been reported by Reddy *et al*., (2007). The health risk of consumption of shell fish species due to the bioavailability of trace metals like Cu, Cd, Cr, Hg, Pb and Zn in Maliston Bay, eastern Adriatic was assessed by Gaspic *et al*., (2007) and inferred that there is no health risk for moderate shell fish consumers. Metal concentrations was measured monthly in an annual cycle in the tissues of *Nereis diver color* rag worms and sediment from two Moroccan Atlantic Coastal lagoons: Khnifiss and Oualidia (Idardare *et al*., 2008). Fevzi Yilmaz (2009) compared heavy metal concentrations (Cd,

Cu, Mn, Pb, and Zn) in tissues of three economically important fish (*Anguilla anguilla, Mugil cephalus* and *Oreochromis niloticus*) inhabiting Köycegiz - Mugla (Turkey). The disturbances caused by the land based inputs of eight trace metals (Cd, Hg, Pb, Cr, Ni, Tl, Zn & Cu) in the Moroccan Mediterranean coast using two species of mollusks was discussed by Blinda *et al*., (2005). They concluded heavy-metal contents in organism are due to the surrounding environment acting as vectors of these metallic pollutants.

Saha *et al*., (2006) and Alam *et al*., (2010) recorded bioaccumulation of trace metals in soft bottom polychaetes along with host sediments from the intertidal regions of Indian Sundarban mangrove wetland. The investigations indicated the possibility of developing a standard test protocol for bioaccumulation by polychaetous annelids. Rejomon *et al*., (2010) estimated the concentration of Fe,Co,Ni,Cu,Zn,Cd and Pb in the muscle tissue of marine fishes like *Lates calcarifer*, *Nemipterus japonicas*, *Caranx melampygus*, *Rastrelliger kanagurta* and *Cyanoglossus macrostomus* in the continental shelf waters off Cochin and Mangalore of southwest coast of India. The fish species showed a great capacity to accumulate metals, with highest bioaccumulation for the essential element iron and lowest bioaccumulation for the non essential element lead.

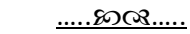
1.6 Aim and Scope of the Present Study

The great bulk of monitoring studies conducted by many countries have been concerned with obtaining information on heavy metal concentrations in water, sediment and biota, of their respective coastal region with the emphasis on the latter being often to allay public health concerns. Invertebrates are considered excellent indicator organisms because of their ability in concentrating metals, among other pollutants. There has been a dearth in studies on documenting the seasonal variation of heavy metals in water, sediment and benthic biota in the coastal waters of India. Besides measuring concentrations of these metals in aquatic organisms and its host environment, there is a need to study effects of concentrated metals on organisms and on ecosystem. This will

require careful evaluation of effects of metals on various trophic levels in marine ecosystem and movement of metals through food web. Sediments being the ultimate repository of contaminants, this can act as a source of contaminants in benthic fauna for accumulation and finally find its way into seafood consumers. The current study is mainly based on heavy metal contamination in marine environment, its accumulation in sediment dwelling fauna (polychaetes and flatfish) and to evaluate the metal toxicity flow through a benthic food chain (sediment – polychaetes - flatfish). The metals discussed in this study include copper (Cu), lead (Pb), chromium (Cr), nickel (Ni), zinc (Zn), cadmium (Cd), and mercury (Hg). These metals have been selected due to their diverse application in a majority of the commodities produced by the modern society, their toxic effect on living organism and their levels are easily measurable in the marine samples.

The present work aims at:

- To establish the physico-chemical characteristics of coastal waters of central (Cochin, Chettuva) and northern (Ponnani, Calicut and Kasargod) Kerala.
- To study the concentration of selected heavy metals (Cu, Pb, Cr, Ni, Zn, Cd, and Hg) in the water and sediment of the central and northern coast of Kerala.
- Bioaccumulation of heavy metals in sediment living polychaete worms and flatfish and to express it as a biological indicator.
- To prove and correlate the heavy metal transport through food chain relationship.



Chapter 2

MATERIALS AND METHODS

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2.1 Geographical and Environmental Background of the Study Area

The Kerala coastline extending up to 570 km in length consists of beaches, ridges, riverine deposits, backwaters and coastline. The coastal land is characterized by paddy fields, coconut plantations and extensive network of backwaters inter- connected with rivers and canals in the landside with most of them open into the coastal region.

Winds in this region are stronger (8- 10 m/s) north easterlies during post monsoon (October – January) and pre monsoon (February – May), while south westerly during monsoon (June – September). The current direction is from south to north during November – January, and it reverses in February with strong north to south currents from May to October (Shirodkar *et al.*, 2009).

The onset of south west monsoon occurs in May and June and continues through October. From November to February, the coast is influenced by lighter, drier northeast winds. The upwelling period (June to October) of southwest monsoon is associated with algal blooms and the favorable productivity factors support large fisheries along the west coast, which contributes 60% to the total fish catches along the Indian coast (Naqvi *et al.*, 2000).

The coastal towns and villages generate about 351 MLD of untreated sewage and it is disposed in the backwaters which ultimately impinge into the coastal environment. An estimated 17,104 m^3/ day of treated effluents from the industries are also discharged into the coastal waters.

2.2 Sampling

For this study five different transects from central (Cochin, Chettuva) and northern (Ponnani, Calicut and Kasargod) Kerala coastal waters of southwest India were selected (Fig. 2A). Seasonal sampling representing post monsoon (January $I^{st} – 5^{th}$), pre monsoon (April $I^{st} – 6^{th}$) and monsoon (September $16^{th} – 21^{st}$) were carried out onboard *CRV* Sagar Purvi/Paschimi during the year 2008. Sampling was carried out in six sampling points (0.5, 1.0, 3.0, 5.0, 7.5 and 10.0 km) at each transects extending from bar mouth to offshore perpendicular to the

coast. The locations from where the samples were obtained are given in Table 2.1.The selection of locations was based on the inflow of pollutants from different sources.

Cochin : Cochin coastal areas along the south-west coast of the Arabian Sea receives water, sediment and silt from the extensive Vembanad Lake system at Ernakulam (Cochin barmouth) and at Munambam (Azheekode barmouth), discharged from the lower reaches of Periyar River. The urbanization, industrialization (70 large scale and 30580 small scale industrial units) and related anthropogenic activities produce a large quantity of sewage and effluents laden with toxic contaminants that are discharged into the Cochin barmouth through the backwaters. More than 240 industrial units operating in Edayar village of Eloor panchayath make this part of the river into a cesspit of chemical pollutants. The major polluting industries in the region include fertilizer plant, oil refinery, rare earth processing plant, minerals and retiles plant, zinc smelter plant, insecticide factory and organic chemical pollutant. The volume of industrial effluents from Eloor- Kalamasery belt is about 2.6 million litres per day (Menon *et al.*, 2000; Greenpeace, 2003) much of which is discharged directly into the Periyar River from where it is emptied into Cochin coastal waters. Frequent instances of fish kill along this belt especially during the south-west monsoon are a common affair (Unnithan *et al.*, 1977; Greenpeace, 2003). Cochin backwater (300 sq. km) is a positive estuarine system receiving freshwater discharge from three major rivers of Kerala namely, Periyar, Muvattupuzha and Chalakudy (Sankaranarayanan *et al.*, 1986). The common contaminants of Cochin backwaters are acids, alkalis, suspended solids, fluorides, free ammonia, insecticides, dyes, trace metals and radioactive nuclei (Lakshmanan *et al.*, 1987; Menon *et al.*, 2000). The effluents from Ambalamugal located 16 km east of Cochin, which is an industrial complex with a giant fertilizer plant and an oil refinery, are discharged into Chitrapuzha which ultimately flows into the Cochin backwaters. In addition, the area is listed as one of the top 50 destinations in the global tourism map, shipping and port activities thus altogether increasing the pressure on the ecosystem.

Chettuva: is an important fish landing centre of Thrissur district. The discharges from the establishments in the great temple town of Guruvayur in Kerala, where millions of pilgrims visit each year in to the streams/ canals finally joins the backwaters and empties into sea through an outlet at Chettuva. There also numerous canals which bring untreated domestic and industrial (7800 registered small scale units in the district) discharges from the hinterland and finally impinges into the Chettuva coastal waters.

Ponnani: is an important fishing centre of Malappuram District and has a minor port. The longest river in the state, the Bharathapuzha with a total length of 251 km after flowing through Coimbatore district in Tamil Nadu and Palakkad district in Kerala enters into the sea at Ponnani. There are numerous small scale industries (34 large scale and 3700 registered small scale units in the district) operating in and around the region which includes textiles, agro based, engineering, chemical, leather tanning, fish processing, metal plating industries etc. which discharge their effluents in open drains and river, finally impinges into the coastal waters. Water that flows through or over land may accumulate pollutants and carry them into rivers and estuaries. There is also inflow of agricultural wastes into the coastal waters as agriculture predominates in the region's economy. As far as fisheries is concerned the use of mechanized boats are prevalent here.

Calicut: represents one of the industrially advanced areas of the Kerala state. There are about 20 large scale industrial units and about 1564 registered forest based industrial units. Another major industry is the tile industry which includes production of ceramics, crockery, stoneware pipes and insulation materials. Other important industries include textiles, plywood, general engineering, automobiles, plastics, steel fabrication and fish processing. Calicut Corporation has a 15 km length coastal area and most of the slums of the city are situated in this coastal area. The open defecation, dumping of wastes directly to seashore and discharging of drainage into coastal area leads to marine water pollution. The small scale industrial activities like paint factory, soap factory and oil mills discharge their effluents into pits or open drains in adjacent areas. Most of these

units use chemicals for their production process and they do not have waste treatment systems. These pollution problems aggravate the misery of the inhabitants of coastal belt of Calicut.

Kasargod: Kasaragod district occupies northern part of Kerala. The majority of the 12 rivers of the district like Chandragiri, Kumbala, Bakel etc are polluted with effluents discharged from industries located on the banks (5559 registered small scale industrial units in the district,majority of which are textiles followed by engineering units and agro based industries), dumping of municipality wastes, solid wastes, and septic discharges. The main occupation of the people here is agriculture as such this has lead to the usage of chemicals (pesticides and insecticides) which finally reaches the coastal water. Fishing and animal husbandry are other fields in which the people are engaged in. It is also one of the major fish landing centers in the district.

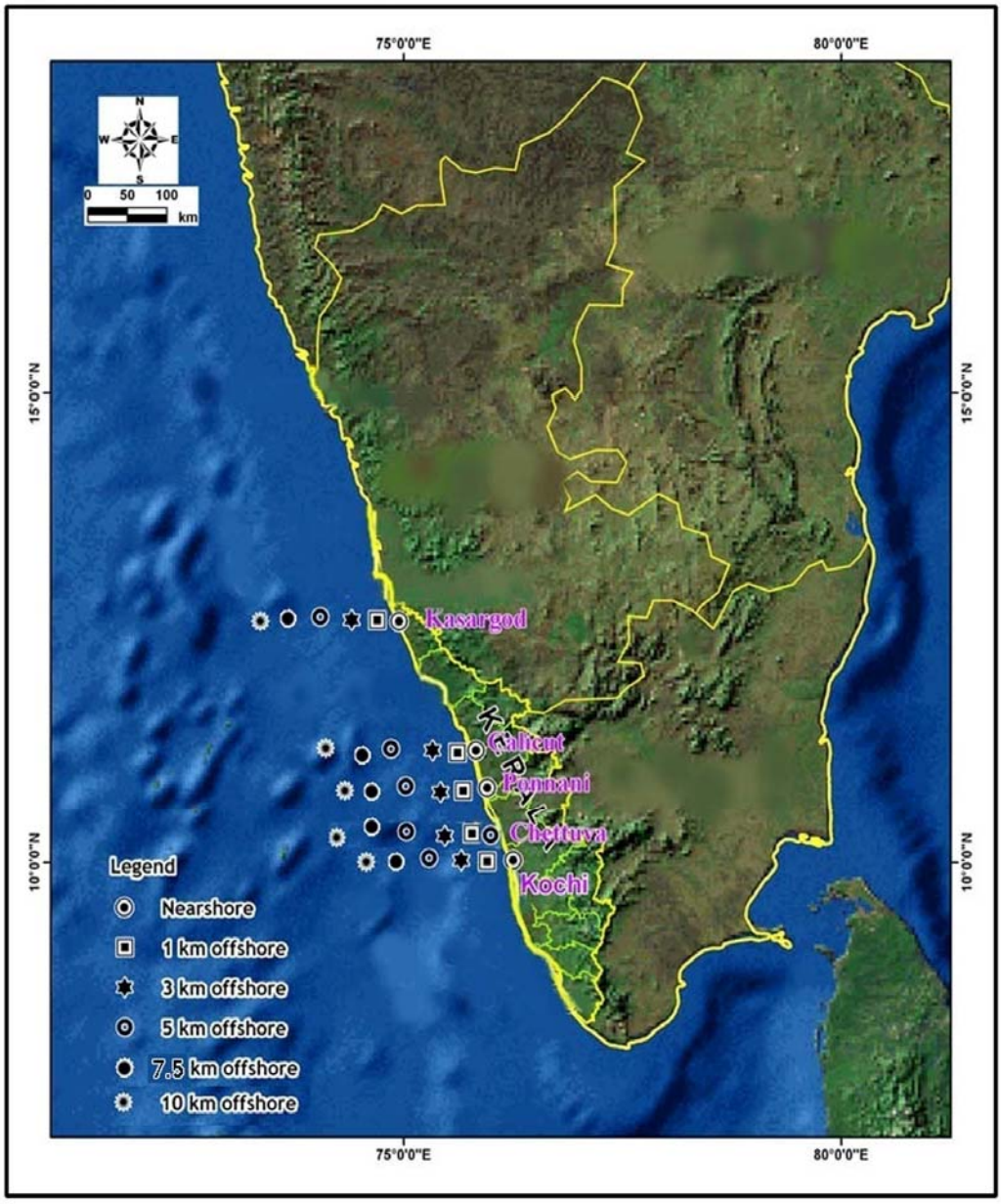


Figure 2A. Area of investigation along the central and northern coast of Kerala.

Table 2.1: Location of sampling points along the central and northern coast of Kerala.

Transect	Station	Latitude	Longitude	Depth(m)
Cochin	0.5 km	09^{0}57'6.9" N	76^{0}14'29" E	8.6
	1.0 km	09^{0}56'16" N	76^{0}13'55" E	11.5
	3.0 km	09^{0}56'16" N	76^{0}12'50" E	8.4
	5.0 km	09^{0}56'14" N	76^{0}11'48" E	9.2
	7.5 km	09^{0}56'15" N	76^{0}10'41" E	10.1
	10 km	09^{0}56'18" N	76^{0}09'13" E	11.9
Chettuva	0.5 km	10^0 16' 45" N	76^{0}07'23" E	4.5
	1.0 km	10^0 16' 21" N	76^{0}06'54" E	6.1
	3.0 km	10^0 16' 33" N	76^{0}05'03" E	9.3
	5.0 km	10^0 16' 34" N	76^{0}04'36" E	14.2
	7.5 km	10^0 16' 32" N	76^{0}02'11" E	17.8
	10.0 km	10^0 16' 32" N	76^{0}00'30" E	19.2
Ponnani	0.5 km	10^0 47' 06" N	75^{0}54' 45" E	5.4
	1.0 km	10^0 47' 06" N	75^{0}54' 20" E	6.2
	3.0 km	10^0 47' 06" N	75^{0}53' 48" E	7.1
	5.0 km	10^0 47' 07" N	75^{0}52' 13" E	12.3
	7.5 km	10^0 47' 07" N	75^{0}50' 33" E	16.8
	10.0 km	10^0 47' 06" N	75^{0}49' 49" E	20.4
Calicut	0.5 km	11^0 13' 33'' N	75^{0}47' 30 "E	5.7
	1.0 km	11^0 13' 33'' N	75^{0}46' 30 "E	7.1
	3.0 km	11^0 13' 33'' N	75^{0}45' 02 "E	9.9
	5.0 km	11^{0}13' 34 " N	75^{0}43' 11 "E	12.8
	7.5 km	11^{0}13' 34 " N	75^{0}41' 32 "E	15.7
	10.0 km	11^{0}13' 33 " N	75^{0}40' 11 "E	19.0
Kasargod	0.5 km	12^0 28' 59'' N	74^{0}58' 48 "E	3.8
	1.0 km	12^0 28' 59'' N	74^{0}58' 20 "E	7.9
	3.0 km	12^0 28' 59'' N	74^{0}57' 15 "E	10.8
	5.0 km	12^0 28' 59'' N	74^{0}56' 11 "E	14.5
	7.5 km	12^0 28' 56'' N	74^{0}54' 01 "E	17.6
	10.0 km	12^0 28' 56'' N	74^{0}53' 19 "E	21.9

2.3 Shipboard Sampling

Sampling program involved measurements of hydrographic, chemical and biological properties of the near shore coastal waters. Sampling and analysis of water, sediment and biological samples from 1.0 km to 10.0 km offshore from barmouth of each coastal transect was made onboard coastal research vessels and 0.5 km (from the barmouth) sampling was depended on fiber boats and the measurements in shore based laboratories. Samples were collected for duplicate and repeat analysis.

2.4 Sampling and Sub sampling

Prior to sampling, the sampler and the sampling bottles was acid washed with 1N HCl. Sample bottles were rinsed two times with the environmental sample and then the sample was collected. For plankton sampling, the nets were thoroughly washed and air dried to avoid clogging of meshes.

Water samples were collected using Teflon coated Niskin samplers (to avoid any form of metal contact with samples). The sample is collected with a help of a 5 litre Niskin sampler, all water samples were collected from the knob of the Niskin sampler using silicon rubber tubes. The prioritized individual sub sampling steps followed are given below:

1) for dissolved gases, and pH
2) for nutrients and physical parameters,
3) trace metals, and
4) for biological Chlorophylls.

For dissolved oxygen, the samples were fixed by employing Winkler's reagent on board vessel itself. Temperature and pH were measured immediately after collection using mercury thermometer and standard probes (WTW Multi Line P4).

Nutrient samples were stored in refrigeration maintained at $4^{o}C$ and ice box was used for transportation to the laboratory.

Metal samples were collected in acid-washed and pre cleaned high density polyethylene (HDPE) bottles. Separate good quality glass bottles were used for mercury samples. Disposable, clean gloves were used while sampling and handling samples for metals and mercury analysis. All samples (dissolved metals) bottles were stored in metal free plastic bags till analysis, so as to avoid contamination.

Filtration was carried out *in situ* for Chlorophylls.

Sediment samples were stored in metal free plastic bags for metals. The samples were stored in ice boxes for transportation to the laboratory and put to dry at low temperatures (about 60 ^{o}C) in petridishes.

2.5 Collection of Sediment and Biological Samples

Van Veen grab with a sampling area of 0.04m^2 was employed as a standard sediment sampler, since it is (i) an efficient sampler for the range of soft sediments encountered in the near shore area, (ii) reliable and simple to operate and (iii) widely applied, which allows data comparison with other marine areas. Van Veen grab made of stainless steel was made use of for sediment collection and benthos.

2.6 Storage and Preservation of Samples

Sample collection and preservation is given below.

Sl. No	Samples types	Actions	Preservation method
1	Nutrients (Nitrate, Nitrite, Phosphate, Silicate)	Filtered immediately with 0.45μM filter paper.	Kept the sample in chill condition (refrigerator / ice) till the samples arrived up to laboratory.
2	TP and TN	No filtration. Collected water in a cleaned plastic bottles (250 ml capacity)	Kept the sample in chill condition (refrigerator / ice) till the samples arrived up to laboratory.
3	DO	Collected the bubble free water and fixed with Winkler A & B	
4	Temperature, pH and Salinity	• Certified mercury thermometer 0- 50^{o}c with 0.1^{0}c accuracy. • pH measured by pH electrode with pH meter standardised and calibrated with 4.00, 7.00 and 10.00 prior to the sample measurement. • Measured with standard probes (WTW Multi Line P4).	
5	Sediment	Sampled with stainless steel grab and collected the sediment with a plastic scoop and kept in plastic bag with proper labeling.	Kept the sample in chill condition (i.e refrigerator /ice) till the samples arrive up to laboratory.
6	Dissolved metals	Collected the water with sufficient care avoiding the atmospheric as well as metal contaminants and filtererd immediately and kept in a HDPE bottles.	Acidified to pH $<$ 2 and kept the sample in chill condition (i.e refrigerator /ice) till the samples arrive up to laboratory.
7	Chlorophyll *a*	On board, collected immediately and filtered with GF/F paper.	Kept in aluminium foil and stored in chill condition.
8	Marine Phytoplankton	Filtered through 50 μ sieve.	Preserved by adding 4% formaldehyde.
9	Marine Polychaete	Polychaete embedded sediment washed through 0.5 mm sieve and depurated for 48 hrs in sea water.	Kept frozen in polypropylene containers.
10.	Flat Fish (*Cyanoglossus macrostomus*)	Brought from artisanal fisherman	Kept frozen in ice box.

2.7 Analysis of Physico-chemical Parameters

2.7.1 Temperature

A calibrated mercury thermometer (0-50°C with 0.1° accuracy) is allowed to stand in seawater sample and the reading is recorded after 2 min.

2.7.2 pH (Hydrogen ion concentration)

The electrodes of a pH meter was duly calibrated using buffer solution of pH 4.0, 7.0 and 10.0 range is introduced in seawater sample and pH is recorded possessing resolution of 0.01 and an accuracy of ± 0.05 pH.

2.7.3 Salinity

Measured with WTW Multi Line P4 probe and reading recorded as practical salinity unit (psu).

2.7.4 Total Suspended Solids

Suspended sediment concentration (SSC) was determined as the weight of material retained on a WCN Cellulose Nitrate filter (0.45 micron pore size) per litre after drying the filter for 2 h at 50^0 C.

2.7.5 Dissolved Oxygen (DO)

DO in water reacts with manganous (II) hydroxide in strongly alkaline medium forming manganese (III) hydroxide (cloudy precipitate). When acidified to pH less than 2.5, the manganese (III) hydroxide is dissolved to liberate manganese which is a strong oxidizing agent in acidic media. It reacts with iodide ions (previously added), liberating equivalent amount of free iodine, which is titrated against standard thiosulphate solution using starch as an indicator. Colour change is from blue to colourless.

2.7.6 Biochemical Oxygen Demand (BOD)

The biochemical oxygen demand (BOD) is an empirical test to assess water quality in terms of "Organic Matter" as an approximate index. This test measures the amount of oxygen utilized for the biochemical degradation of

organic materials (carbonaceous demand) and to oxidize inorganic materials such as sulfides and ferrous ion, over a specified time. The dissolved oxygen is analyzed both at the start and after a specific time of incubation, usually five days, at 20°C in a BOD incubator. The dissolved oxygen in the bottle is measured by Winkler's titration method.

2.8 Determination of Nutrients in Seawater

Nutrients (ammonia, nitrite, nitrate, phosphate and silicate) were estimated spectophotometrically as per standard methods (Grasshoff, 1999).

2.8.1 Ammonia – Nitrogen

The ammonia in the seawater reacts with sodium hypochlorite and phenol in alkaline condition to produce indophenols blue. Sodium nitroprusside is used as a catalyst and colour intensifier. After mixing with citrate buffer, phenol and hypochlorite, the solution is kept in the dark for at least 3hrs. The measurement for absorbance is carried out at 630 nm.

For the determination of ammonia –N extra care was taken in the analysis. Glassware's exclusively meant for the determination of ammonia was used.

2.8.2 Nitrite- Nitrogen (NO_2 - N)

The method of nitrite determination depends on reaction with an aromatic amine, sulphanilamide, which is then coupled with n-(1-naphthyl) – ethylene diamine dihydrochloride, to form an azo dye. The absorbance of the dye is measured spectrophotometrically at 543 nm.

2.8.3 Nitrate – Nitrogen (NO_3 -N)

Nitrate in seawater is quantitatively reduced to nitrite by heterogeneous reduction involving copper – cadmium granules. Nitrite thus produced is determined by diazotising with sulphanilamide and coupling with n – (1- naphthyl) – ethylene diamine to form an azo dye. The absorbance of the dye is measured

spectrophotometrically at 543 nm. Correction was made for nitrite present in the sample.

2.8.4 Inorganic Phosphate (PO_4-P)

Phosphate in seawater is allowed to react with acid Ammonium molybdate, forming a phosphomolybdate complex, which is reduced by ascorbic acid, in presence of antimonyl ions (to accelerate to reaction) to a blue coloured complex containing 1: 1 atomic ratio of phosphate and antimonyl ions. The blue colour forming through the reaction is measured at 880nm using 5cm cell (cuvette). To avoid interference by silicate the pH is kept below 1.

2.8.5 Inorganic Silicate ($Si(OH)_4$)

The seawater sample is allowed to react with molybdate under conditions, which result in the formation of silicomolybdate, phosphomolybdate and arsenomolybdate complexes. A reducing solution, containing ascorbic acid and oxalic acid is then added which reduces the silicomolybdate complex to give a blue reduction compound and simultaneously decomposes any phosphomolybdate so that interference from phosphate and arsenate is eliminated. The intensity is measured at 810 nm.

2.8.6 Total Phosphorus and Total Nitrogen (TP, TN)

Total dissolved parameters (TP or TN) include all forms of dissolved inorganic and organic species. Unfiltered water sample is oxidized with the help of strong oxidizing agent (alkaline persulphate) by autoclaving in closed conditions. The organic forms of phosphate and nitrate and also their inorganic forms in lower oxidation states are finally oxidized to inorganic phosphate and nitrate respectively.

2.9 Biological Characteristics

2.9.1 Chlorophyll *a*:

Filtered one litre of water sample through a Whatman 47 mm Ø GF/C fiber (0.7 µm nominal pore size) with a drop of $MgCO_3$ suspension. The

contents in the filter were extracted in 90% acetone, refrigerated in dark for 20 to 24 hrs, centrifuged, and the light absorbance at 750, 664, 647 and 630 nm of the sample was recorded in a spectrophotometer (Shimadzu UV 1800), as per Lorenzen (1967).

2.9.2 Primary Productivity:

Productivity is measured by light and dark oxygen bottle experiment. The dissolved oxygen of the control bottle is measured initially and the difference in dissolved oxygen content in the light and dark bottles is calculated per day using Winkler method. The dark bottle is wrapped with aluminium foil and kept in a black cloth bag so as protect from sunlight. The light and dark bottle is then incubated for a period of 8 hours on board by suspending it in sea water. After sunset the bottles are taken out and 1 ml of Winkler A and 1ml of Winkler B are added and after fixation, 1ml H_2SO_4 is added to liberate I_2 which is titrated against standard sodium thiosulphate solution.

2.9.3 Marine Phytoplankton:

Phytoplankton samples were collected by filtering 1l of surface water through 50µm sieve. The filtrate was preserved in plastic bottles using 4% formaldehyde. The abundance of phytoplankton was determined by counting with 1 ml concentrated samples using a Sedge Wick Rafter counting slide at a magnification of 400 X under an inverted microscope (Olympus CX41). Major phytoplankton group was identified up to genus level and expressed as % (Tomas, 1997).

2.10 Determination of Dissolved Metals in Seawater:

Prior to the collection of water samples, High density polyethylene sampling bottles were pre-cleaned by soaking them in 5-10 % HNO_3 (55 %, chemically pure, Merck Chemicals) for 24 hours and then rinsed thoroughly with deionized water. Approximately 1 liter of marine surface water was collected and the samples were preserved by lowering their pH below 2 with concentrated HNO_3. The samples were transported to the laboratory and stored

at 4 ºC prior to extraction and analysis. Water samples were collected in triplicate at each site and each sample was analyzed individually. All glassware and apparatus used in the following extraction procedures was pre-cleaned in 5-10 % HNO_3 for 24 hours and then rinsed thoroughly with deionized water.

The method explored for matrix separation and pre concentration was liquid-liquid extraction using ammonium pyrrolidine dithiocarbamate (APDC) and methyl isobulyl ketone (MIBK). Upon addition to the aqueous sample (pH adjusted to 4.5 by adding acetate buffer), APDC forms complexes with metals. These APDC-metal chelates are more miscible in organic than aqueous solutions and can be extracted into a small volume of organic solvent such as MIBK (Subramanian and Meranger, 1979). The metals in organic solvent are then separated from the seawater by back extraction into aqueous phase in acidic medium (0.2 ml Conc. HNO_3) (Brooks *et al.*, 1967). Extraction for each sample was done in triplicate and the concentration of heavy metals was determined by ICP-OES (Thermo Electron IRIS INTREPID II XSP DUO). The average value of triplicate analysis for each heavy metal is reported as its concentration. For the determination of mercury, preconcentration of mercury in sea water is achieved by complexing it with dithiazone at low pH (pH < 2). The complex is extracted in carbon tetrachloride and back extracted into hydrochloric acid. The acid extract is shaken with sodium nitrite to decompose the dithiazone and to revert mercury to aqueous phase. Excess of nitrite is reduced with hydroxylamine hydrochloride. Inorganic mercury compounds in the final solution are reduced to elemental mercury with stannous chloride and measured by cold vapour Atomic Absorption Spectrophotometry (Mercury Analyzer MA 5840) (Grasshoff, 1999). The recoveries > 90% for each metal were observed from the spiked standards in metal free sea water employing the above extraction method. The limits of detection (LODs) for Cu, Pb, Cr, Ni, Zn, Cd and Hg were 0.0097, 0.0042, 0.0071, 0.0016, 0.0018, 0.0027 ppm and 1.0 ppb respectively.

2.11 Texture of Sediments:

The sediment textural characteristics (sand, silt, and clay) were determined by pipette analysis after removing the inorganic carbonates using 10% HCl and organic matter using 15% H_2O_2. This analysis is based on Stoke's law. Sediment was dispersed in sodium hexametaphoshate overnight and then wet sieved through a 63 μm sieve to collect the sand fraction. The mud fraction was divided into silt and clay fractions by the timed gravimetric extraction of dispersed sediments (Folk, 1974).

2.12 Organic Matter in Sediments:

Organic Matter in the sediment samples was determined using wet digestion (chromic acid) followed by back titration with ferrous ammonium sulfate using ferroin as indicator and the colour change is from yellow orange to wine red(El Wakeel and Riley, 1957). The amount of total organic matter (TOM) was obtained by multiplying the organic carbon values with 1.724 (Nelson and Sommers, 1996).

2.13 Heavy Metal Analysis in Sediments:

For the analysis of total heavy metal in sediment, 1.0 g of finely powdered and dried (70^0C), sediment sample was digested in a mixture of HF–$HClO_4$–HNO_3 (1:2:3) (Loring and Rantala, 1992) in a microwave digester. The digestion was repeated until a clear solution was obtained, which ensured complete digestion. For the quantification of Hg, wet sediment samples were digested in Bethge apparatus in a mixture of nitric and sulfuric acid (3: 1) (Thompson *et al.*, 1980). ICP-OES was used to quantify the heavy metals (Cu, Pb, Cr, Ni, Zn and Cd). Total mercury was determined using cold vapour atomic absorption spectrometry (Mercury Analyzer, MA 5840). Quality assurance was established using a Certified Marine Sediment Reference Material (BCSS-1) from the National Research Council of Canada and the recovery was above 90% (Table 2.2). The precision of analysis was ascertained by triplicate analysis and the results are expressed as $\mu g\ g^{-1}$ on dry weight basis.

Table 2.2 Recoveries of heavy metals from certified reference materials μg g^{-1}.

Metal	Cd	Cr	Cu	Pb	Hg	Ni	Zn
BCSS-1							
Certified	0.25 ± 0.04	123 ± 14	18.5 ± 2.7	22.7 ± 3.4	-	55.3 ± 3.6	119 ± 12
Measured (n=5)	0.23 ± 0.06	111 ± 16	17.9 ± 1.8	21.3 ± 3.2	BDL*	52.7 ± 3.4	106 ± 22

Notes: Certified material: mean ± standard deviation; Measured: mean ± standard deviation; BDL*: below detectable limit.

2.14 Marine Polychaetes Sampling and Sample Preparation:

Macro polychaetes were separated by washing the sediments kept on 0.5mm sieves using a backwash technique with seawater. Polychaetes were carefully handpicked, depurated onboard with seawater collected from the same location on a clean plastic container for 48 hours and kept frozen in polypropylene containers. Identification of the polychaete was carried out using standard identification manuals (Fauvel, 1953; Fauchald, 1977). The polychaetes pooled from the study area are presented in Table 2.3. The frozen specimens were transported to the laboratory for further analysis. In the laboratory, *G. longipinnis* specimens of uniform size (1.80–2.10 cm) were segregated according to sampling transect to attenuate the possible variation in metal concentration. Specimens were then washed with deionised water to remove mucus and salt, macerated and air dried at 60^{o}C for 48 hours in a hot air oven before digestion. Dried tissue (0.250 g) was digested using 2mL HNO_3 (65%) and 1mL H_2O_2 (30%) in a Teflon vessel kept overnight and digested at 80^{0}C for 2 hours (Saha *et al.*, 2006). After digestion, the residue was transferred into an Erlenmeyer flask and the volume reduced to almost dryness. The processed sample was leached with 6M HCl solutions and was made up to 25mL with deionised water. All the glassware used was acid washed (diluted HNO_3) and subsequently rinsed in double-distilled water. The heavy metals in the solution were analyzed in ICP- OES and Hg by cold vapor atomic absorption spectroscopy (Mercury Analyzer MA 5840). Quality assurance was established using Certified Biological Reference Material (dogfish muscle, DORM-2) from the National Research Council of Canada (NRCC) and the

recovery was above 90% (Table 2.4). The precision of analysis was ascertained by triplicate analysis and the results are expressed as µg g^{-1} on dry weight basis.

Table 2.3 List of benthic polychaete genera assembled along the Kerala coast during the present study

Sl. No.	Polychaete genera	Cochin	Chettuva	Ponnani	Calicut	Kasargod
1	*Arabella*	–	–	✓	✓	✓
2	*Ancistrocyllis*	✓	–	✓	–	–
3	*Capitella*	✓	✓	–	✓	–
4	*Chaetopterus*	✓	–	✓	–	–
5	*Cossura*	–	✓	✓	✓	✓
6	*Cirratulus*	–	–	✓	–	–
7	*Diopatra*	✓	–	–	–	–
8	*Euclymene*	–	✓	✓	✓	✓
9	*Glycera*	✓	✓	✓	✓	✓
10	*Lumbrineries*	✓	✓	–	–	–
11	*Magelona*	✓	✓	✓	–	–
12	*Nephtys*	–	✓	✓	✓	–
13	*Neries*	✓	✓	–	✓	–
14	*Notomastus*	–	✓	–	–	–
15	*Prionospio*	–	✓	✓	✓	✓
16	*Polydora*	✓	–	–	–	–
17	*Pista*	✓	–	–	✓	✓
18	*Sternapsis*	–	–	✓	✓	✓
19	*Sabella*	✓	✓	✓	–	–
20	*Scoloplos*	–	–	✓	✓	✓
21	*Terebella*	✓	–	–	✓	✓

Table 2.4: Mean and SD of metal concentrations determined in the international standards: DORM 2 and DOLT 2 (µg g^{-1} dry weight)

Metal	Cd	Cr	Cu	Pb	Hg	Ni	Zn
NRCC DORM-2 Dogfish muscle							
Certified	0.043 ± 0.008	34.7 ± 5.5	2.42 ± 0.2	0.065 ± 0.007	4.64 ± 0.26	19.4 ± 3.1	25.6 ± 2.3
Measured (n=3)	0.039 ± 0.009	32.7 ± 2.8	2.06 ± 0.01	BDL*	4.44 ± 0.18	17.8 ± 2.8	25.4 ± 1.9
NRCC DOLT-2 Dogfish liver							
Certified	20.80 ± 0.50	0.37 ± 0.08	25.80 ± 1.10	0.22 ± 0.02	2.14 ± 0.28	0.20 ± 0.02	85.80 ± 2.50
Measured (n=3)	21.60 ± 1.80	0.46 ± 0.10	26.0 ± 1.0	0.16 ± 0.09	2.01 ± 0.11	0.35 ± 0.12	83.20 ± 4.30

Notes: Certified material: mean ± standard deviation; Measured: mean ± standard deviation. BDL*, below detectable limit.

2.15 Sample Preparation and Heavy Metal Analysis in Flatfish:

Fish were collected at the harbor where local anglers regularly fished. Flatfish were thawed and dissected into various tissues (liver, muscle, and gill) and thoroughly rinsed with deionised water to remove any sediment or detrital material. About 20 specimens of the studied species were collected during the period of study (post monsoon 2008 to monsoon 2008) from each transects. Fishes obtained were of different size and weight for each transect. Fish samples were stored in prewashed polyethylene bags and brought to the laboratory in frozen gel ice. In the laboratory, the length and weight of each fish were measured. Gills and liver are chosen as target organs for assessing metal accumulation. Muscle is chosen because of its public concern. Different organs were kept separately and are homogenized to make a composite sample. The composite samples were weighed in clean, labeled petri dishes and were frozen. Pulverization and homogenization were achieved by grinding the tissue samples. An exact weight of wet sample (triplicate, each 0.2 – 0.3 g) was placed in Teflon vessels followed by addition of 5ml nitric acid and 2 ml perchloric acid. The vessels were allowed to predigest overnight at room temperature and digestion was carried out in a microwave digester with the microwave procedure consisting of three steps: 2 min at 600 W, 2 min at 0 W; and 45 min at 450 W (Barwick and Maher, 2003).

The digested sample was allowed to cool at room temperature, diluted with deionized water, filtered and the volume was made upto 25ml with HCl (0.1N). The samples were analyzed using ICP –OES. For the determination of mercury, 1.0 g of homogenized wet sample was digested with 5ml of nitric acid and 2 ml of perchloric acid, and the mixture was heated at 50^0C until all the materials were dissolved (UNEP, 1984). After cooling to room temperature , the sample solution was diluted using deionized water,filtered and made upto 10.0 ml , and then subjected to Hg determination using cold – vapor atomic absorption spectrophotometer (Mercury Analyzer, MA 5840).The results of the heavy metals were expressed as $\mu g\ g^{-1}$ wet wt. A DORM-2 and DOLT-2 certified dogfish tissue was used as the calibration verification standard. Recoveries greater than 90% and less than 110% were accepted to validate the

calibration (Table 2.4). All specimens were run in batches that included blanks, a standard calibration curve, and one duplicate.

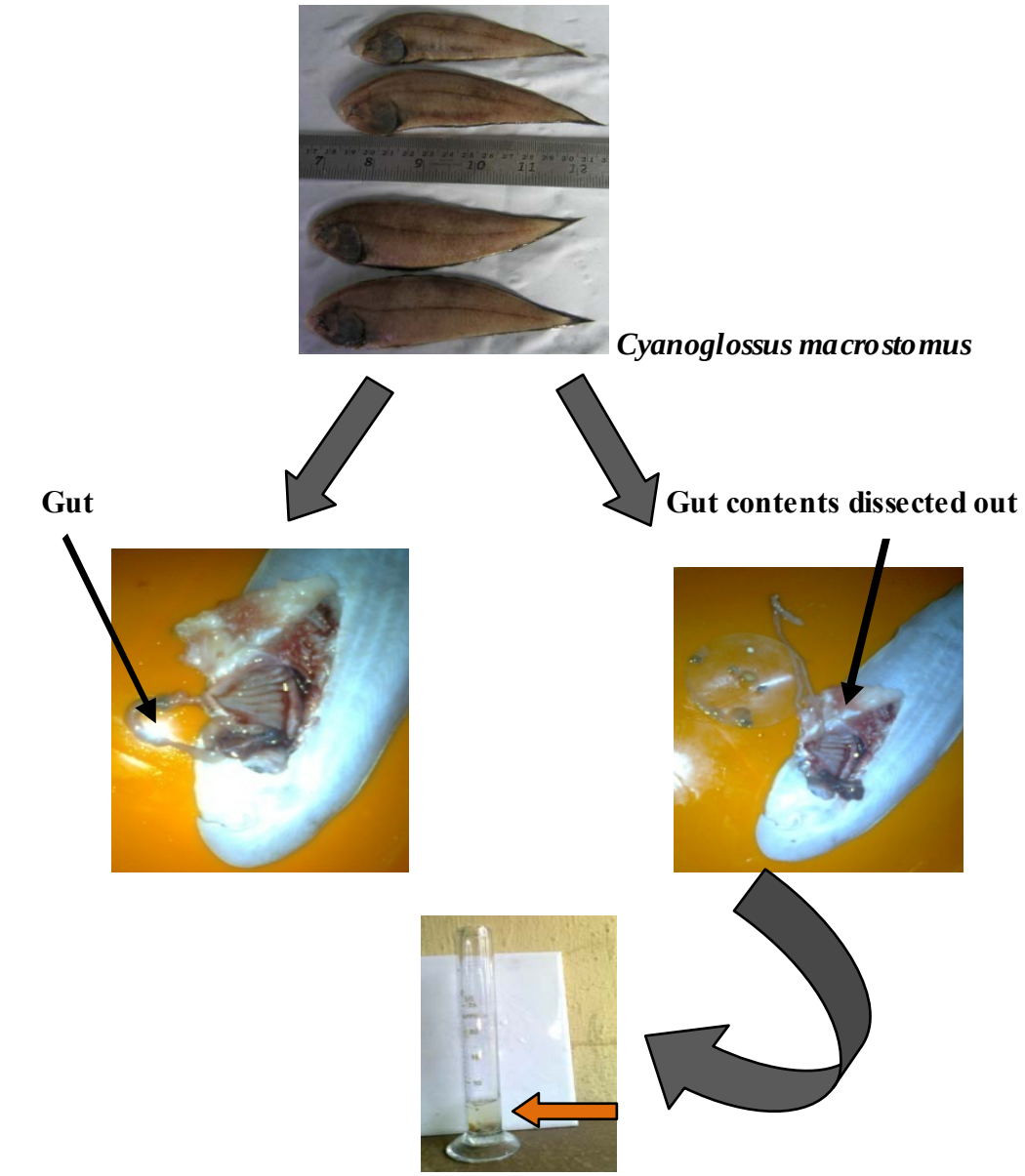
The muscle tissue was also determined in dry weight basis. For this, the dissected muscle of the fish samples was dried in an oven at 65°C and stored in a vacuum dessicator. The dried muscle was powdered and aliquots of about 300mg were digested in microwave digester with 5ml of nitric acid (65%, suprapur, Merck) and 2 ml of perchloric acid (suprapur, Merck). The digests were diluted to 25ml with HCl (0.1N) and metals were analyzed by ICP OES.

2.16 Gut Content Analysis of Flatfish:

Several attempts have been made to study the food and feeding habits of marine fishes. The true benthic fishes, *Cyanoglossids* (Flatfishes) are well adapted to live in benthic zone of marine ecosystem, which is clearly reflected in its morphological characteristics. The most noticeable characteristics are tongue shaped flat body having its eyes on one side. Flat fishes prefer the major part of its diet which includes the live zoobenthic invertebrates and vertebrates. It also finds its food from the detritus settlement. Thus through its feeding regime it can be grouped under both carnivorous and as detritivorous.

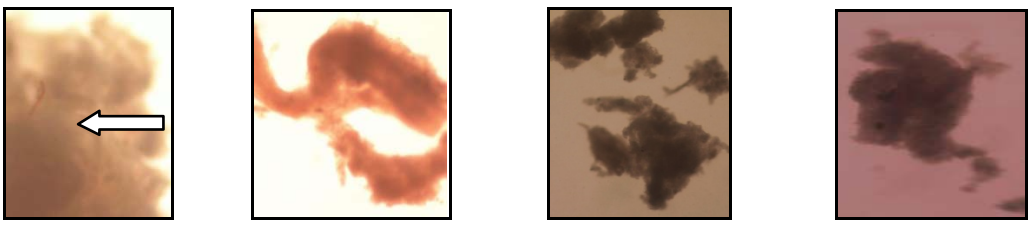
Different methods are adopted to study the food and feeding habits of fishes. Volumetric method was the most commonly used method. In the present study biomass of gut contents was calculated through this method (Fig 2B).

A total of 18 to 30 specimens were collected by its availability from the fish landing centers of Cochin, Chettuva, Ponnani, Calicut and Kasargod. Fish samples were taken seasonally from the predetermined fish vendors giving importance in the freshness keeping of caught fish. After taking the morphometric measurements such as average body length and weight (ABL and ABW), each fishes were dissected out and the gut contents were carefully removed and examined in fresh condition. The percentage of each food item was determined under a dissection microscope (Olympus SZ- ST) by examining the total biomass of gut contents estimated using volumetric method.



Gut content biomass estimation by volumetric method

Gut contents in magnified view



Semi digested Polychaete | **Polychaetes** | **Semi digested matter** | **Miscellaneous items**

Figure 2B: Schematic representation of gut content analysis in Malabar Sole (*Cyanoglossus macrostomus*)

2.17 Statistical Analyses:

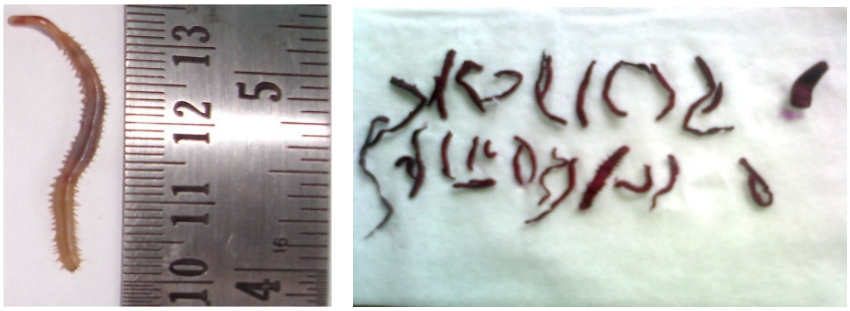
Principal component analysis (PCA) is one of the best statistical tools for extracting linear relationships among a set of variables (Iyer *et al*., 2003). This can be a valuable tool for resource managers for it can provide information regarding the driving environmental variables effect on ecologic response variables (Hobbie, 2000). The PCA was carried out with factors having eigen vectors greater than one (Kaiser criterion). Correlation matrix was used in PCA. The principal components were extracted in decreasing order of importance so that the first PC accounts for as much of the variation as possible and each successive component accounts are lesser. The most significant variables in the components represented by high loadings (> 0.6) are taken into consideration for evaluating the components (Mahloch, 1974). During PCA the loadings were suppressed to less than 0.1 in absolute value and thus small values are replaced with blanks. The quality of data for factor analysis is confirmed with Kaiser-Meyer-Olkin (KMO) test. The Principal component loading of water and sediment quality variables obtained for each season were analyzed. The factor loading were categorized as strong (> 0.75), moderate (0.75-0.50) and weak (0.50 – 0.40) according to Liu *et al*., (2003). Pearson correlation was also performed to find out the significant relation between variables. Multivariate statistical approaches such as PCA and Regression Analysis (Pearson correlation) have been used by researchers for deriving the significance of specific parameters among the data generated (Shirodkar *et al*., 2009; Singh *et al*., 2004). The statistical package, SPSS 11.0 was employed for doing the PCA and Regression analysis.

1. Photographs of the studied transects (a) Cochin (b) Chettuva (c) Ponnani (d) Calicut (e) Kasargod

(a) (b) (c)

(d) (e)

2. Photographs of (a) Polychaeta *Glycera longipinnis* (b) Polychaetes (c) Flatfish (Malabar Sole, *Cyanoglossus macrostomus*) pooled along the Central and Northern Coast of Kerala.



(a) (b)

(c)

Chapter 3

GENERAL HYDROGRAPHY

3.1 Introduction
3.2 Results
3.3 Discussion
3.4 Statistical Analyses
3.5 Conclusion

3.1 Introduction

Over the last several decades coastal regions throughout the world have experienced increased incidence of harmful or toxic algal blooms. These blooms occur as a result of key nutrients such as nitrogen (N) and phosphorus (P), because the supply rates of these nutrients most often control or "limit" aquatic plant primary production and biomass formation (Paerl, 2009). The direct influences of human population growth, urbanization, agricultural and industrial expansion have accelerated nutrient over-enrichment in receiving waters (Nicholas, 2006). Increased nutrient supply in coastal waters can cause several environmental modifications, such as increase in productivity and fishery potential (Menon *et al.*, 2000). However, continual nutrient enrichment promotes accelerated production of plant-based organic matter (i.e., eutrophication) to the extent that excessive production; including noxious algal blooms, shift in species composition, zones of bottom water hypoxia which is highly detrimental for biological diversity (Glibert *et al.*, 2001; Kemp *et al.*, 2005). The interplay of nutrients, expressed as the stoichiometric ratio of their supply and subsequent shifts in this ratio during uptake by the biota has become an important topic in contemporary biogeochemical studies (Boyd and Hurd, 2010). In many urbanized coastal regions, anthropogenic inputs have altered the composition of nutrient stoichiometry, which may, in turn, exacerbate certain toxic species to proliferate (Jickells, 1988). This is particularly true in the coastal waters of Kerala, southwest coast of India where nutrient availability is strongly influenced from riverine flux, domestic sewage effluents, seasonal upwelling phenomena and the critical social situation leading to consider economical enrichment as a priority compared to the respect of the environmental input. Considering the important role nutrients play on the productivity potential of coastal waters, limited studies haveonly been made to evaluate their seasonal and spatial behavior (Rajendran *et al.*, 1980; Varshney *et al.*, 1983; Panigrahy *et al.*, 1984; Choudhary and Panigrahy, 1991; Madhupratap *et al.*, 2001; Prasannakumar *et al.*, 2002; Sasmal *et al.*, 2005). This chapter therefore discusses the seasonal and spatial variability in the

nutrient distribution, stoichiometry, and phytoplankton biomass in the coastal waters of central and northern coast of Kerala.

3.2 Results

3.2.1 Physico- chemical Parameters

Water Temperature

Temperature is a commonly measured water quality parameter, and is a critical factor influencing chemical and biological processes in coastal water. Efficient photosynthesis takes place over the whole range of temperature encountered in the marine environment (i.e., from -2^{0}C in the polar regions to > 30^{o}C in tropical lagoons). Phytoplankton will only tolerate quite limited changes of temperature and are rapidly killed at temperature of 10^0 - 15^{0}C above that at which they are adapted to live. Increased temperature decreases the level of oxygen that can be dissolved in the water column. Water temperature influences the rate of plant photosynthesis, the metabolic rates of aquatic organisms, and the sensitivity of organisms to toxic wastes, parasites, diseases, and other stresses.

Among the transects, significant changes in the temporal and spatial variation of water temperature were discerned (Table 3.1, Fig. 3A, Fig. 3B). The surface water temperature in post monsoon varied from 28.00 to 28.40 ^{0}C at Cochin, 28.00 to 29.00 ^{0}C at Chettuva, 28.10 to 28.60 ^{0}C at Ponnani, 28.90 to 30.0 ^{0}C at Calicut, and 27.90 to 28.60^{0}C at Kasargod. In pre monsoon the surface water temperature at Cochin varied from 28.50 to 29.00 ^{0}C, 29.20 to 30.10 ^{0}C at Chettuva, 28.20 to 29.00 ^{0}C at Ponnani, 29.40 to 29.50 ^{0}C at Calicut and 29.20 to 30.00 ^{0}C at Kasargod. In monsoon it varied from 27.50 to 28.20 ^{0}C at Cochin, 27.10 to 28.10 ^{0}C at Chettuva, 27.40 to 27.80 ^{0}C at Ponnani, 28.00 to 28.90 ^{0}C at Calicut, 28.00 to 29.10 ^{0}C at Kasargod. The maximum surface water temperature of 30.10 ^{0}C was recorded at Chettuva in pre monsoon, while the minimum water temperature of 27.10 ^{0}C was also observed at Chettuva in monsoon.

Significant changes in bottom water temperature was also observed and it varied from 28.00 to 28.60 ^{0}C at Cochin, 28.00 to 28.50 ^{0}C at Chettuva, 28.20 to 28.40 ^{0}C at Ponnani, 28.10 to 29.00 ^{0}C at Calicut, 28.30 to 28.90 ^{0}C at Kasargod in post monsoon. In pre monsoon, it varied in the range from 28.10 to 28.90 ^{0}C at Cochin, 28.40 to 29.80 ^{0}C at Chettuva, 28.00 to 30.00 ^{0}C at Ponnani, 28.90 to 29.50 ^{0}C at Calicut, 28.80 to 29.50 ^{0}C at Kasargod in bottom water. In monsoon the bottom water temperature varied from 27.00 to 27.90 ^{0}C at Cochin, 25.50 to 28.20 ^{0}C at Chettuva, 26.90 to 28.10 ^{0}C at Ponnani, 25.50 to 29.80 ^{0}C at Calicut, 26.70 to 28.70 ^{0}C at Kasargod. The maximum bottom water temperature of 30.00 ^{0}C was recorded at Ponnani in pre monsoon, while the minimum water temperature of 25.50 ^{0}C was observed at Calicut and Chettuva in monsoon.

The average surface water temperature in the study area varied between 28.20 – 29.60, 28.65 – 29.68 and 27.60 – 28.50 ^{0}C and in bottom waters it ranged between 28.28 – 28.58, 28.38 – 29.45, 27.08 – 27.88 ^{0}C in post monsoon, pre monsoon and monsoon respectively (Fig. 3A3 (a), Fig. 3A4 (a)).

pH (Hydrogen ion concentration)

During photosynthesis, hydrogen atoms are used by phytoplankton and the pH of sea water will rise becoming more basic. Respiration and breakdown of organic matter will lower the pH making the water more acidic. Sea water is a natural buffer. Wide spatial and temporal fluctuation was observed in its distribution among the transects (Table 3.1, Fig. 3C, Fig. 3D). The values of pH in surface water in post monsoon ranged from 7.82 to 8.10 at Cochin, 7.40 to 8.10 at Chettuva, 7.90 to 8.10 at Ponnani, 7.90 to 8.10 at Calicut and 7.80 to 8.20 at Kasargod. In pre monsoon the pH values in surface water ranged from 7.80 to 8.17 at Cochin, 8.11 to 8.21 at Chettuva, 7.75 to 8.29 at Ponnani, 8.02 to 8.33 at Calicut and 8.01 to 8.29 at Kasargod. In monsoon the values of pH ranged from 7.50 to 8.01 at Cochin, 7.47 to 7.95 at Chettuva, 7.72 to 8.10 at Ponnani, 7.56 to 8.15 at Calicut, 7.52 to 8.14 at Kasargod. The maximum pH of 8.33 was recorded at Calicut in pre monsoon, while the minimum pH of 7.47 was observed at Chettuva in monsoon.

Variation of pH similar to that of the surface water was also observed in bottom waters and it ranged from 7.80 to 8.15 at Cochin, 7.50 to 8.20 at Chettuva, 7.90 to 8.10 at Ponnani, 8.00 to 8.10 at Calicut, 7.90 to 8.20 at Kasargod in post monsoon. In pre monsoon, it ranged from 7.90) to 8.21 at Cochin, 8.02 to 8.23 at Chettuva, 8.01 to 8.29 at Ponnani, 8.04 to 8.27 at Calicut, 8.02 to 8.29 at Kasargod. In monsoon, pH of bottom water ranged from 7.58 to 7.80 at Cochin, 7.55 to 8.08 at Chettuva, 7.70 to 8.06 at Ponnani, 7.64 to 8.12 at Calicut, 7.60 to 8.01 at Kasargod. The maximum pH of 8.29 in bottom water was recorded at Ponnani and Kasargod in pre monsoon, while the minimum pH of 7.55 was observed at Chettuva in monsoon.

The average surface values of pH in the present study ranged from 7.83 – 8.07, 8.04 –8.20, 7.79 –7.96 and bottom values ranged between 7.98 – 8.08, 8.09 – 8.21, 7.66 – 7.96 during post monsoon, pre monsoon and monsoon respectively (Fig. 3A3 (b), Fig. 3A4 (b)).

Salinity

Salinity is the amount of salts dissolved in water expressed in parts per thousand (ppt) or practical salinity unit (psu). It controls the type of species that can live in the medium but also influences physical and chemical processes such as flocculation and the amount of DO in the water column. Variations in salinity have some effect on the rate of photosynthesis; most marine phytoplankton will grow well at salinity of 15 or even less. Some species like diatoms grow poorly at salinities greater than 35 and this perhaps explains their preference for coastal waters.

Surface and bottom water salinity varied according to seasons between transect (Table 3.1, Fig. 3E, Fig. 3F). In post monsoon, salinity of surface water varied from 28.80 to 32.30 psu at Cochin, 27.80 to 32.20 psu at Chettuva, 28.30 to 32.10 psu at Ponnani, 27.50 to 32.0 psu 7at Calicut and 28.10 to 33.10 psu at Kasargod. In pre monsoon, salinity of surface water varied from 25.20 to 32.90 psu at Cochin, 30.50 to 33.40 psu at Chettuva, 30.80 to 33.40 psu at Ponnani, 30.50 to 33.30 psu at Calicut and 30.10 to 33.10 psu at Kasargod. In monsoon,

salinity of surface water varied from 18.50 to 31.10 psu at Cochin, 23.90 to 32.20 psu at Chettuva, 15.50 to 33.30 psu at Ponnani, 23.50 to 32.70 psu at Calicut and 23.80 to 32.20 psu at Kasargod. The maximum salinity of 33.40 psu in surface water was recorded at Chettuva and Ponnai in pre monsoon, while the minimum salinity of 15.50 psu was observed at Ponnani in monsoon.

Due to the shallowness of the water column and riverine influenc fluctuation of salinity in bottom waters was also discerned. It varied from 27.80 to 32.40 psu at Cochin, 28.20 to 32.60 psu at Chettuva, 26.80 to 32.10 psu at Ponnani, 32.00 to 32.40 psu at Calicut, 28.70 to 33.10 psu at Kasargod in post monsoon. In pre monsoon, it varied from 26.50 to 33.80 psu at Cochin, 30.20 to 33.70 psu at Chettuva, 29.00 to 33.70 psu at Ponnani, 30.70 to 33.40 psu at Calicut, 30.20 to 33.40 psu at Kasargod. In monsoon, a band of low salinity water was developed along the shoreline of this study due to the influence of strong fresh water discharges from the adjoining major rivers. It varied from 19.00 to 31.90 psu at Cochin, 26.60 to 32.50 psu at Chettuva, 15.80 to 32.90 psu at Ponnani, 26.20 to 32.90 psu at Calicut, 25.60 to 33.20 psu at Kasargod. The maximum salinity of 33.80 psu in the bottom water was recorded at Cochin in pre monsoon, while the minimum salinity of 15.80 psu was discerned at Ponnani in monsoon.

Average surface salinity in the study area fluctuated seasonally, between 30.87 – 31.72, 30.85 – 32.77, 27.48 – 30.12 psu and in bottom water between 30.70– 32.27, 31.78 – 32.92, 27.25 – 31.48 psu during post monsoon, pre monsoon and monsoon respectively (Fig. 3A3 (c), Fig. 3A4 (c)).

Dissolved Oxygen (DO)

Dissolved oxygen concentrations in seawater are controlled by fluxes through the atmospheric water interface and by biological assimilation and dissimilation. DO is a sensitive indicator for biological and chemical processes. The amount of oxygen that water can hold depends on temperature and salinity. Waves and wind help put up oxygen in water and through phytoplankton

synthesis. Above 5 mg O_2 l^{-1} most marine plants and animals have plenty of oxygen. Low DO signifies stressed environment.

DO consumption and production is influenced by plant and algal biomass, light intensity and water temperature which are subject to diurnal and seasonal variations (Connell and Miller, 1984). Naturally, DO concentrations vary over a 24-h period due to tidal exchange, as a result wide variations was observed in the distribution of DO among the transects, both in surface and bottom water of this study (Table 3.2, Fig. 3G, Fig. 3H). In post monsoon, values of DO in surface water ranged from 4.76 to 5.32 mg O_2 l^{-1} , 4.82 to 5.18 mg O_2 l^{-1} , 4.22 to 4.78 mg O_2 l^{-1} , 3.86 to 6.48 mg O_2 l^{-1} and 4.44 to 5.27 mg O_2 l^{-1} at Cochin, Chettuva, Ponnani, Calicut and Kasargod respectively. In pre monsoon, DO ranged from 3.06 to 4.12 mg O_2 l^{-1} at Cochin, 5.14 to 5.84 mg O_2 l^{-1} at Chettuva, 4.82 to 6.80 mg O_2 l^{-1} at Ponnani, 4.12 to 6.72 mg O_2 l^{-1} at Calicut, 5.12 to 6.30 mg O_2 l^{-1} at Kasargod. In monsoon DO in surface water ranged from 4.29 to 5.32 mg O_2 l^{-1} at Cochin, 4.12 to 5.26 mg O_2 l^{-1} at Chettuva, 5.14 to 6.04 mg O_2 l^{-1} at Ponnani, 3.29 to 4.32 mg O_2 l^{-1} at Calicut and 3.22 to 4.14 mg O_2 l^{-1} at Kasargod. The maximum DO of 6.80 mg O_2 l^{-1} was reported at Calicut and the minimum DO value of 3.06 mg O_2 l^{-1} was observed at Cochin both in pre monsoon.

Dissolved Oxygen in the bottom water ranged from 4.52 to 5.68 mg O_2 l^{-1} at Cochin, 4.54 to 4.79 mg O_2 l^{-1} at Chettuva, 4.06 to 5.12 mg O_2 l^{-1} at Ponnani, 3.76 to 4.72 mg O_2 l^{-1} at Calicut and 4.28 to 5.12 mg O_2 l^{-1} at Kasargod in post monsoon. In pre monsoon, it varied in the range from 3.04 to 3.98 mg O_2 l^{-1} at Cochin, 4.18to 5.02 mg O_2 l^{-1} at Chettuva, 4.85 to 6. 20 mg O_2 l^{-1} at Ponnani, 3.98 to 6.50 mg O_2 l^{-1} at Calicut, 3.22 to 5.26 mg O_2 l^{-1} at Kasargod. Dissolved oxygen in the bottom waters in monsoon was found to vary from 3.96 to 5.42 mg O_2 l^{-1} at Cochin, 3.46 to 5.61 mg O_2 l^{-1} at Chettuva, 5.01 to 5.80 mg O_2 l^{-1} at Ponnani, 3.18 to 4.06 mg O_2 l^{-1} at Calicut, 3.07 to 4.80 mg O_2 l^{-1} at Kasargod. The maximum DO value of 6.50 mg O_2 l^{-1} in bottom water was recorded at Calicut, while the minimum value of 3.04 mg O_2 l^{-1} was observed at Cochin. Both the maximum and minimum value of DO was discerned in pre monsoon.

An average concentration of DO for surface water in this study varied between 4.56 – 5.23, 5.53 – 5.93, 3.62 – 5.62 mg O_2 l^{-1} and in bottom waters it was in the range 4.46 – 4.88, 3.49 – 5.33, 3.70- 5.23 mg O_2 l^{-1} during post monsoon, pre monsoon and monsoon respectively (Fig. 3A3 (e), Fig. 3A4 (e)).

Biochemical Oxygen Demand (BOD)

BOD is the amount of oxygen utilized by microorganisms to degrade organic matter present in water. High BOD value indicates high organic load and thus heavily polluted. The importance of BOD in pollution monitoring has been well established (Reish, 1972). Waters with BOD less than 3 mg O_2 l^{-1} are known to have received no significant pollution discharges. BOD values of more than 8 mg O_2 l^{-1} are indicative of moderate pollution (Martin, 1970) and BOD values of 12 mg O_2 l^{-1} or more are considered grossly polluted.

Depending on the time of sampling, the tidal changes and the release of the sewage through the outfall; wide spatial and temporal variation in BOD values was noted in this study (Table 3.2, Fig. 3I, Fig. 3J). In post monsoon, BOD values in surface water of this study ranged from 1.38 to 1.87 mg O_2 l^{-1} at Cochin, 0.54 to 1.98 mg O_2 l^{-1} at Chettuva, 0.36to 1.39 mg O_2 l^{-1} at Ponnani, 0.80 to 1.64 mg O_2 l^{-1} at Calicut and 0.39 to 0.96 mg O_2 l^{-1} at Kasargod. In pre monsoon, BOD values ranged from 2.14 to 2.78 mg O_2 l^{-1} at Cochin, 0.40 to 0.91 mg O_2 l^{-1} at Chettuva, 0.34 to 1.09 mg O_2 l^{-1} at Ponnani, 1.45 to 2.39 mg O_2 l^{-1} at Calicut, 0.83 to 2.80 mg O_2 l^{-1} at Kasargod. In monsoon, BOD values ranged from 1.56 to 3.45 mg O_2 l^{-1} at Cochin, 0.88 to 1.76 mg O_2 l^{-1} at Chettuva, 1.12 to 2.76 mg O_2 l^{-1} at Ponnani, 1.19 to 2.33 mg O_2 l^{-1} at Calicut, 1.24 to 1.90 mg O_2 l^{-1} at Kasargod. The maximum BOD value of 3.45 mg O_2 l^{-1} was recorded at Cochin in monsoon, while the minimum value of 0.39 mg O_2 l^{-1} was observed at Kasargod in post monsoon.

BOD in the bottom water in post monsoon ranged from 0.58 to 1.99 mg O_2 l^{-1} at Cochin, 0.72 to 2.12 mg O_2 l^{-1} at Chettuva, 0.47 to 1.36 mg O_2 l^{-1} at Ponnani, 0.60 to 2.12 mg O_2 l^{-1} at Calicut, 0.32 to 1.76 mg O_2 l^{-1} at Kasargod. In pre monsoon, BOD ranged from 2.42 to 3.04 mg O_2 l^{-1} at Cochin, 0.43 to

1.43 mg O_2 l^{-1} at Chettuva, 0.82 to 1.12 mg O_2 l^{-1} at Ponnani, 0.86 to 3.01 mg O_2 l^{-1} at Calicut, 0.76 to 1.60 mg O_2 l^{-1} at Kasargod. BOD was found to vary in the range from 1.19 to 2.99 mg O_2 l^{-1} at Cochin, 1.14 to 1.94 mg O_2 l^{-1} at Chettuva, 1.60 to 2.94 mg O_2 l^{-1} at Ponnani, 0.94 to 3.29 mg O_2 l^{-1} at Calicut, 0.87 to 2.35 mg O_2 l^{-1} at Kasargod in monsoon. The maximum BOD value of 3.04 mg O_2 l^{-1} was reported at Cochin in pre monsoon, while the minimum BOD value of 0.32 mg O_2 l^{-1} was recorded at Kasargod in post monsoon.

An average concentration of BOD for surface water in this study varied between 0.70 –1.65, 0.62 – 2.45, 1.06 – 2.66 mg O_2 l^{-1} and in bottom waters it was in the range 0.78 – 1.25, 0.81 – 1.20, 1.44 – 2.09 mg O_2 l^{-1} during post monsoon, pre monsoon and monsoon respectively (Fig. 3A3 (f), Fig. 3A4 (f)).

Total Suspended Solids (TSS)

Suspended material concentration is the amount of material that is suspended in the water column. It refer to any matter suspended in water or everything that retained by a filter i.e. usually 0.45µm in size (American Public Health Association, 1998). Elevated levels of suspended material and turbidity occur naturally through erosion, storm runoff, and the input of plant material on a seasonal basis. However, these parameters can also indicate degraded water quality if the elevated levels are caused by excessive erosion due to upland development, organic material due to nutrient enrichment, or uncontrolled discharges from sewage treatment plants and industrial facilities. Small particles can scatter light that tend to reduce the depth to which light can penetrate; which in turn affect the growth of aquatic plants. High TSS can lower the production of dissolved oxygen; high absorption of heat from sunlight, thus increasing the temperature which can result to lower oxygen level; low visibility which will affect the fish' ability to hunt for food; clog fish' gills; prevent development of egg and larva. It can also be an indicator of higher concentration of bacteria, nutrients and pollutants in the water. Some of the factors that affect the concentration of TSS are high flow rate, soil erosion, urban run-off, septic and wastewater effluents, decaying plants and animals and bottom-feeding fish.

Among the transects, significant spatial and temporal variation was observed in the distribution of TSS in the coastal water (Table 3.2, Fig. 3K, Fig. 3L). In post monsoon the value of TSS in the surface water varied from 6.08 to 19.39 mg l^{-1} at Cochin, 5.20 to 11.10 mg l^{-1} at Chettuva, 7.70 to 20.76 mg l^{-1} at Ponnani, 4.52 to 7.72 mg l^{-1} at Calicut and 3.98 to 10.56 mg l^{-1} at Kasargod. In pre monsoon, the values of TSS varied from 6.12 to 30.28 mg l^{-1} at Cochin, 6.96to 12.76 mg l^{-1} at Chettuva, 5.74 to 11.32 mg l^{-1} at Ponnani, 5.74 to 12.76 mg l^{-1} at Calicut and 5.12 to 10.36 mg l^{-1} at Kasargod. In monsoon, the value of TSS varied from 15.39 to 34.96 mg l^{-1} at Cochin, 8.38 to 21.12 mg l^{-1} at Chettuva, 10.89 to 22.67 mg l^{-1} at Ponnani, 8.12 to 15.52 mg l^{-1} at Calicut, 5.72 to 16.39 mg l^{-1} at Kasargod. The maximum TSS value of 34.96 mg l^{-1} was recorded at Cochin in monsoon, while the minimum TSS value of 3.98 mg l^{-1} was reported at Kasargod in post monsoon.

The values of TSS in bottom water varied from 7.70 to 13.48 mg l^{-1} at Cochin, 5.20 to 14.40 mg l^{-1} at Chettuva, 3.40 to 16.28 mg l^{-1} at Ponnani, 6.56 to 18.24 mg l^{-1} at Calicut, 2.87 to 14.34 mg l^{-1} at Kasargod in post monsoon. In pre monsoon, the values of TSS varied from 7.18 to 16.66 mg l^{-1} at Cochin, 5.24 to 13.40 mg l^{-1} at Chettuva, 5.06 to 12.32 mg l^{-1} at Ponnani, 5.28 to 15.66 mg l^{-1} at Calicut, 4.76 to 11.80 mg l^{-1} at Kasargod. In monsoon, TSS in bottom water varied in the range from 11.08 to 23.90 mg l^{-1} at Cochin, 7.92 to 13.86 mg l^{-1} at Chettuva, 10.54 to 23.89 mg l^{-1} at Ponnani, 5.81 to 17.14 mg l^{-1} at Calicut, 5.14 to 19.27 mg l^{-1} at Kasargod. The maximum TSS value of 23.90 mg l^{-1} was recorded at Cochin in monsoon, while the minimum TSS value of 2.87 mg l^{-1} was reported at Kasargod in post monsoon.

An average values of TSS for surface water varied between 5.70 – 13.60, 7.47 – 13.02, 9.48 – 20.86 mg l^{-1} and in bottom water it was in the range of 6.38 – 10.61, 7.56 – 11.54, 10.41– 17.18 mg l^{-1} during post monsoon, pre monsoon and monsoon respectively in the study area (Fig. 3A3 (d), Fig. 3A4 (d)).

3.2.2 Nutrients

A nutrient element is one that is involved in the production of organic matter by photosynthesis. This term has been applied mostly for inorganic

nitrogen compounds, phosphorus and silicon. In addition to the above elements certain trace metals are also called nutrient elements, eg. Iron plays an important role in controlling the growth of marine plant.

Nitrogen

For the synthesis of their cellular amino acids phytoplankton requires some form of nitrogen. They satisfy their needs by utilizing nitrite (NO_2^-), nitrate (NO_3^-) and ammonium ($NH_3 + NH_4^+$) ions. Nitrogen is a key component in i) chlorophyll, the green pigment in primary producers that absorbs sunlight during photosynthesis, ii) amino acids, the building blocks of proteins, and iii) genetic material, including deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). Nitrogen ranks as the fourth most abundant chemical element in living tissue, behind oxygen, carbon, and hydrogen.

Ammonium- N ($NH_3 + NH_4^+$)

Soluble and particulate organic nitrogen compounds resulting from decaying organisms together with those excreted by plants are rapidly broken down to NH_3 by various species of proteolytic bacteria. Ammonia is excreted directly by animals together with urea and peptides. NH_3 is toxic to fish and other marine organism, while ammonium ion (NH_4^+) is not toxic.

The concentration of ammonium-N showed temporal and spatial pattern in its distribution among the transects (Table 3.3, Fig. 3M, Fig. 3N). In post monsoon the concentration of ammonium-N in surface water varied from 0.09 to 0.76 µmol l^{-1} at Cochin, 0.11 to 0.27 µmol l^{-1} at Chettuva, 0.06 to 0.24 µmol l^{-1} at Ponnani, 0.14 to 0.34 µmol l^{-1} at Calicut and 0.12 to 0.44 µmol l^{-1} at Kasargod. In pre monsoon, the concentration of ammonium-N varied from 0.21 to 0.66 µmol l^{-1} at Cochin, 0.06 to 0.36 µmol l^{-1} at Chettuva, 0.13 to 0.26 µmol l^{-1} at Ponnani, 0.04 to 0.23 µmol l^{-1} at Calicut and 0.05 to 0.32 µmol l^{-1} at Kasargod. In monsoon, the concentration of ammonium –N varied from 0.28 to 0.97 µmol l^{-1} at Cochin, 0.05 to 0.37 µmol l^{-1} at Chettuva, 0.06 to 0.35 µmol l^{-1} at Ponnani, 0.22 to 0.55 µmol l^{-1} at Calicut and 0.13 to 0.56 µmol l^{-1} at Kasargod. The maximum concentration of ammonia –N of 0.97 µmol l^{-1} was

recorded at Cochin in monsoon, while the minimum value of 0.04 µmol l^{-1} was reported at Calicut in pre monsoon.

In post monsoon, the concentration of ammonium-N in bottom waters varied from 0.06 to 0.17 µmol l^{-1} at Cochin, 0.07 to 0.12 µmol l^{-1} at Chettuva, 0.12 to 0.18 µmol l^{-1} at Ponnani, 0.07 to 0.16 µmol l^{-1} at Calicut and 0.06 to 0.24 µmol l^{-1} at Kasargod. In pre monsoon the concentration of ammonium-N varied from 0.13 to 0.36 µmol l^{-1} at Cochin, 0.06 to 0.18 µmol l^{-1} at Chettuva, 0.05 to 0. 23 µmol l^{-1} at Ponnani, 0.08 to 0.26 µmol l^{-1} at Calicut and 0.08 to 0.25 µmol l^{-1} at Kasargod. In monsoon, the concentration of ammonium-N varied from 0.08 to 0.37 µmol l^{-1} at Cochin, 0.14 to 0.32 µmol l^{-1} at Chettuva, 0.04 to 0.37 µmol l^{-1} at Ponnani, 0.05 to 0.21 µmol l^{-1} at Calicut, 0.08 to 0.26 µmol l^{-1} at Kasargod. The maximum concentration of ammonia –N of 0.37 µmol l^{-1} in bottom water was recorded at Cochin and Ponnani, while the minimum value of 0.04 µmol l^{-1} was reported at Ponnani in monsoon.

The average values of NH_4 – N in surface water in this study, ranged from 0.16 – 0.30, 0.13 –0.38, 0.16 – 0.50 µmol l^{-1} and in bottom water it ranged from 0.10 – 0.16, 0.13 – 0.22, 0.11 – 0.21 µmol l^{-1} during post monsoon, pre monsoon and monsoon respectively (Fig. 3A5 (a), Fig. 3A6 (a)).

Nitrite –N (NO_2^- - N)

It is the intermediate product in microbial redox processes of nitrogenous compounds. Nitrite is a byproduct of oxidized NH_3 or NH_4^+, an intermediary in the conversion of NH_3 or NH_4^+ into NO_3. This process is completed through nitrification which is done by the highly aerobic, gram-negative, chemoautotropic bacteria found naturally in the system. The conversion is quick, thus high nitrite concentrations are not commonly found. Increased nitrite concentration is formed at low oxygen levels. Upwelling leads to higher values of nitrite (1-2 µmol l^{-1}). Pollution also leads to very high values of nitrite in water.

Among the transects, wide spatial and temporal variation was observed in its distribution (Table 3.3, Fig. 3O, Fig. 3P). In post monsoon the concentration

of nitrite-N in surface water varied from 0.22 to 0.82 µmol/l at Cochin, 0.01 to 0.12 µmol l^{-1} at Chettuva, 0.02 to 0.14 µmol l^{-1} at Ponnani, 0.02 to 0.16 µmol l^{-1} at Calicut and 0.02 to 0.12 µmol l^{-1} (0.5 km) at Kasargod. In pre monsoon, the concentration of nitrite-N varied from 0.02 to 1.08 µmol l^{-1} at Cochin, 0.02 to 0.12 µmol l^{-1} at Chettuva, 0.02 to 0.14 µmol l^{-1} at Ponnani, 0.02 to 0.56 µmol l^{-1} at Calicut, 0.02 to 0.14 µmol l^{-1} at Kasargod. In monsoon, the concentration of nitrite-N in surface water varied from 0.08 to 0.44 µmol l^{-1} at Cochin, 0.02 to 0.16 µmol l^{-1} at Chettuva, 0.02 to 0.34 µmol l^{-1} at Ponnani, 0.02 to 0.45 µmol l^{-1} at Calicut and 0.08 to 0.16 µmol l^{-1} at Kasargod. The maximum nitrite-N concentration of 0.82 µmol l^{-1} was reported at Cochin and the minimum nitrite-N concentration of 0.01 µmol l^{-1} was observed at Chettuva in post monsoon.

The concentrations of nitrite-N in bottom waters varied from 0.14 to 1.58 µmol l^{-1} at Cochin, 0.01 to 0.14 µmol l^{-1} at Chettuva, 0.02 to 0.28 µmol l^{-1} at Ponnani, 0.02 to 0.28 µmol l^{-1} at Calicut, 0.02 to 0.23 µmol l^{-1} at Kasargod in post monsoon. In pre monsoon, the concentration of nitrite-N varied from 0.02 to 1.24 µmol l^{-1} at Cochin, 0.04 to 0.16 µmol l^{-1} at Chettuva, 0.02 to 0.39 µmol l^{-1} at Ponnani, 0.02 to 0.72 µmol l^{-1} at Calicut, 0.04 to 0.44 µmol l^{-1} at Kasargod. The concentrations of nitrite-N in bottom water varied from 0.02 to 0.52 µmol l^{-1} at Cochin, 0.04 to 0.21 µmol l^{-1} at Chettuva, 0.06 to 0.19 µmol l^{-1} at Ponnani, 0.02 to 0.42 µmol l^{-1} at Calicut and 0.09 to 0.39 µmol l^{-1} at Kasargod in monsoon. The maximum nitrite-N concentration of 1.54 µmol l^{-1} in bottom water was reported at Cochin in post monsoon. The minimum nitrite-N concentration of 0.01 µmol l^{-1} was observed at Chettuva in post monsoon.

The average NO_2-N concentrations were always less than 0.5 µmol l^{-1}, it fluctuated from 0.05 – 0.42, 0.06 – 0.16, 0.07 – 0.18 µmol l^{-1} in surface water and in bottom water it ranged from 0.05 – 0.47, 0.06 – 0.26, 0.10 – 0.21 µmol l^{-1} in post monsoon, pre monsoon and monsoon respectively along the central and northern coast of Kerala (Fig. 3A5 (b), Fig. 3A6 (b)).

Nitrate- N (NO_3^--N)

Nitrate is formed through nitrification process, i.e. oxidation of NO_2 into NO_3 by the action of aerobic bacteria. Nitrate not taken up directly by aquatic plants is denitrified in anaerobic sediments and micro zones. In tropical systems, denitrification will be most intense in the following areas: (a) where detritus accumulates; (b) in water bodies subject to enhanced nutrient loading from pollution; (c) in water bodies with long residence times. Generally, it is stable over a wide range of environmental conditions and is highly soluble in water. Compared with other inorganic nitrogen compounds, it is also the least toxic. However, high levels can affect osmoregulation, oxygen transport, eutrophication and algal bloom (Lawson, 1995).

Wide fluctuation in spatial and temporal distribution of nitrate-N was discerned in this study (Table 3.3, Fig. 3Q, Fig. 3R). In post monsoon, the concentration of nitrate-N in surface water varied from 3.30 to 9.37 µmol l^{-1} at Cochin, 0.34 to 1.86 µmol l^{-1} at Chettuva, 0.76 to 2.76 µmol l^{-1} at Ponnani, 0.32 to 3.48 µmol l^{-1} at Calicut and 1.10 to 3.18 µmol l^{-1} at Kasargod. In pre monsoon, the concentration of nitrate-N in surface water varied from 0.38 to 5.36 µmol l^{-1} at Cochin, 0.32 to 2.68 µmol l^{-1} at Chettuva, 0.24 to 5.32 µmol l^{-1} at Ponnani , 0.80 to 3.38 µmol l^{-1} at Calicut and 0.30 to 5.59 µmol l^{-1} at Kasargod. In monsoon, the concentration of nitrate-N in surface water varied from 0.76 to 5.99 µmol l^{-1} at Cochin, 0.96 to 3.96 µmol l^{-1} at Chettuva, 2.51 to 6.96 µmol l^{-1} at Ponnani, 1.17 to 6.68 µmol l^{-1} at Calicut, 7.56 to 12.76 µmol l^{-1} at Kasargod. The maximum concentration of 12.76 µmol l^{-1} of nitrate- N in surface water was reported at Kasargod in monsoon and the minimum concentration of 0.24 µmol l^{-1} was discerned at Ponnani in pre monsoon.

In post monsoon the concentration of nitrate-N in bottom waters varied from 6.70 to 13.32 µmol l^{-1} at Cochin, 0.55 to 3.40 µmol l^{-1} at Chettuva, 0.68 to 3.67 µmol l^{-1} at Ponnani, 0.68 to 3.08 µmol l^{-1} at Calicut and 1.46 to 3.21 µmol l^{-1} at Kasargod. In pre monsoon, the concentration of nitrate-N varied from 0.25 to 6.38 µmol l^{-1} at Cochin, 0.48 to 1.26 µmol l^{-1} at Chettuva, 0.40 to 3.09 µmol l^{-1} at Ponnani, 0.50 to 8.44 µmol l^{-1} at Calicut, 0.52 to 5.20 µmol l^{-1} at

Kasargod. In monsoon, the concentration of nitrate - N varied from 0.92 to 7.98 µmol l^{-1} at Cochin, 5.68 to 11.56 µmol l^{-1} at Chettuva, 1.99 to 5.2 µmol l^{-1} at Ponnani, 3.46 to 4.29 µmol l^{-1} at Calicut and 5.31 to 9.88 µmol l^{-1} at Kasargod. The maximum and minimum concentration of 13.32 µmol l^{-1} and 0.25 µmol l^{-1} of nitrate- N in bottom water was reported at Cochin in post monsoon and pre monsoon respectively.

The average NO_3-N concentrations in this study showed a variation of 0.89– 6.55, 0.90– 1.89, 2.20 – 10.80 µmol l^{-1} in surface water and in bottom water it varied from 1.18 – 9.55, 0.92 – 2.97, 3.18 – 8.20 µmol l^{-1} in post monsoon, pre monsoon and monsoon respectively in the study area (Fig. 3A5 (c), Fig. 3A6 (c)).

Total Nitrogen (TN)

It involves both dissolved and particulate inorganic and organic nitrogen forms. Marked regional variation in its distribution was discerned along the coastal waters (Table 3.3, Fig. 3S, Fig. 3T). In post monsoon, the concentration of total nitrogen in surface water varied from 15.68 to 21.62 µmol l^{-1} at Cochin, 7.68 to 18.95 µmol l^{-1} at Chettuva, 9.26 to 21.69 µmol l^{-1} at Ponnani, 8.60 to 14.36 µmol l^{-1} at Calicut and 8.76 to 16.36 µmol l^{-1} at Kasargod. In pre monsoon, the concentration of total nitrogen in surface water varied from 8.80 to 12.69 µmol l^{-1} at Cochin, 11.37 to 17.35 µmol l^{-1} at Chettuva, 5.16 to 11.27 µmol l^{-1} at Ponnani, 10.32 to 15.68 µmol l^{-1} at Calicut and 7.39 to 13.16 µmol l^{-1} at Kasargod. In monsoon, the concentration of total nitrogen varied from 24.89 to 30.84 µmol l^{-1} at Cochin, 16.38 to 24.28 µmol l^{-1} at Chettuva, 5.91 to 23.52 µmol l^{-1} at Ponnani, 12.67 to 27.20 µmol l^{-1} at Calicut and 13.60 to 22.70 µmol l^{-1} at Kasargod. The maximum concentration of total nitrogen in surface water of 30.84 µmol l^{-1} was reported at Cochin in monsoon and the minimum concentration of 5.16 µmol l^{-1} was observed at Ponnani in pre monsoon.

In post monsoon, total nitrogen in bottom water varied from 12.30 to 22.90 µmol l^{-1} at Cochin, 9.24 to 20.26 µmol l^{-1} at Chettuva, 12.26 to 19.59 µmol l^{-1} at Ponnani, 11.56 to 20.06 µmol l^{-1} at Calicut and 11.06 to 19.36 µmol l^{-1}

at Kasargod. In pre monsoon, the concentration of total nitrogen varied from 10.98 to 14.75 µmol l^{-1} at Cochin, 12.39 to 15.94 µmol l^{-1} at Chettuva, 8.35 to 14.18 µmol l^{-1} at Ponnani, 13.02 to 16.29 µmol l^{-1} at Calicut and 8.80 to 17.45 µmol l^{-1} at Kasargod. In monsoon, total nitrogen varied from 10.90 to 29.80 µmol l^{-1} at Cochin, 16.78 to 22.65 µmol l^{-1} at Chettuva, 9.78 to 22.36 µmol l^{-1} at Ponnani, 8.16 to 16.78 µmol l^{-1} at Calicut and 8.90 to 17.90 µmol l^{-1} at Kasargod. The maximum concentration of total nitrogen of 29.80 µmol $l^{-1}$was recorded at Cochin and the minimum value of 8.16 µmol l^{-1} was reported at Calicut both in monsoon.

The average levels of TN displayed marked variations in this study and its concentration in surface water varied from 10.93 – 18.20, 8.62 -15.37, 11.34 -27.74 µmol l^{-1} and in bottom water it varied from 14.92– 9.21,12.13– 4.88 and 10.70– 22.01 µmol l^{-1} in post monsoon, pre monsoon and monsoon respectively in the study area (Fig. 3A5 (d), Fig. 3A6 (d)).

Inorganic Phosphate (PO_4^{3-})

Phosphorus is also a key component in DNA, and it is found in adenosine triphosphate (ATP), a molecule that is important in energy transfer and storage in living cells. Phytoplankton normally satisfies their requirements by direct assimilation of ortho–phosphate. Weathering of rocks liberates phosphorus as soluble alkali phosphates and colloidal calcium phosphates which finally reach the sea by various means. In addition to this, anthropogenic inputs of fertilizers (superphosphate) and detergents (alkyl phosphates) also increase amount of phosphorus in sea water.

In general, two forms of phosphorus exist in sea water such as - inorganic and organic. Inorganic phosphate exists as PO_4^{3-} ions and HPO_4^{2-} ions. The condensed phosphate as P_2O_7 ions exists in estuarine and coastal waters and plays an important role in energy transformation processes in the biological systems and the organic phosphates exists as phospholipids, phosphonucleotides originated from decomposition and excretion of organisms. Therefore, determination of

phosphates includes two phases such as determination of inorganic phosphate-P and total phosphorus that includes all forms of phosphorus.

Among the transects, marked fluctuations was observed in its temporal and spatial distribution (Table 3.4, Fig. 3U, Fig. 3V). In post monsoon the concentration of inorganic phosphate in surface water varied from 1.15 to 2.17 µmol l^{-1} at Cochin, 0.42 to 0.74 µmol l^{-1} at Chettuva, 1.04 to 1.95 µmol l^{-1} at Ponnani, 0.09 to 1.84 µmol l^{-1} at Calicut and 0.50 to 1.47 µmol l^{-1} at Kasargod. In pre monsoon, the concentration of inorganic phosphate in surface water varied from 0.87 to 1.57 µmol l^{-1} at Cochin, 0.72 to 1.46 µmol l^{-1} at Chettuva, 0.39 to 1.27 µmol/l at Ponnani, 0.27 to 2.08 µmol l^{-1} at Calicut and 0.25 to 0.58 µmol l^{-1} at Kasargod. In monsoon, the concentration of inorganic phosphate in surface water varied from 0.11to 1.43 µmol l^{-1} at Cochin, 0.14 to 0.82 µmol l^{-1} at Chettuva, 0.14 to 0.64 µmol l^{-1} at Ponnani, 0.09 to 0.46 µmol l^{-1} at Calicut and 1.18 to 1.51 µmol l^{-1} at Kasargod. The maximum concentration of inorganic phosphate of 2.17 µmol l^{-1} was recorded at Cochin in post monsoon, while the minimum value of 0.09 µmol l^{-1} was reported at Calicut in post monsoon and monsoon.

The concentration of inorganic phosphate in bottom water ranged from 1.38 to 2.75 µmol l^{-1} at Cochin, 0.58 to 1.45 µmol l^{-1} at Chettuva, 1.18 to 1.56 µmol l^{-1} at Ponnani, 0.95 to 2.17 µmol l^{-1} at Calicut and 1.12 to 2.10 µmol l^{-1} at Kasargod in post monsoon. In pre monsoon the concentration of inorganic phosphate ranged from 1.04 to 2.18 µmol l^{-1} at Cochin, 0.72 to 0.90 µmol l^{-1} at Chettuva, 0.49 to 1.10 µmol l^{-1} at Ponnani, 0.64 to 2.14 µmol l^{-1} at Calicut, 0.25 to 1.24 µmol l^{-1} at Kasargod. In monsoon, the concentration of inorganic phosphate ranged from 0.17 to 1.24 µmol l^{-1} at Cochin, 0.08 to 0.90 µmol l^{-1} at Chettuva, 0.24 to 1.24 µmol l^{-1} at Ponnani, 0.09 to 0.66 µmol l^{-1} at Calicut and 0.16 to 0.64 µmol l^{-1} at Kasargod. The maximum concentration of inorganic phosphate of 2.75 µmol l^{-1} was recorded at Cochin in post monsoon, while the minimum value of 0.08 µmol l^{-1} was reported at Chettuva in monsoon.

The average surface concentration of inorganic phosphate in this study varied from 0.85 - 1.65, 0.44 - 1.11, 0.43 -1.31 µmol l^{-1} and in bottom water it varied from 0.97 - 1.65, 0.57 - 1.04, 0.17 - 0.66 µmol l^{-1} in post monsoon, pre monsoon and monsoon respectively (Fig. 3A5 (f), Fig. 3A6 (e)).

Total Phosphorus

It involves both dissolved and particulate inorganic and organic phosphorus forms. Its concentration was found to vary both spatially and temporally among the transects (Table 3.4, Fig. 3W, Fig. 3X). In post monsoon the concentration of total phosphorous in surface water varied from 1.56 to 2.76 µmol l^{-1} at Cochin, 0.56 to 0.97 µmol l^{-1} at Chettuva, 1.21 to 2.95 µmol l^{-1} at Ponnani, 0.86 to 3.69 µmol l^{-1} at Calicut and 1.08 to 2.02 µmol l^{-1} at Kasargod. In pre monsoon the concentration of total phosphorus in surface water varied from 1.91 to 3.02 µmol l^{-1} at Cochin, 1.38 to 2.29 µmol l^{-1} at Chettuva, 1.58 to 2.78 µmol l^{-1} at Ponnani, 0.96 to 2.76 µmol l^{-1} at Calicut and 0.98 to 2.50 µmol l^{-1} at Kasargod. In monsoon the concentration of total phosphorus in surface water varied from 0.38 to 1.82 µmol l^{-1} at Cochin, 0.37 to 1.96 µmol l^{-1} at Chettuva, 0.42 to 1.76 µmol l^{-1} at Ponnani, 0.31 to 1.08 µmol l^{-1} at Calicut and 1.29 to 1.82 µmol l^{-1} at Kasargod. The maximum concentration of 3.69 µmol l^{-1} was reported at Calicut in post monsoon and the minimum concentration of 0.31 µmol l^{-1} was observed at Calicut in monsoon.

In post monsoon total phosphorous in bottom water varied from 2.42 to 3.27 µmol l^{-1} at Cochin, 0.71 to 1.91 µmol l^{-1} at Chettuva, 1.68 to 2.36 µmol l^{-1} at Ponnani, 1.32 to 3.54 µmol l^{-1} at Calicut, 1.86 to 3.01 µmol l^{-1} at Kasargod. In pre monsoon the concentration of total phosphorous in bottom water varied from 1.32 to 3.16 µmol l^{-1} at Cochin, 1.24 to 2.10 µmol l^{-1} at Chettuva, 1.95 to 3.41 µmol l^{-1} at Ponnani, 1.36 to 3.77 µmol l^{-1} at Calicut, 1.06 to 3.08 µmol l^{-1} at Kasargod. In monsoon the concentration of total phosphorous in bottom water varied from 0.31 to 2.12 µmol l^{-1} at Cochin, 0.96 to 2.48 µmol l^{-1} at Chettuva, 0.59 to 2.34 µmol l^{-1} at Ponnani, 0.53 to 1.16 µmol l^{-1} at Calicut and 0.32 to 0.74 µmol l^{-1} at Kasargod. The maximum concentration of total phosphorus of 3.77 µmol l^{-1} in bottom water was reported at Calicut in pre

monsoon and the minimum concentration of 0.31 µmol l^{-1} was discerned at Cochin in monsoon.

In surface water the average TP value varied from 0.71 – 2.18, 1.50 – 2.25, 0.62 –1.48 µmol l^{-1} and in bottom water it varied in the range 1.20 –2.82, 1.86 – 2.36 and 0.54 –1.35 µmol l^{-1} during post monsoon, pre monsoon and monsoon respectively in the study area (Fig. 3A5 (g), Fig. 3A6 (f)).

Inorganic Silicate ($Si(OH)_4$)

Silicon, after oxygen is the most common abundant element in the upper lithosphere. The principal sources of dissolved silicate in sea water are from rivers. The sea contains several groups of plants (eg. Diatoms and some Chrysophta) and animals (eg. Radioalarians, Pteropods and Sponges) having silicified structures that take up dissolved silicate and deposit as hydrated silica.

The distribution of SiO_4-Si significantly varied between regions at all seasons (Table 3.4, Fig. 3Y, Fig. 3Z). In post monsoon the concentration of inorganic silicate in surface water varied from 3.12 to 19.46 µmol l^{-1} at Cochin, 7.48 to 13.40 µmol l^{-1} at Chettuva, 5.52 to 18.36 µmol l^{-1} at Ponnani, 7.44 to 12.72 µmol l^{-1} at Calicut and 5.56 to 10.36 µmol l^{-1} at Kasargod. In pre monsoon, the concentration of inorganic silicate varied from 3.65 to 14.20 µmol l^{-1} at Cochin, 2.21 to 7.48 µmol l^{-1} at Chettuva, 2.50 to 7.02 µmol l^{-1} at Ponnani, 3.22 to 6.58 µmol l^{-1} at Calicut and 2.26 to 6.78 µmol l^{-1} at Kasargod. In monsoon, the concentration of Inorganic silicate varied from 7.89 to 24.36 µmol l^{-1} at Cochin, 7.16 to 15.26 µmol l^{-1} at Chettuva, 7.44 to 23.66 µmol l^{-1} at Ponnani, 6.84 to 13.56 µmol l^{-1} at Calicut and 5.40 to 14.10 µmol l^{-1} at Kasargod. The maximum concentration of Inorganic silicate of 24.36 µmol l^{-1}in the surface water was recorded at Cochin in monsoon and the minimum concentration of 2.26 µmol l^{-1} was observed at Kasargod in pre monsoon.

The concentration of Inorganic silicate in bottom waters varied from 3.50 to 15.38 µmol l^{-1} at Cochin, 4.60 to 18.09 µmol l^{-1} at Chettuva, 6.04 to 17.65 µmol l^{-1} at Ponnani, 6.12 to 12.48 µmol l^{-1} at Calicut, 8.60 to 18.60 µmol l^{-1} at Kasargod in post monsoon. In pre monsoon the concentration of Inorganic

silicate varied from 4.22 to 14.86 µmol l^{-1} at Cochin, 3.98 to 9.02 µmol l^{-1} at Chettuva, 4.37 to 9.56 µmol l^{-1} at Ponnani, 1.92 to 6.76 µmol l^{-1} at Calicut, 2.50 to 6.84 µmol l^{-1} at Kasargod. In monsoon, the concentration of inorganic silicate in bottom water varied from 7.12 to 19.20 µmol l^{-1} at Cochin, 6.14 to 21.30 µmol l^{-1} at Chettuva, 6.48 to 26.44 µmol l^{-1} at Ponnani, 4.28 to 15.39 µmol l^{-1} at Calicut and 9.40 to 19.68 µmol l^{-1} at Kasargod. The maximum concentration of inorganic silicate of 26.44 µmol l^{-1} was recorded at Ponnani in monsoon, while the minimum value of 1.92 µmol l^{-1} was reported at Calicut in pre monsoon.

The average surface concentration of SiO_4-Si was in the range 7.19 – 9.80, 4.25 – 7.63 and 9.26 – 14.06 µmol l^{-1} and in bottom water it varied between 7.96 – 13.04, 4.11 – 8.79, and 8.05 – 13.11 µmol l^{-1} in post monsoon, pre monsoon and monsoon respectively in the study area (Fig. 3A5 (i), Fig. 3A6 (g)).

3.2.3 Biological Characteristics

Chlorophyll *a*

Chlorophyll a is a green pigment found in phytoplankton, which represents the first trophic level in the primary production cycle. The amount of chlorophyll a in the water column is indicative of the biomass of phytoplankton, which in turn can indicate nutrient levels in the water column (or excess nutrients if the chlorophyll a values are elevated). Excessive nutrients and plant growth can in turn decrease DO levels and increase turbidity.

There was considerable difference in the phytoplankton pigment concentration (chlorophyll *a*) in surface coastal waters between stations studied seasonally during the present study (Table 3.5, Fig. 3A1) Near shore areas studied in all transects exhibited maximum pigment concentrations all over the study period. In post monsoon the concentration of chlorophyll *a* varied from 12.11 to 24.87 mg m^{-3} at Cochin, 6.56 to 13.82 mg m^{-3} at Chettuva, 6.57 to 13.65 mg m^{-3} at Ponnani, 5.07 to 11.76 mg m^{-3} at Calicut and 4.10 to 9.79 mg m^{-3} at Kasargod. In pre monsoon the concentration of chlorophyll *a* varied from 10.87 to 27.18 mg m^{-3} at Cochin, 4.67 to 11.97 mg m^{-3} at Chettuva, 4.02 to 11.18

mg m^{-3} at Ponnani, 8.68 to 16.20 mg m^{-3} at Calicut and 8.02 to 12.79 mg m^{-3} at Kasargod. In monsoon the concentration of chlorophyll *a* varied from 17.02 to 30.69 mg m^{-3} at Cochin, 7.10 to 15.79 mg m^{-3} at Chettuva, 7.65 to 15.10 mg m^{-3} at Ponnani, 10.72 to 17.79 mg m^{-3} at Calicut and 10.11 to 15.01 mg m^{-3} at Kasargod. The maximum concentration of chlorophyll *a* of 30.69 mg m^{-3} was reported at Cochin in monsoon and the minimum concentration of 4.02 mg m^{-3} was discerned at Ponnani in pre monsoon.

The mean concentration of Chlorophyll *a* in surface waters varied from 7.11 – 19.62, 7.45 – 18.08, 10.12 – 22.07 mg m^{-3} during post monsoon, pre monsoon and monsoon respectively along the study area(Fig. 3A7 (a)).

Primary Productivity

In aquatic sciences, the organisms that can perform oxygenic photosynthesis are collectively known as phytoplankton. Through photosynthesis, they convert inorganic carbon and nutrients into biomass and produce oxygen, in a process known as primary production (PP). The organic matter produced in such a way then becomes the base for most life in the ocean, providing the building blocks and metabolic energy required by higher trophic levels for maintenance, growth and reproduction. Significant spatial and temporal differences in the primary productivity occurred along the coastal region of the study area (Table 3.5, Fig. 3A2). In post monsoon the primary production varied from 20.16 to 28.12 mgC m^{-3} hr^{-1} at Cochin, 14.09 to 22.61 mgC m^{-3} hr^{-1} at Chettuva, 14.02 to 22.16 mgC m^{-3} hr^{-1} at Ponnani, 11.11 to 18.06 mgC m^{-3} hr^{-1} at Calicut and 9.66 to 12.62 mgC m^{-3} hr^{-1} at Kasargod. In pre monsoon, the primary production varied from 12.78 to 22.18 mgC m^{-3} hr^{-1} at Cochin, 11.57 to 19.49 mgC m^{-3} hr^{-1} at Chettuva, 11.68 to 19.92 mgC m^{-3} hr^{-1} at Ponnani, 10.96 to 20.70 mgC m^{-3} hr^{-1} at Calicut and 12.52 to 17.16 mgC m^{-3} hr^{-1} at Kasargod. In monsoon the primary production varied from 12.23 to 17.46 mgC m^{-3} hr^{-1} at Cochin, 10.92 to 16.07 mgC m^{-3} hr^{-1} at Chettuva, 10.11 to 16.75 mgC m^{-3} hr^{-1} at Ponnani, 9.91 to 16.91 mgC m^{-3} hr^{-1} at Calicut and 9.17 to 12.87 mgC m^{-3} hr^{-1} at Kasargod. The maximum primary production of

28.12 mgC m^{-3} hr^{-1} was reported at Cochin in post monsoon and the minimum of 9.17 mgC m^{-3} hr^{-1} was discerned at Kasargod in monsoon.

The mean concentration of primary productivity in surface waters varied from 10.94 – 24.25, 14.66 – 16.28, 10.57 -14.11 mgC m^{-3} hr^{-1} during post monsoon, pre monsoon and monsoon respectively along the study area (Fig. 3A7 (b)).

Phytoplankton

Phytoplanktonic organisms can be found across the entire world's ocean inhabiting the lighted upper layer known as the euphotic zone. However according to their growth requirements, different phytoplankton groups will be more abundant under different environmental conditions.

The species distribution chart (Fig. 3A8) indicates *Chaetoceros*, contributing to > 20 % of the phytoplankton population in post monsoon and monsoon at each transect, except at Ponnani where the community structure was dominated by *Skeletonema* (> 25%). The seasonal shift in population was explicit in pre monsoon, where *Skeletonema* contributing > 22% at Cochin and Ponnani, *Asterionella* (>23%) at Chettuva and *Leptocylindrus* (19%) at Calicut and Kasargod.

Table 3.1: Water Temperature, pH and Salinity of surface and bottom water among different seasons of the central and northern coast of Kerala.

Station Name	Distance from the shore (km)	Source	Water Temperature (°C)			pH			Salinity(psu)		
			POM	PM	M	POM	PM	M	POM	PM	M
Cochin	0.5	S	28.40	29.00	27.80	7.82	7.80	7.50	28.80	25.20	18.50
		B	28.60	28.70	27.30	7.80	7.90	7.62	27.80	26.50	19.00
	1	S	28.40	28.80	28.20	7.95	7.80	7.70	30.60	29.20	24.60
		B	28.30	28.90	27.90	7.80	7.90	7.59	30.10	30.10	29.30
	3	S	28.20	28.50	27.80	8.01	8.15	7.90	32.20	32.20	28.90
		B	28.50	28.10	27.00	8.10	8.21	7.58	32.00	33.30	29.60
	5	S	28.10	28.50	27.90	8.10	8.17	7.95	31.90	32.90	30.80
		B	28.20	28.30	27.20	8.12	8.14	7.60	32.40	33.50	30.50
	7.5	S	28.10	28.60	28.00	8.10	8.17	8.01	32.30	32.90	31.00
		B	28.10	28.20	27.20	8.12	8.18	7.80	32.20	33.50	31.20
	10	S	28.00	28.50	27.50	8.10	8.16	8.01	32.30	32.70	31.10
		B	28.00	28.10	27.00	8.15	8.21	7.78	32.20	33.80	31.90
Chettuva	0.5	S	28.20	30.10	27.10	7.40	8.14	7.47	27.80	30.50	23.90
		B	28.50	29.80	28.20	7.50	8.02	7.60	28.20	30.20	26.60
	1	S	28.10	29.90	27.70	7.50	8.11	7.70	29.20	32.80	27.80
		B	28.50	29.60	28.00	7.90	8.14	7.55	31.80	33.10	28.80
	3	S	29.00	29.90	27.90	7.90	8.21	7.74	31.80	33.20	30.20
		B	28.00	28.80	27.40	8.00	8.21	7.92	32.10	33.50	30.70
	5	S	28.00	29.50	28.10	8.00	8.21	7.93	32.20	33.40	31.30
		B	28.30	29.00	26.50	8.10	8.23	7.93	32.10	33.50	32.10
	7.5	S	28.50	29.30	28.00	8.10	8.19	7.95	32.10	33.40	32.00
		B	28.20	28.80	26.90	8.20	8.21	8.05	32.30	33.50	32.00
	10	S	28.50	29.20	28.00	8.10	8.20	7.95	32.10	33.30	32.20
		B	28.00	28.40	25.50	8.20	8.21	8.08	32.60	33.70	32.50
Ponnani	0.5	S	28.10	28.20	27.50	7.90	7.75	7.72	28.30	30.80	15.50
		B	28.20	28.00	28.10	7.95	8.01	7.70	26.80	29.00	15.80
	1	S	28.30	28.60	27.40	7.90	8.08	7.91	31.50	32.50	17.80
		B	28.40	28.50	26.90	8.10	8.11	7.94	31.20	33.00	18.10
	3	S	28.20	28.80	27.50	8.00	8.13	8.10	31.70	33.20	32.40

		B	28.20	28.90	27.70	8.10	8.17	8.06	31.30	33.20	32.20
	5	S	28.30	29.00	27.80	8.00	8.29	7.98	31.20	33.40	33.30
		B	28.40	30.00	27.10	8.00	8.29	7.92	31.00	33.40	32.40
	7.5	S	28.50	28.90	27.80	8.10	8.23	8.01	32.00	33.30	33.30
		B	28.20	28.80	27.50	7.95	8.27	7,95	31.80	33.50	32.10
	10	S	28.60	28.90	27.70	8.10	8.19	8.01	32.10	33.30	33.30
		B	28.30	28.50	26.90	7.90	8.26	8.04	32.10	33.70	32.90
Calicut	0.5	S	28.90	29.40	28.90	7.90	8.02	7.56	27.50	30.50	23.50
		B	28.60	29.40	29.80	8.00	8.04	7.64	32.10	30.70	26.20
	1	S	29.00	29.50	28.80	7.90	8.08	7.67	31.90	32.70	27.60
		B	28.50	29.40	27.90	8.10	8.11	8.03	32.00	33.10	28.90
	3	S	30.00	29.40	28.00	8.10	8.19	8.07	32.00	33.30	31.90
		B	29.00	29.30	28.50	8.10	8.13	8.12	32.40	33.30	32.10
	5	S	30.00	29.50	28.20	7.90	8.25	8.15	31.50	33.30	32.50
		B	28.90	29.40	27.80	8.00	8.27	7.95	32.30	33.30	32.40
	7.5	S	29.90	29.40	28.40	8.10	8.27	8.05	32.00	33.30	32.50
		B	28.40	29.50	27.80	8.10	8.25	8.03	32.40	33.30	32.50
	10	S	29.80	29.50	28.50	8.10	8.33	8.02	32.00	33.30	32.70
		B	28.10	28.90	25.50	8.10	8.27	7.97	32.40	33.40	32.90
Kasargod	0.5	S	27.90	29.90	28.00	7.80	8.01	7.52	28.10	30.10	23.80
		B	28.70	29.30	28.10	7.90	8.02	7.60	28.70	30.20	25.60
	1	S	28.30	29.70	28.40	7.95	8.12	7.66	30.10	31.80	26.50
		B	28.50	29.50	28.70	8.10	8.15	7.83	32.00	32.50	31.10
	3	S	28.50	29.60	28.10	8.10	8.24	7.98	33.10	32.60	30.20
		B	28.50	28.90	27.10	8.00	8.26	7.89	33.00	33.20	32.70
	5	S	28.50	29.20	28.20	8.20	8.24	8.14	32.90	32.60	31.20
		B	28.30	29.00	26.70	8.10	8.26	7.91	33.10	33.30	33.10
	7.5	S	28.60	29.70	28.70	8.18	8.27	8.12	33.00	32.90	32.20
		B	28.50	28.80	27.00	8.18	8.29	7.95	33.00	33.30	33.20
	10	S	28.60	30.00	29.10	8.20	8.29	8.08	33.10	33.10	32.20
		B	28.90	29.00	27.20	8.20	8.29	8.01	33.10	33.40	33.20
NOTE: S- surface water, B - bottom water, POM - post monsoon, PM - pre monsoon, M - monsoon											

Table 3.2: Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD) and Total Suspended Solids (TSS) of surface and bottom water among different seasons of the central and northern coast of Kerala.

Station Name	Distance from the shore (km)	Source	DO (mg O_2 l^{-1})			BOD (mg O_2 l^{-1})			TSS(mg l^{-1})		
			POM	PM	M	POM	PM	M	POM	PM	M
Cochin	0.5	S	4.76	3.98	4.29	1.39	2.16	3.45	19.39	30.28	34.96
		B	4.52	3.48	3.96	1.76	2.42	2.99	13.48	16.66	23.90
	1	S	5.12	4.12	4.90	1.87	2.14	1.56	12.38	16.26	20.87
		B	4.56	3.78	4.58	1.99	2.56	1.19	10.79	13.24	19.34
	3	S	4.92	3.06	5.19	1.64	2.78	2.94	7.71	9.30	18.17
		B	4.60	3.12	5.42	0.58	2.90	2.70	8.78	10.40	15.39
	5	S	5.18	3.14	5.32	1.74	2.6	3.01	6.08	8.27	17.65
		B	5.02	3.98	5.29	1.28	3.04	2.34	9.21	11.34	18.90
	7.5	S	5.08	3.12	5.26	1.38	2.3	2.78	6.96	7.89	18.11
		B	4.92	3.56	4.32	1.29	2.87	1.86	9.98	10.40	14.46
	10	S	5.32	3.14	5.04	1.86	2.69	2.19	6.40	6.12	15.39
		B	5.68	3.04	4.35	1.28	2.89	1.49	7.70	7.18	11.08
Chettuva	0.5	S	5.12	5.14	5.12	1.98	0.86	1.76	11.10	12.76	21.12
		B	4.79	4.88	4.78	2.12	1.09	1.90	14.40	13.40	11.08
	1	S	4.98	5.81	4.94	1.45	0.40	0.92	8.92	10.18	18.60
		B	4.72	5.02	4.86	0.96	0.43	1.14	9.90	9.14	7.92
	3	S	4.82	5.60	4.12	0.70	0.48	0.89	8.80	9.16	15.37
		B	4.62	4.97	4.78	0.80	0.51	1.94	10.20	7.78	13.86
	5	S	5.14	5.84	4.27	0.54	0.43	0.94	6.80	9.26	12.79
		B	4.54	4.80	5.61	0.72	0.52	1.82	7.06	8.14	13.34
	7.5	S	4.92	5.36	4.82	1.32	0.86	0.88	6.76	7.88	8.47
		B	4.62	4.78	4.86	0.90	0.89	1.19	5.98	6.87	10.42
	10	S	5.18	5.42	5.26	0.56	0.91	0.94	5.20	6.96	8.38
		B	4.66	4.18	3.46	0.72	1.43	1.89	5.20	5.24	8.96
Ponnani	0.5	S	4.76	4.82	5.14	1.39	1.09	2.76	20.76	11.32	22.67
		B	5.12	4.85	5.16	1.36	1.12	2.18	14.39	12.32	23.89
	1	S	4.34	5.02	5.76	0.97	0.78	2.36	18.20	9.56	16.46
		B	4.06	4.98	5.12	0.82	0.86	2.94	16.28	9.37	19.39
	3	S	4.22	6.52	5.74	1.14	0.34	1.14	15.20	8.46	12.49
		B	4.14	6.20	5.80	1.26	0.82	2.15	13.28	9.39	16.32
	5	S	4.66	6.40	6.04	0.64	0.44	1.68	10.40	6.17	12.16
		B	4.48	5.70	5.10	0.72	1.10	1.69	11.10	5.96	12.32
	7.5	S	4.60	6.02	5.76	0.90	0.54	1.12	9.34	6.78	10.89
		B	4.69	5.80	5.21	0.65	1.02	1.73	5.21	6.17	11.67
	10	S	4.78	6.80	5.29	0.36	0.52	1.20	7.70	5.74	11.76
		B	4.76	5.96	5.01	0.47	0.92	1.60	3.40	5.06	10.54

Calicut	0.5	S	4.76	4.12	3.79	1.39	2.39	2.33	7.72	12.76	15.52
		B	4.62	3.98	3.18	2.12	2.39	2.69	7.18	15.66	17.14
	1	S	4.12	4.56	4.32	0.89	2.19	1.24	6.39	12.58	14.66
		B	3.76	4.39	4.06	1.82	3.01	0.94	6.56	13.47	16.60
	3	S	3.86	4.80	3.56	1.64	2.12	1.33	4.52	10.38	11.82
		B	4.48	4.88	3.76	1.10	1.96	3.29	7.80	10.99	8.12
	5	S	6.12	6.48	3.29	0.81	1.72	1.56	4.80	8.66	10.46
		B	4.56	6.22	3.97	0.96	0.86	2.17	18.24	9.32	7.87
	7.5	S	6.02	6.12	3.40	0.92	1.45	1.29	4.89	6.80	8.12
		B	4.60	5.98	3.66	0.88	1.02	1.89	9.88	7.63	6.90
	10	S	6.48	6.72	3.34	0.80	1.76	1.19	5.90	5.74	8.76
		B	4.72	6.50	3.56	0.60	1.83	1.56	7.60	5.28	5.81
Kasargod	0.5	S	5.08	5.12	4.14	0.96	1.14	1.24	10.56	9.34	16.39
		B	5.12	4.76	4.8	1.76	1.55	2.11	14.34	11.8	19.27
	1	S	5.27	5.72	3.86	0.86	0.94	1.28	10.47	10.36	11.66
		B	4.86	5.26	4.19	0.72	0.86	0.87	9.98	10.58	17.29
	3	S	4.52	6.30	3.22	0.80	0.83	1.90	9.80	8.34	9.56
		B	4.28	5.23	3.67	0.64	0.76	1.27	4.30	7.60	11.72
	5	S	4.44	5.60	3.56	0.48	2.80	1.86	5.10	5.78	6.76
		B	4.42	3.22	3.44	0.32	1.60	2.35	3.27	5.44	7.20
	7.5	S	4.80	5.72	3.66	0.72	1.79	1.56	5.19	5.86	6.78
		B	4.56	4.12	3.22	0.78	1.08	0.98	3.49	5.16	6.31
	10	S	4.96	6.19	3.76	0.39	2.19	1.80	3.98	5.12	5.72
		B	4.92	4.95	3.07	0.46	1.36	1.08	2.87	4.76	5.14
NOTE: S- surface water, B - bottom water, POM - post monsoon, PM - pre monsoon, M - monsoon											

Table 3.3: Concentration of Ammonium - N, Nitrite - N, Nitrate – N and Total Nitrogen in surface and bottom water of the central and northern coast of Kerala.

Station Name	Distance from the shore (km)	Source	NH_4^+ (μmol l^{-1})			NO_2^- (μmol l^{-1})			NO_3^- (μmol l^{-1})			Total Nitrogen (μmol l^{-1})		
			POM	PM	M	POM	PM	M	POM	PM	M	POM	PM	M
Cochin	0.5	S	0.76	0.66	0.97	0.38	1.08	0.24	9.37	5.36	5.99	17.39	12.69	26.14
		B	0.17	0.36	0.37	0.42	1.24	0.48	13.32	6.38	7.98	21.38	10.98	29.80
	1	S	0.35	0.46	0.66	0.24	0.30	0.44	7.58	1.98	3.67	17.39	9.58	27.39
		B	0.15	0.16	0.16	0.36	0.16	0.52	11.80	1.86	5.86	18.90	12.62	26.68
	3	S	0.27	0.26	0.42	0.22	0.02	0.12	5.92	0.38	0.92	18.65	11.94	30.84
		B	0.16	0.25	0.27	1.58	0.02	0.11	8.50	0.61	1.42	22.90	14.75	21.80
	5	S	0.18	0.36	0.29	0.82	0.06	0.09	3.30	0.42	0.76	21.62	8.80	27.61
		B	0.06	0.15	0.17	0.16	0.06	0.09	6.70	0.25	1.60	12.30	12.91	26.78
	7.5	S	0.09	0.21	0.36	0.32	0.04	0.10	5.31	0.67	0.92	15.68	11.60	24.89
		B	0.13	0.13	0.08	0.14	0.04	0.06	7.84	0.49	1.28	17.80	14.10	16.12
	10	S	0.16	0.32	0.28	0.53	0.02	0.08	7.81	0.95	0.96	18.44	11.17	29.56
		B	0.07	0.25	0.19	0.18	0.02	0.02	9.15	1.04	0.92	21.99	13.75	10.90
Chettuva	0.5	S	0.27	0.36	0.37	0.12	0.09	0.16	1.86	2.68	3.96	7.68	11.37	18.27
		B	0.12	0.18	0.32	0.14	0.11	0.21	3.40	1.26	11.56	9.24	14.56	16.78
	1	S	0.12	0.14	0.14	0.08	0.12	0.09	0.88	1.24	2.92	11.34	14.38	16.38
		B	0.07	0.15	0.14	0.06	0.16	0.16	1.20	1.04	9.46	14.50	12.39	19.54
	3	S	0.12	0.14	0.16	0.02	0.12	0.08	0.76	0.32	3.64	16.14	17.35	24.28
		B	0.11	0.06	0.26	0.01	0.10	0.06	0.81	0.87	5.68	17.62	15.80	18.70
	5	S	0.11	0.14	0.15	0.02	0.06	0.04	0.85	0.48	1.64	18.95	17.12	21.57
		B	0.12	0.15	0.16	0.02	0.06	0.16	0.55	0.48	9.58	20.26	15.94	22.65
	7.5	S	0.11	0.06	0.08	0.02	0.04	0.06	0.54	0.47	2.10	11.56	16.14	19.88
		B	0.09	0.07	0.16	0.02	0.06	0.08	0.56	0.74	5.99	18.80	15.36	21.87
	10	S	0.22	0.14	0.05	0.01	0.02	0.02	0.34	0.36	0.96	8.39	15.88	19.40
		B	0.08	0.16	0.25	0.01	0.04	0.04	0.58	1.14	6.93	17.65	15.20	21.54
Ponnani	0.5	S	0.24	0.26	0.35	0.12	0.10	0.34	2.38	5.32	6.96	12.39	10.30	23.52
		B	0.18	0.23	0.37	0.28	0.31	0.19	3.67	3.09	4.22	16.30	13.98	20.90
	1	S	0.14	0.14	0.16	0.14	0.14	0.14	2.76	2.38	2.51	10.18	7.92	17.40
		B	0.15	0.15	0.17	0.18	0.10	0.12	3.12	2.66	3.66	13.42	11.50	22.36
	3	S	0.13	0.14	0.16	0.02	0.02	0.06	0.76	0.24	5.50	11.30	9.77	5.91

		B	0.13	0.05	0.06	0.02	0.02	0.08	0.84	0.91	1.99	17.40	14.18	11.20
	5	S	0.13	0.25	0.06	0.02	0.02	0.05	1.04	0.26	3.98	21.69	5.16	6.24
		B	0.13	0.14	0.07	0.04	0.08	0.09	0.84	0.40	2.34	19.59	13.56	9.78
	7.5	S	0.06	0.13	0.07	0.02	0.02	0.02	0.96	0.32	2.78	9.78	7.32	6.83
		B	0.15	0.13	0.09	0.03	0.10	0.08	0.79	0.68	3.09	14.38	11.20	11.28
	10	S	0.16	0.24	0.06	0.02	0.06	0.02	1.46	0.44	3.25	9.26	11.27	8.16
		B	0.12	0.14	0.04	0.02	0.39	0.06	0.68	1.48	5.20	12.26	8.35	10.12
Calicut	0.5	S	0.34	0.23	0.47	0.14	0.56	0.45	3.48	3.38	6.68	14.36	10.32	16.10
		B	0.07	0.26	0.18	0.12	0.72	0.42	3.08	8.44	4.29	17.04	13.56	16.78
	1	S	0.14	0.23	0.55	0.16	0.24	0.15	2.46	2.27	4.29	12.37	11.58	22.32
		B	0.16	0.14	0.21	0.28	0.27	0.04	2.18	5.99	3.88	20.06	16.29	12.40
	3	S	0.25	0.14	0.39	0.02	0.04	0.04	0.42	0.86	4.31	11.36	13.46	27.20
		B	0.14	0.08	0.06	0.04	0.06	0.06	0.68	0.50	3.89	14.32	13.65	9.30
	5	S	0.16	0.04	0.39	0.02	0.08	0.02	0.32	0.82	1.26	8.76	15.68	23.78
		B	0.14	0.13	0.07	0.02	0.06	0.04	1.28	0.60	4.01	12.12	13.02	8.44
	7.5	S	0.14	0.07	0.32	0.02	0.04	0.02	0.56	0.80	1.32	8.60	12.56	15.70
		B	0.09	0.09	0.11	0.02	0.04	0.02	1.12	0.92	3.80	11.56	14.32	9.12
	10	S	0.15	0.04	0.22	0.02	0.02	0.03	0.72	0.96	1.17	10.14	15.19	12.67
		B	0.13	0.11	0.05	0.02	0.02	0.02	0.86	1.36	3.46	14.39	13.07	8.16
Kasargod	0.5	S	0.44	0.32	0.56	0.12	0.14	0.16	3.18	5.59	12.76	16.36	10.58	16.80
		B	0.24	0.15	0.26	0.23	0.41	0.32	3.21	5.20	6.39	14.80	13.98	17.80
	1	S	0.14	0.05	0.25	0.08	0.12	0.10	2.14	3.56	12.55	15.38	7.39	13.60
		B	0.23	0.25	0.12	0.10	0.44	0.14	2.38	4.29	6.12	11.06	8.80	9.76
	3	S	0.15	0.06	0.26	0.02	0.02	0.09	1.10	0.86	11.90	13.56	13.16	20.45
		B	0.15	0.14	0.23	0.02	0.04	0.12	1.46	1.08	6.15	17.39	16.20	8.90
	5	S	0.13	0.24	0.37	0.02	0.02	0.08	1.28	0.58	8.90	11.24	12.24	16.89
		B	0.14	0.13	0.16	0.08	0.04	0.39	2.96	1.08	9.88	14.30	14.60	17.90
	7.5	S	0.12	0.09	0.13	0.02	0.02	0.09	1.17	0.46	7.56	12.30	8.90	19.56
		B	0.12	0.08	0.13	0.04	0.06	0.12	1.67	0.82	5.31	14.78	12.90	9.57
	10	S	0.16	0.16	0.24	0.02	0.02	0.10	1.12	0.30	11.14	8.76	11.65	22.70
		B	0.06	0.14	0.08	0.06	0.12	0.09	2.76	0.52	5.80	19.36	17.45	14.50
NOTE: S- surface water, B - bottom water, POM - post monsoon, PM - pre monsoon, M - monsoon														

Table 3.4: Concentration of Inorganic Phosphate (PO_4^{3-}), Total Phosphorus (TP) and Inorganic Silicate ($Si(OH)_4$) in surface and bottom water among different seasons of the central and northern coast of Kerala.

Station Name	Distance from the shore (km)	Source	PO_4^{3-} (μmol l^{-1})			Total Phosphorus (μmol l^{-1})			$Si(OH)_4$ (μmol l^{-1})		
			POM	PM	M	POM	PM	M	POM	PM	M
Cochin	0.5	S	2.17	1.57	1.43	2.76	3.02	1.82	19.46	14.20	24.36
		B	2.36	2.18	1.24	2.98	3.16	2.12	15.38	14.86	19.20
	1	S	2.17	1.14	0.42	2.76	2.02	0.74	13.46	11.36	18.76
		B	2.16	1.92	1.09	3.08	2.76	1.26	12.90	12.80	13.59
	3	S	1.15	1.04	0.23	1.68	1.91	0.57	6.10	7.34	14.80
		B	1.38	1.14	0.22	2.69	1.32	0.46	6.90	4.22	11.68
	5	S	1.71	1.09	0.11	2.54	2.32	0.43	4.08	5.08	10.20
		B	2.75	1.27	0.21	3.27	2.49	1.66	5.18	6.91	7.32
	7.5	S	1.23	0.87	0.14	1.56	2.12	0.38	3.12	4.16	8.32
		B	1.51	1.21	0.18	2.42	1.90	0.52	3.90	6.87	7.34
	10	S	1.48	0.95	0.27	1.59	2.13	0.41	3.40	3.65	7.89
		B	1.61	1.04	0.17	2.45	2.50	0.31	3.50	7.10	7.12
Chettuva	0.5	S	0.74	1.46	0.82	0.97	2.12	1.96	13.40	7.48	15.26
		B	0.82	0.90	0.67	1.01	2.10	1.32	18.09	9.02	21.30
	1	S	0.56	1.32	0.56	0.64	1.98	0.65	12.60	5.58	8.94
		B	0.58	0.40	0.77	0.71	1.67	0.96	13.90	8.12	18.82
	3	S	0.45	0.72	0.14	0.68	2.29	0.56	8.88	3.70	7.16
		B	0.59	0.27	0.08	0.81	1.24	1.47	9.60	3.98	14.40
	5	S	0.59	1.17	0.18	0.64	1.96	0.82	8.24	3.74	8.64
		B	1.45	0.54	0.81	1.91	1.41	2.48	6.00	5.18	8.44
	7.5	S	0.42	0.87	0.16	0.78	1.42	0.56	7.80	2.78	8.32
		B	1.12	0.61	0.72	1.27	1.32	1.79	5.12	5.10	8.10
	10	S	0.45	1.09	0.14	0.56	1.38	0.37	7.48	2.21	8.84
		B	1.23	0.72	0.90	1.47	1.54	1.86	4.60	5.26	6.14
Ponnani	0.5	S	1.08	1.27	0.64	1.40	1.58	1.76	18.36	7.02	23.66
		B	1.56	1.10	0.89	2.19	1.97	2.34	17.65	9.56	26.44
	1	S	1.36	1.12	0.18	1.57	1.98	0.42	14.48	5.26	19.68
		B	1.42	0.86	0.46	1.68	2.16	1.24	14.39	6.18	20.32
	3	S	1.18	1.14	0.14	2.95	2.78	0.45	8.16	3.46	7.44
		B	1.18	0.71	0.24	2.36	1.95	0.59	12.24	4.37	9.84

	5	S	1.95	0.39	0.16	2.04	2.14	0.63	6.38	5.38	8.64
		B	1.27	0.56	1.24	1.84	3.41	1.97	7.92	5.47	6.48
	7.5	S	1.12	0.46	0.16	1.32	1.76	0.47	5.89	3.66	7.80
		B	1.20	0.65	0.43	1.77	1.98	1.02	6.56	4.87	7.90
	10	S	1.04	0.45	0.23	1.21	1.96	0.52	5.52	2.50	7.48
		B	1.18	0.49	0.32	2.13	2.68	0.96	6.04	4.99	7.68
Calicut	0.5	S	1.84	2.08	0.46	3.12	2.76	1.08	12.72	6.58	13.56
		B	2.17	2.14	0.66	3.46	3.77	1.16	10.28	6.76	15.39
	1	S	1.12	0.64	0.18	1.76	1.12	0.39	11.78	5.37	12.62
		B	1.28	0.70	0.41	2.24	2.78	0.77	6.28	5.92	9.19
	3	S	1.36	0.27	0.11	2.57	1.77	0.31	9.30	3.46	7.44
		B	1.99	0.64	0.23	2.08	1.77	0.53	12.48	3.74	8.12
	5	S	1.04	0.56	0.21	3.69	1.23	0.67	8.39	3.22	7.88
		B	1.68	0.92	0.09	3.54	1.99	0.54	7.20	4.46	6.40
	7.5	S	0.42	0.28	0.16	1.10	1.16	0.57	8.56	3.87	7.22
		B	1.08	0.97	0.12	1.80	1.72	0.56	6.12	2.70	4.94
	10	S	0.09	0.49	0.09	0.86	0.96	0.68	7.44	4.08	6.84
		B	0.95	1.23	0.10	1.32	1.36	0.61	7.20	1.92	4.28
Kasargod	0.5	S	1.47	0.58	1.24	2.02	1.14	1.46	10.36	6.78	14.10
		B	2.10	0.89	0.64	2.10	1.56	0.68	18.60	6.84	19.68
	1	S	0.86	0.42	1.18	1.42	0.98	1.29	8.32	4.94	13.30
		B	1.32	0.54	0.19	1.86	1.06	0.32	13.48	4.83	12.90
	3	S	0.50	0.54	1.18	1.38	2.32	1.38	5.56	4.90	9.30
		B	1.73	0.72	0.37	2.17	3.08	0.74	15.40	4.66	12.16
	5	S	1.14	0.25	1.51	1.96	2.50	1.82	6.36	5.10	6.11
		B	1.95	0.25	0.24	3.01	2.31	0.44	12.48	2.50	12.48
	7.5	S	0.62	0.41	1.34	1.08	1.12	1.36	5.92	3.89	7.32
		B	1.12	0.32	0.26	2.10	1.56	0.51	9.68	2.90	9.40
	10	S	0.50	0.45	1.39	1.12	1.27	1.54	6.60	2.26	5.40
		B	1.68	1.24	0.16	2.70	1.77	0.53	8.60	2.93	10.80
NOTE: S- surface water, B - bottom water, POM - post monsoon, PM - pre monsoon, M - monsoon											

Table 3.5: Concentration of Chlorophyll *a* and Primary productivity in surface water among different seasons of the central and northern coast of Kerala.

Station Name	Distance from the shore (km)	Source	Chlorophyll *a* (mg m^{-3})			Primary Productivity (mgC m^{-3} hr^{-1})		
			POM	PM	M	POM	PM	M
Cochin	0.5	S	24.87	27.18	30.69	28.12	22.18	17.46
	1	S	22.92	20.97	25.97	26.34	18.46	14.92
	3	S	19.02	17.84	21.09	26.02	15.63	14.59
	5	S	20.09	15.82	19.76	22.54	15.46	12.74
	7.5	S	18.69	15.79	17.89	22.3	13.19	12.23
	10	S	12.11	10.87	17.02	20.16	12.78	12.71
Chettuva	0.5	S	13.82	11.97	15.79	22.61	19.49	16.07
	1	S	10.64	8.90	11.77	20.20	16.11	14.96
	3	S	8.83	8.20	9.88	19.73	16.02	12.16
	5	S	8.88	6.68	9.88	19.06	13.95	12.92
	7.5	S	6.56	4.68	7.10	14.09	11.92	10.92
	10	S	6.98	4.67	7.78	14.74	11.57	10.98
Ponnani	0.5	S	13.65	11.18	15.10	22.16	19.92	16.75
	1	S	10.67	8.74	11.11	20.95	16.95	14.16
	3	S	8.99	8.98	9.80	19.98	16.92	12.53
	5	S	8.87	6.82	9.09	19.11	13.91	12.80
	7.5	S	6.57	4.98	7.65	14.18	11.92	10.11
	10	S	6.78	4.02	7.98	14.02	11.68	10.92
Calicut	0.5	S	11.76	16.20	17.79	18.06	20.70	16.91
	1	S	11.02	14.20	15.87	15.02	16.80	16.32
	3	S	9.91	14.02	15.19	15.75	16.95	12.59
	5	S	9.09	10.20	12.18	13.61	14.98	11.20
	7.5	S	5.92	10.97	12.20	11.11	14.70	11.95
	10	S	5.07	8.68	10.72	11.17	10.96	9.91
Kasargod	0.5	S	9.79	12.79	15.01	12.62	17.16	12.18
	1	S	8.92	11.02	12.91	12.62	16.98	12.87
	3	S	8.02	10.60	12.11	10.87	14.63	9.64
	5	S	5.92	9.92	10.11	9.92	14.00	9.75
	7.5	S	5.92	8.02	12.07	9.94	12.52	9.17
	10	S	4.10	8.08	14.07	9.66	12.64	9.82
NOTE: S- surface water, B - bottom water, POM - post monsoon, PM - pre monsoon, M - monsoon								

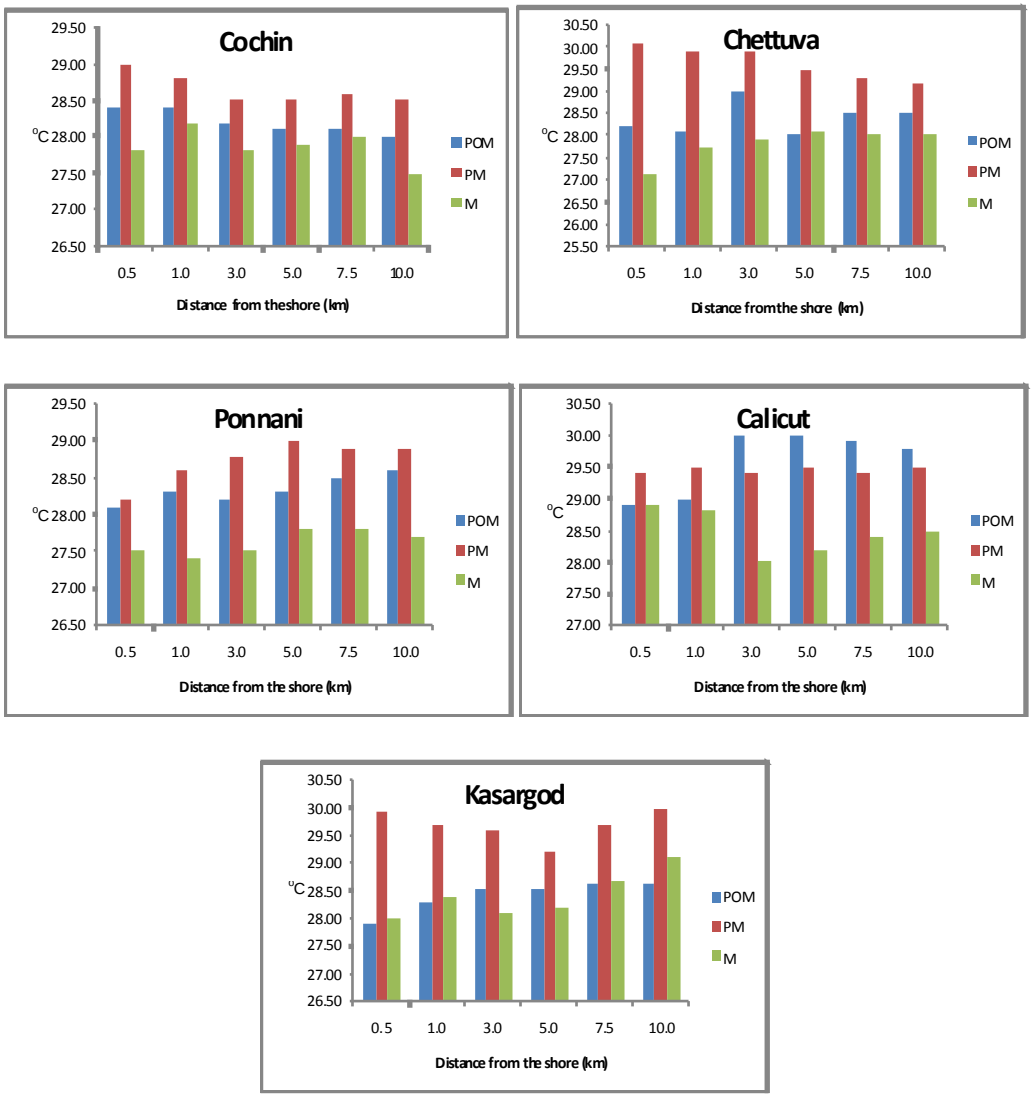


Figure 3A. Seasonal variation of surface water temperature among different transects.

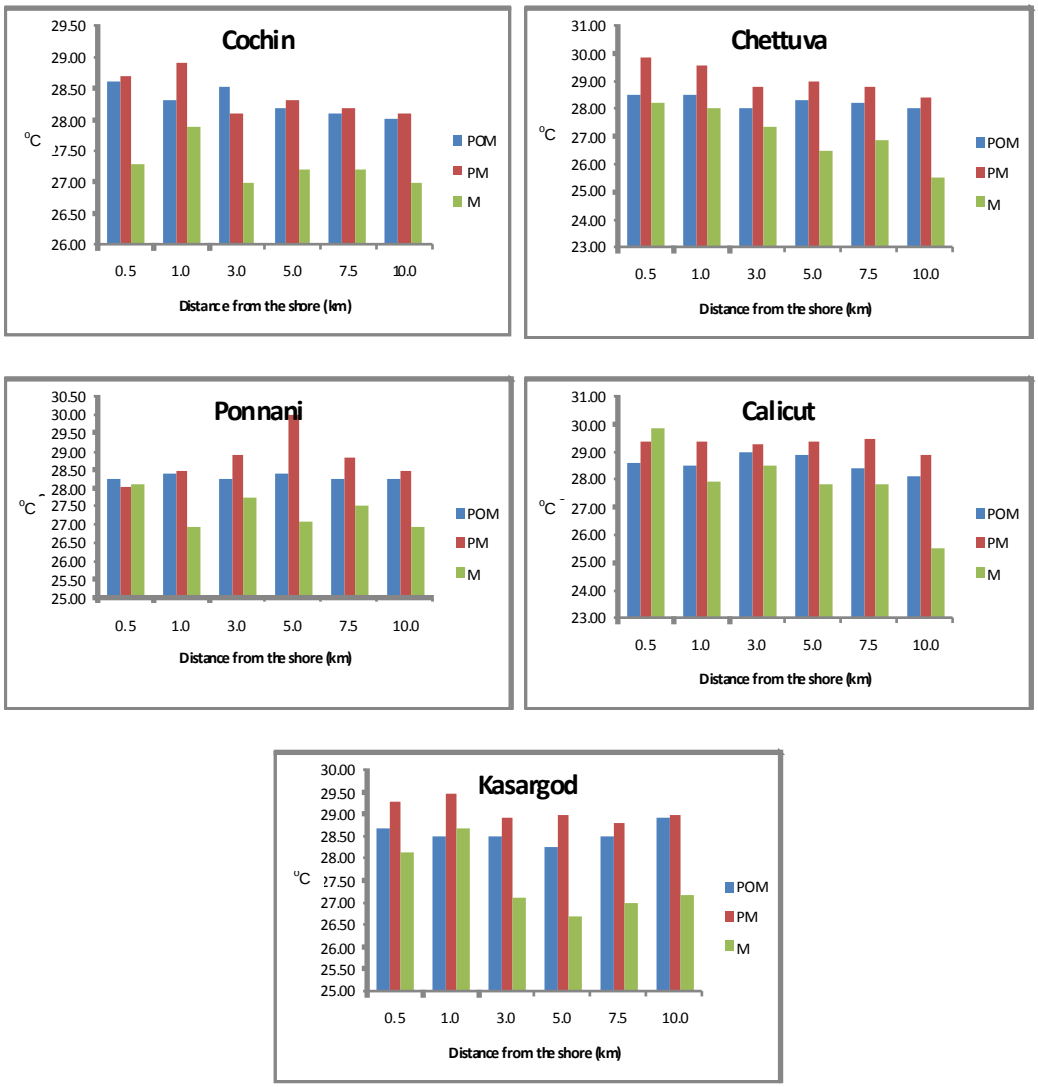


Figure 3B. Seasonal variation of bottom water temperature among different transects.

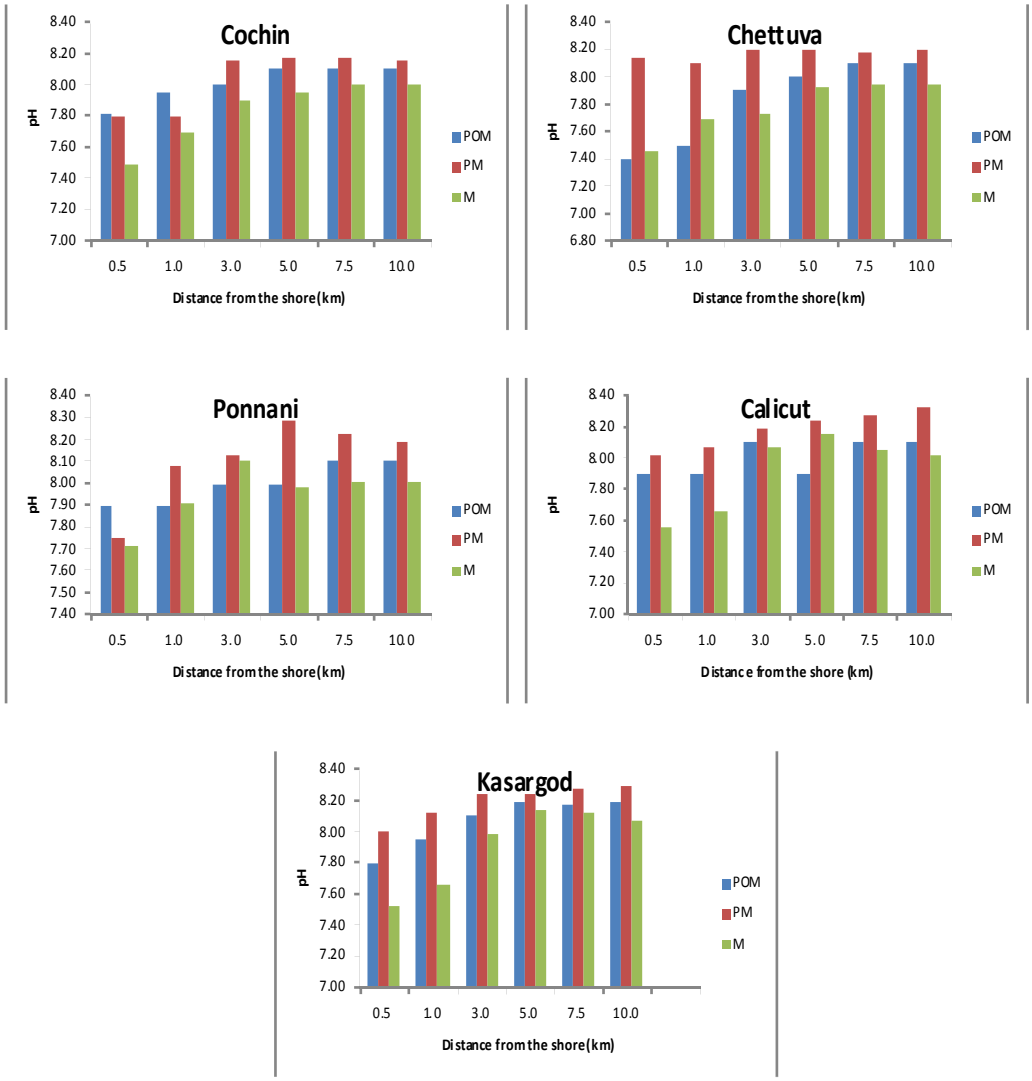


Figure 3C. Seasonal variation of pH in surface water among different transects.

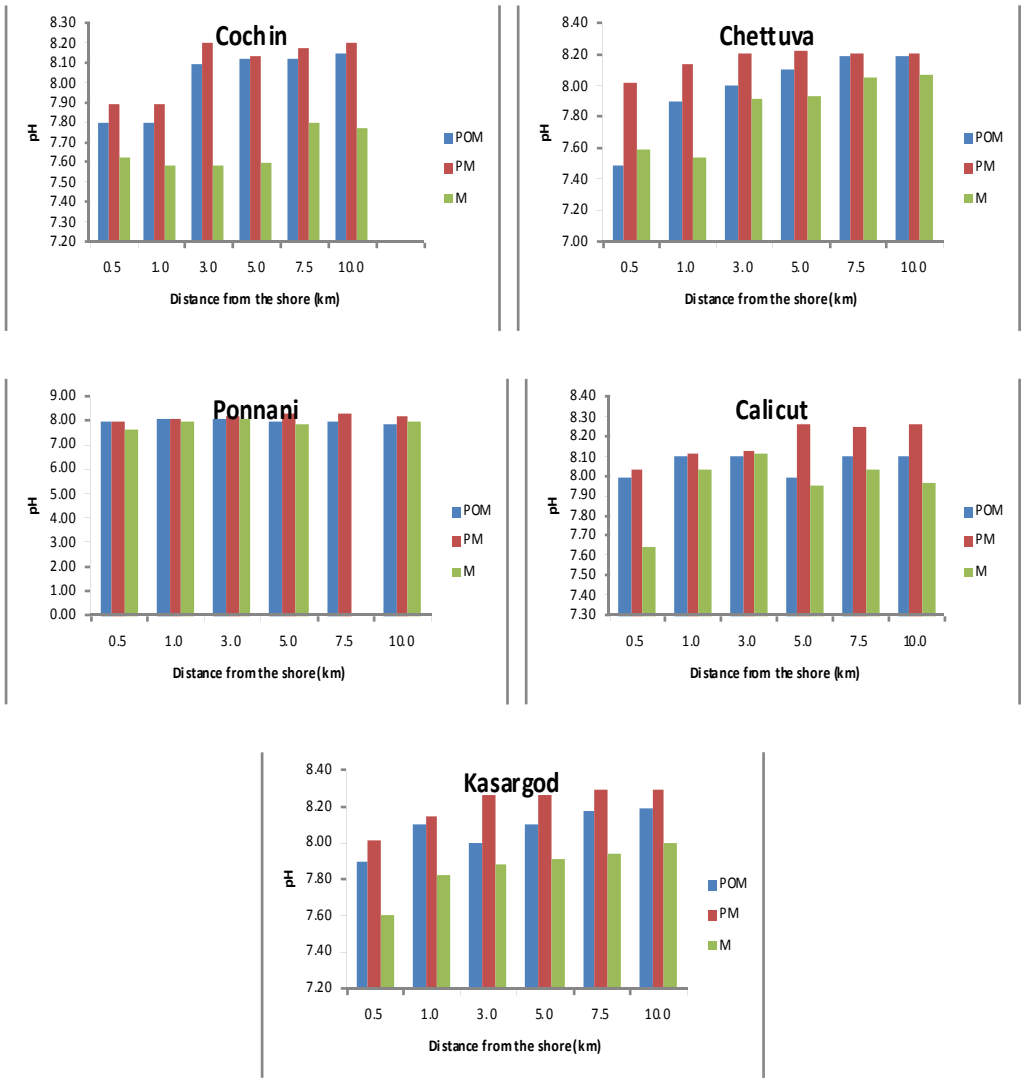


Figure 3D. Seasonal variation of pH in bottom water among different transects.

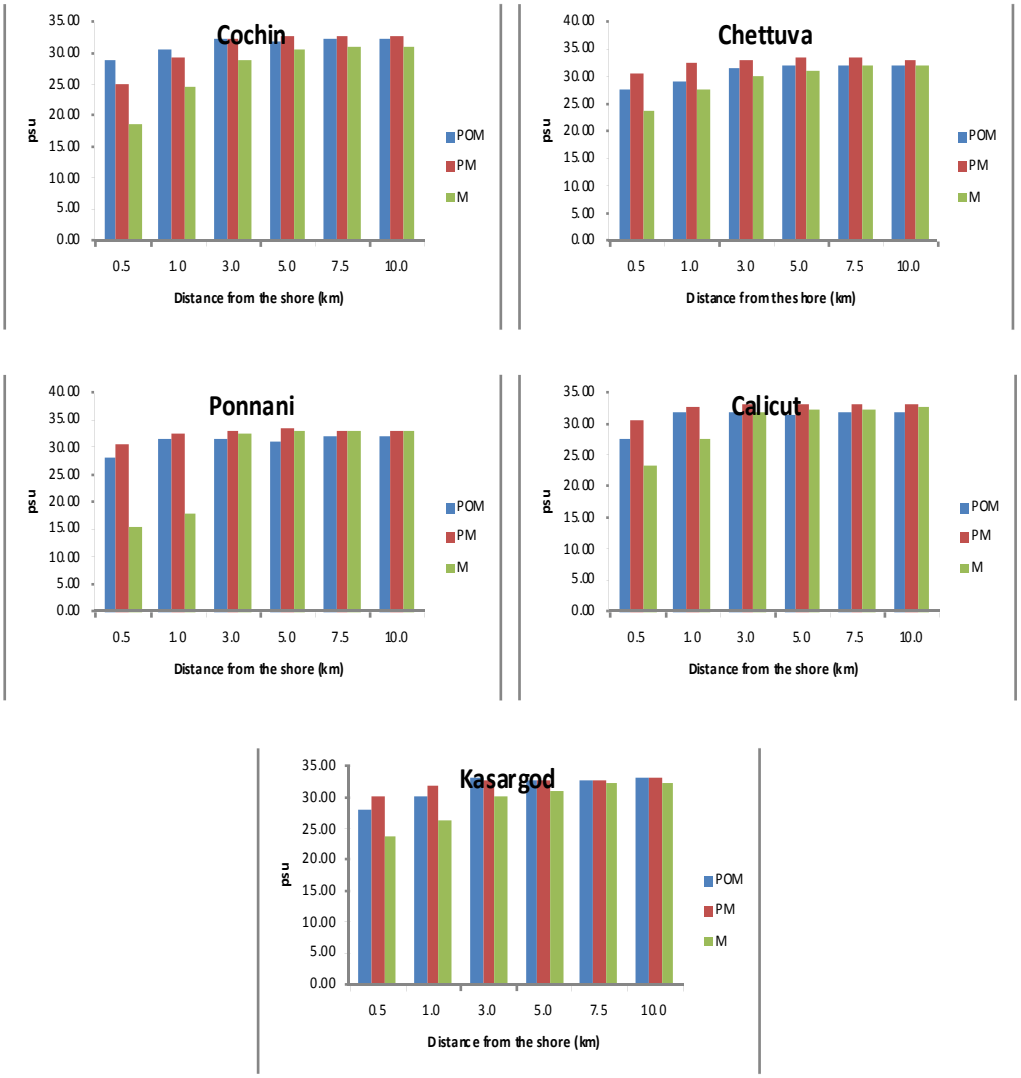


Figure 3E. Seasonal variation of salinity in surface water among different transects.

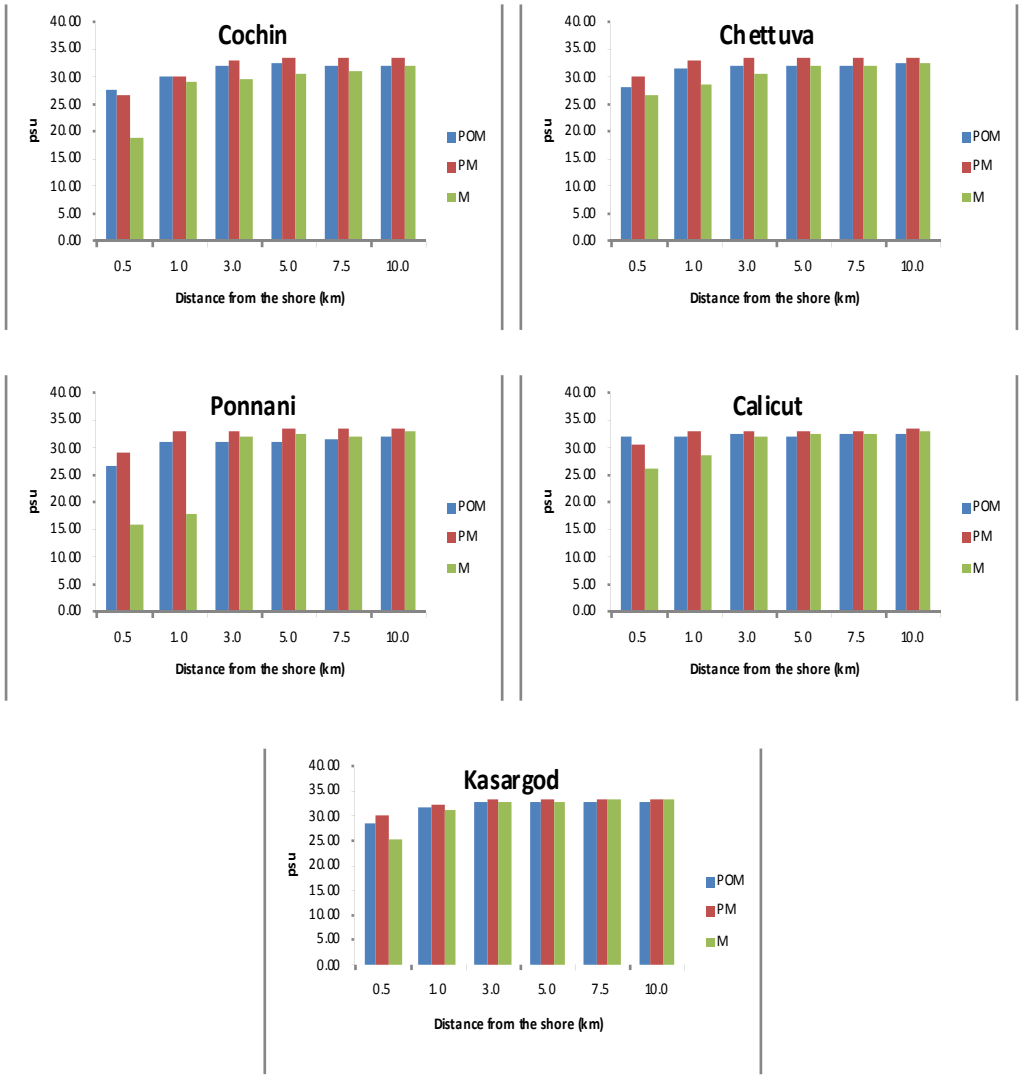


Figure 3F. Seasonal variation of salinity in bottom water among different transects.

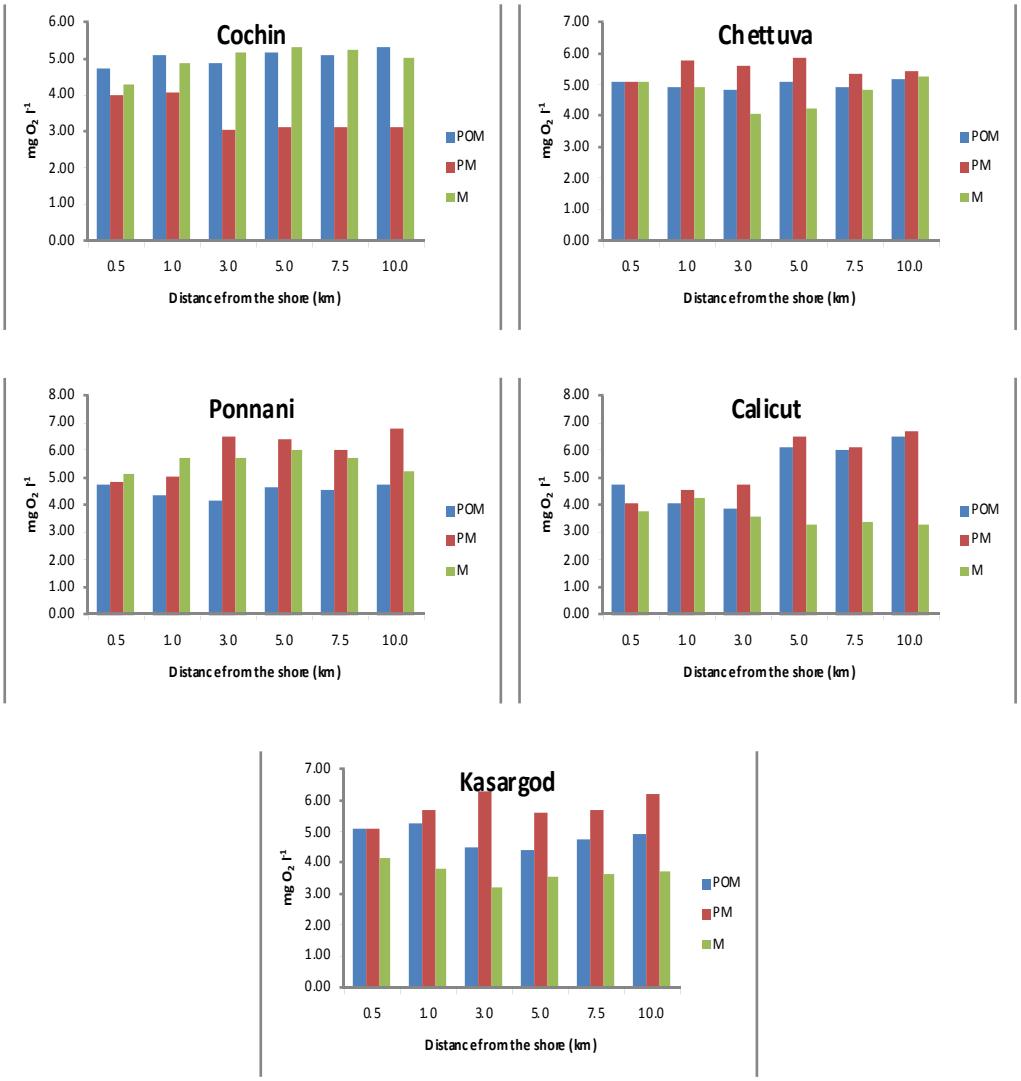


Figure 3G. Seasonal variation of Dissolved Oxygen in surface water among different transects.

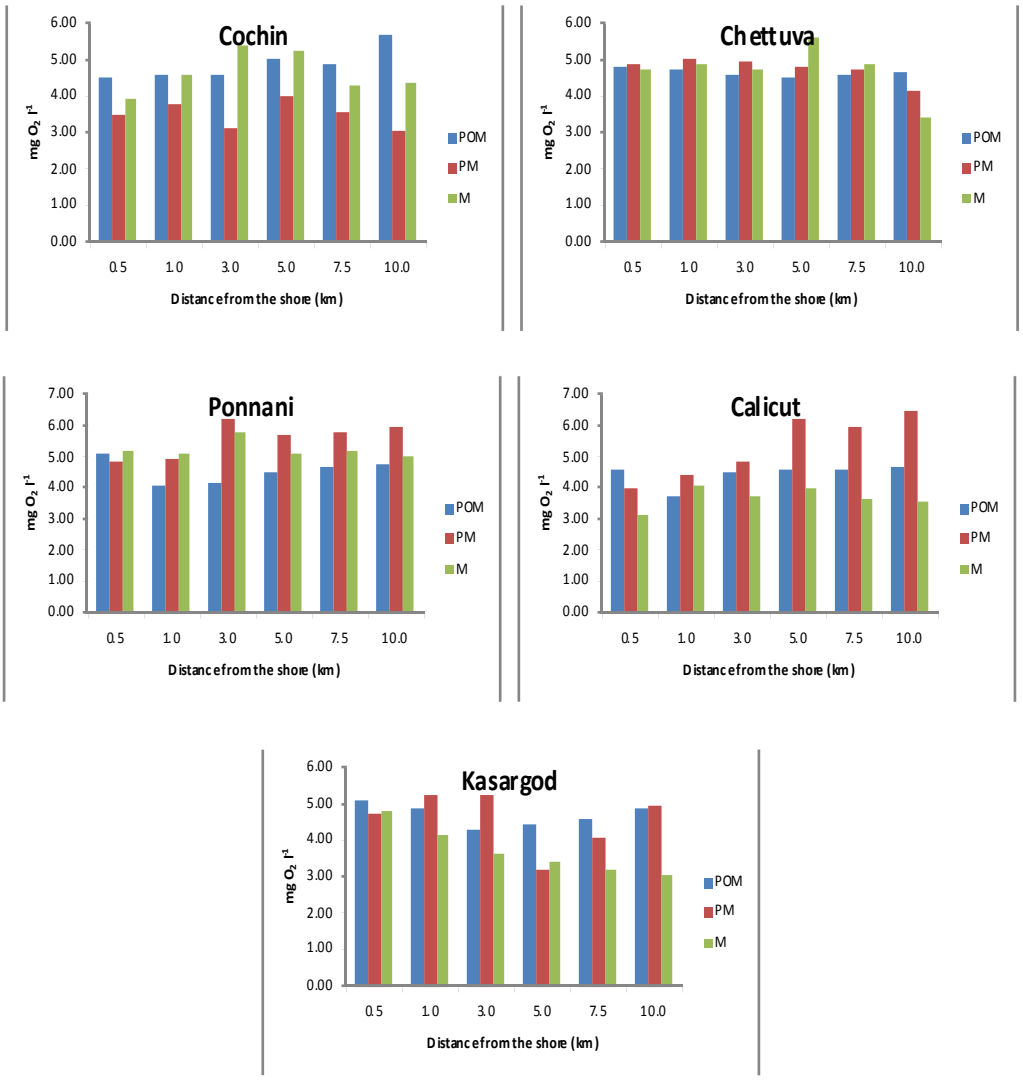


Figure 3H. Seasonal variation of Dissolved Oxygen in bottom water among different transects.

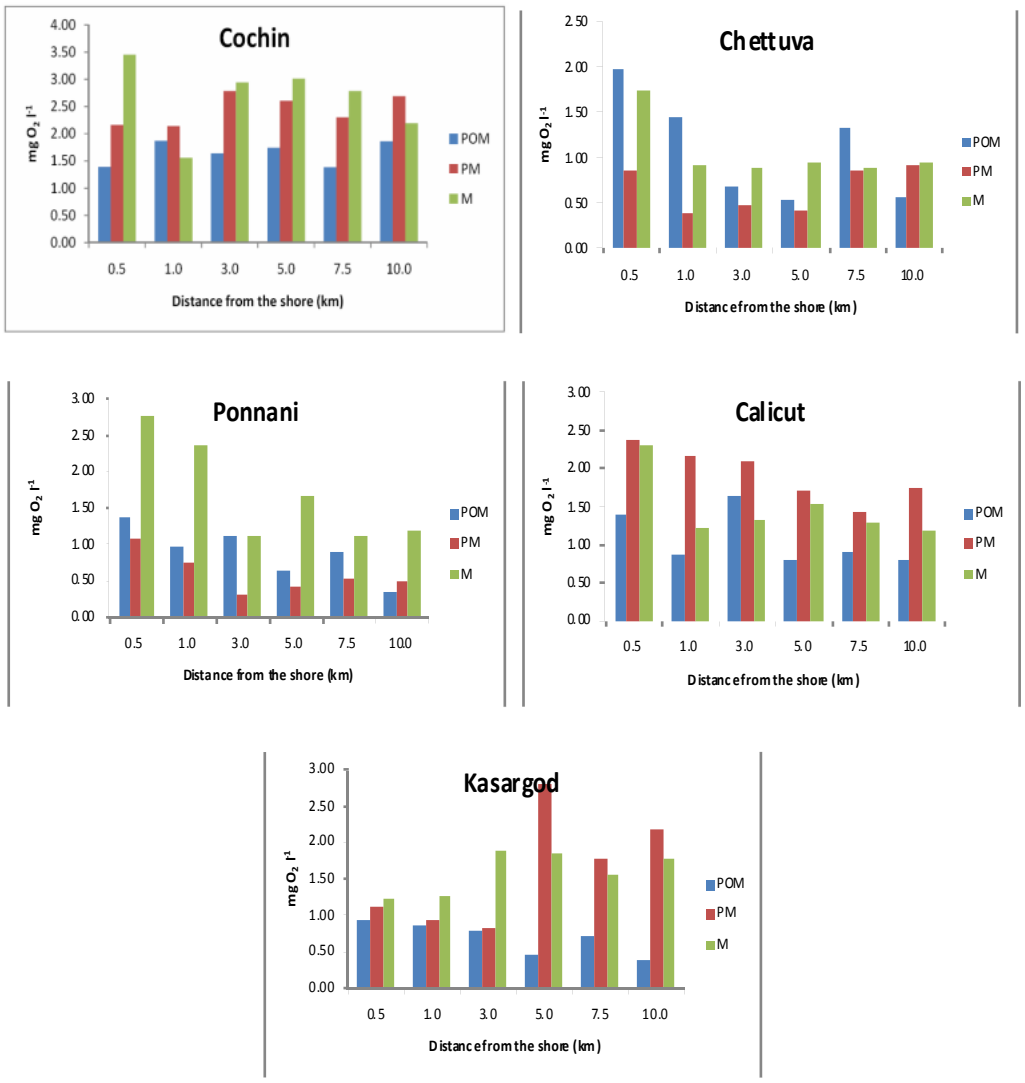


Figure 3I. Seasonal variation of BOD in surface water among different transects.

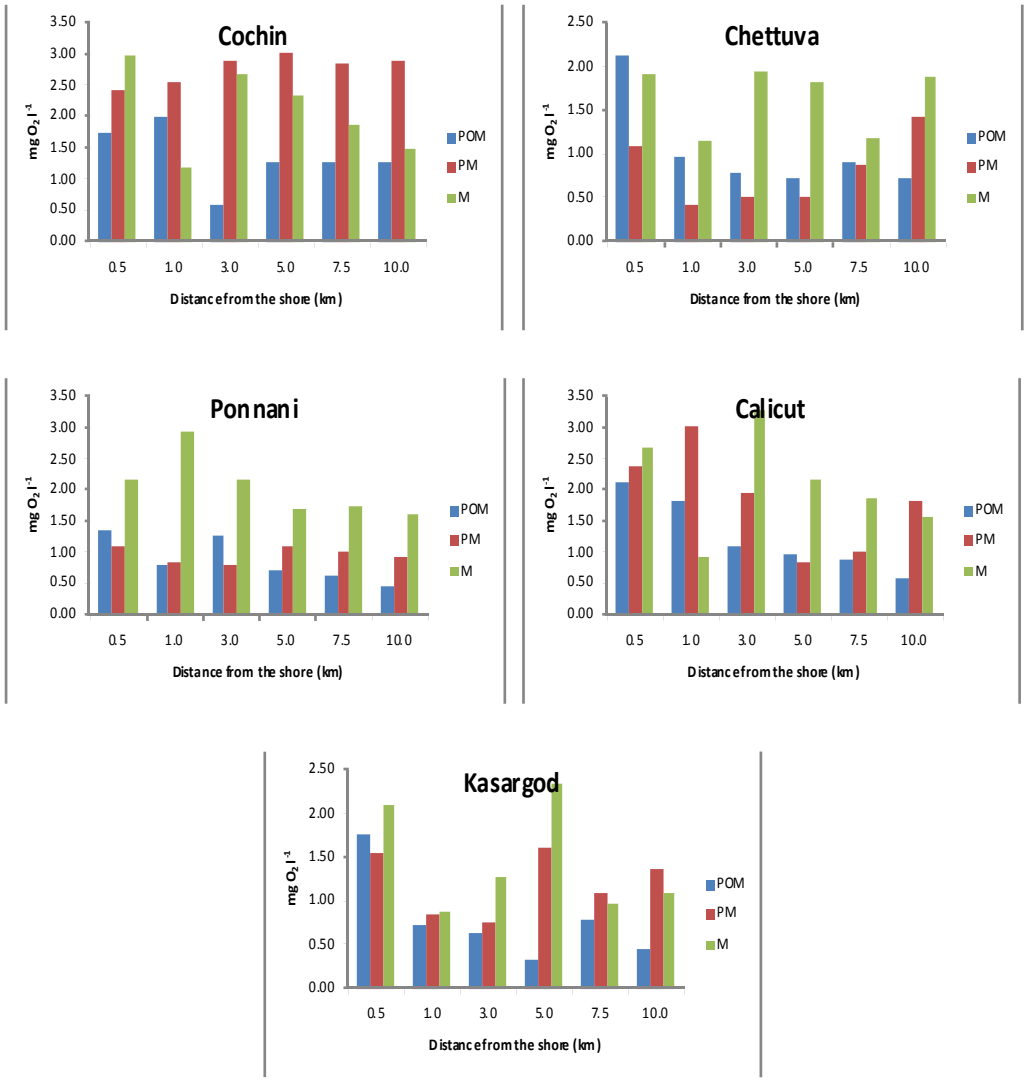


Figure 3J. Seasonal variation of BOD in bottom water among different transects.

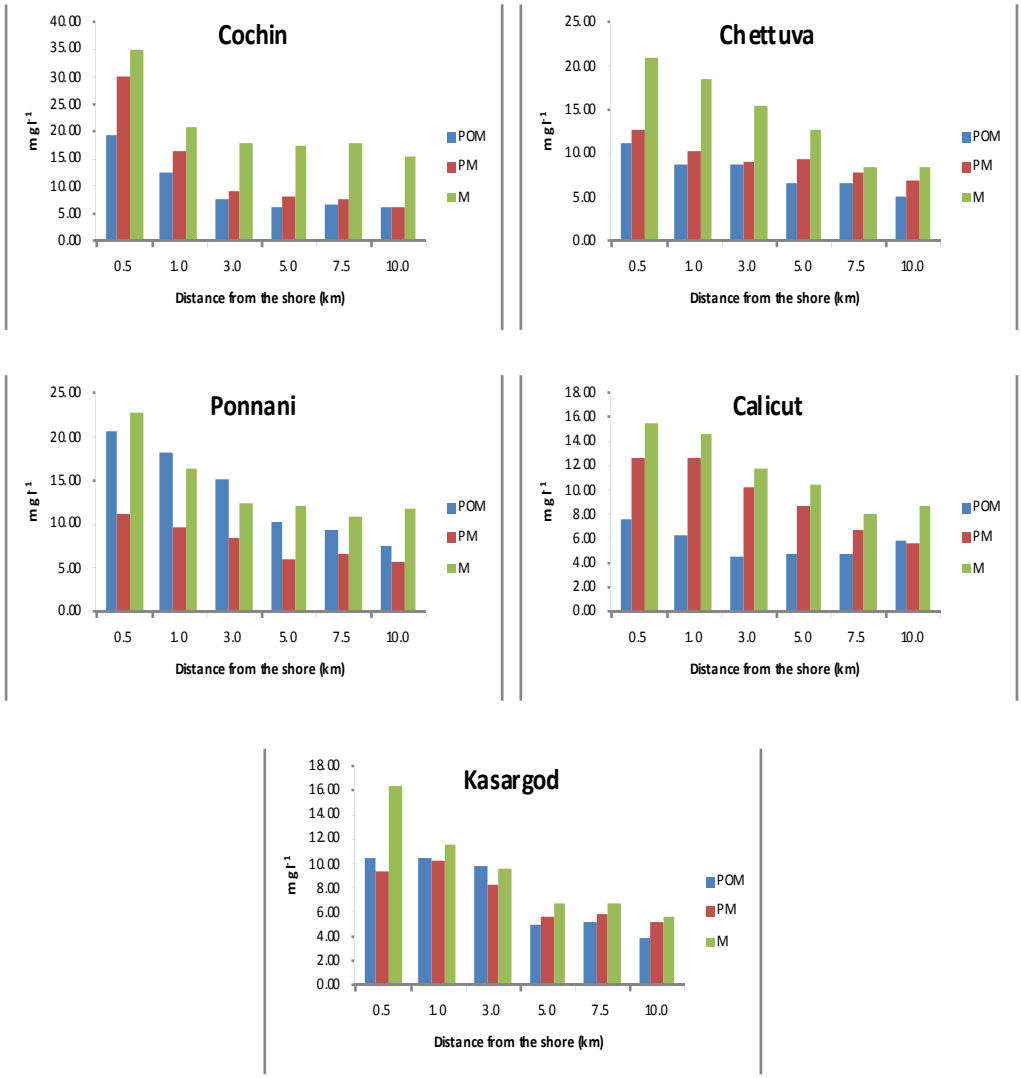


Figure 3K. Seasonal variation of TSS in surface water among different transects.

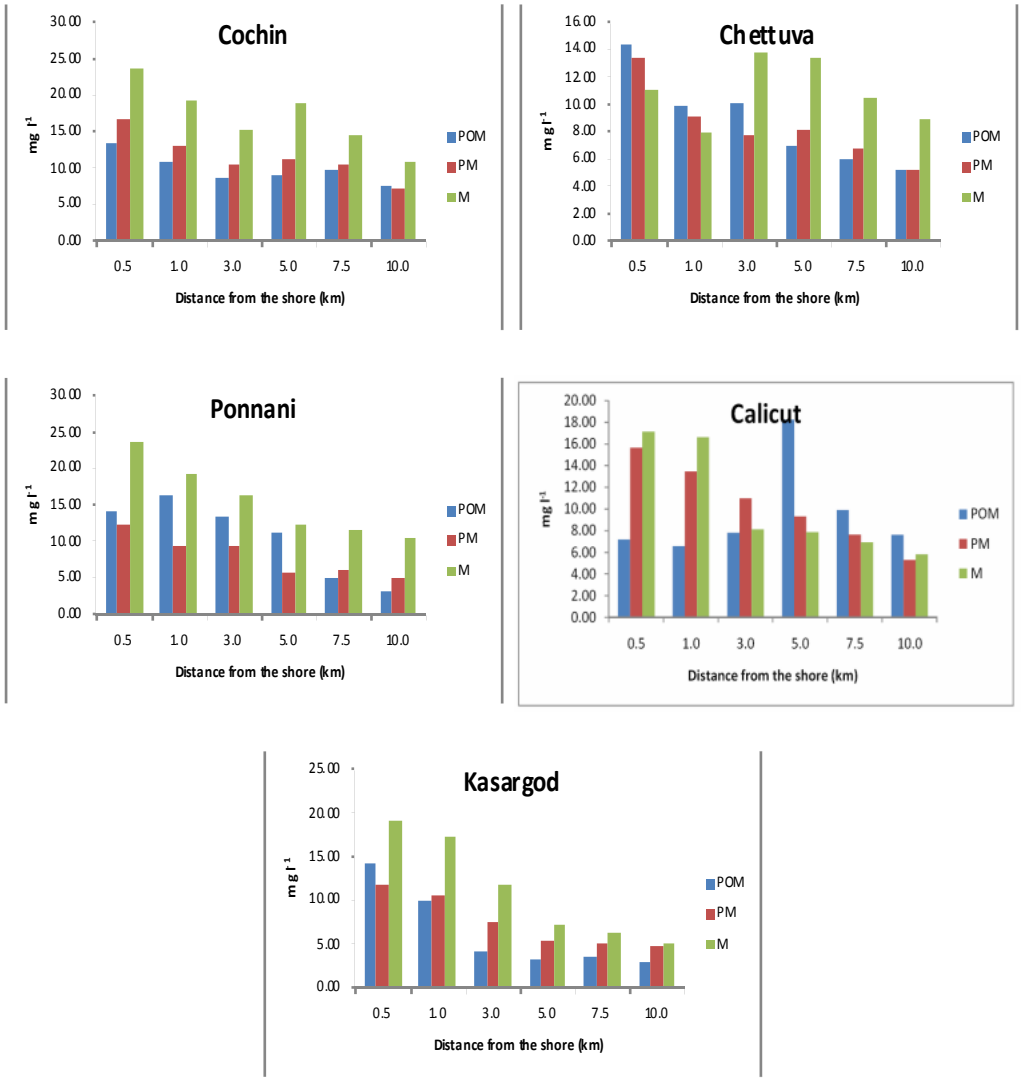


Figure 3L. Seasonal variation of TSS in bottom water among different transects.

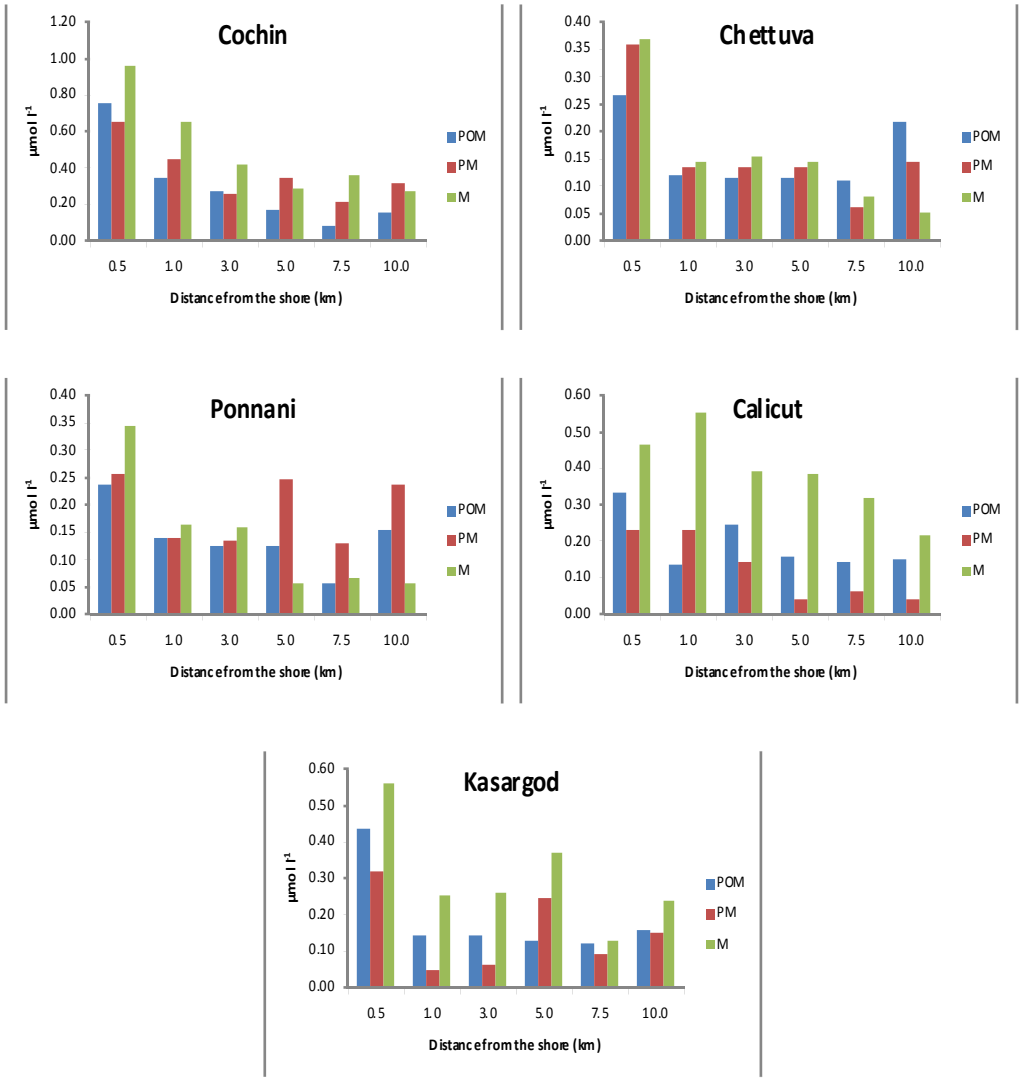


Figure 3M. Seasonal variation of ammonium-N in surface water among different transects.

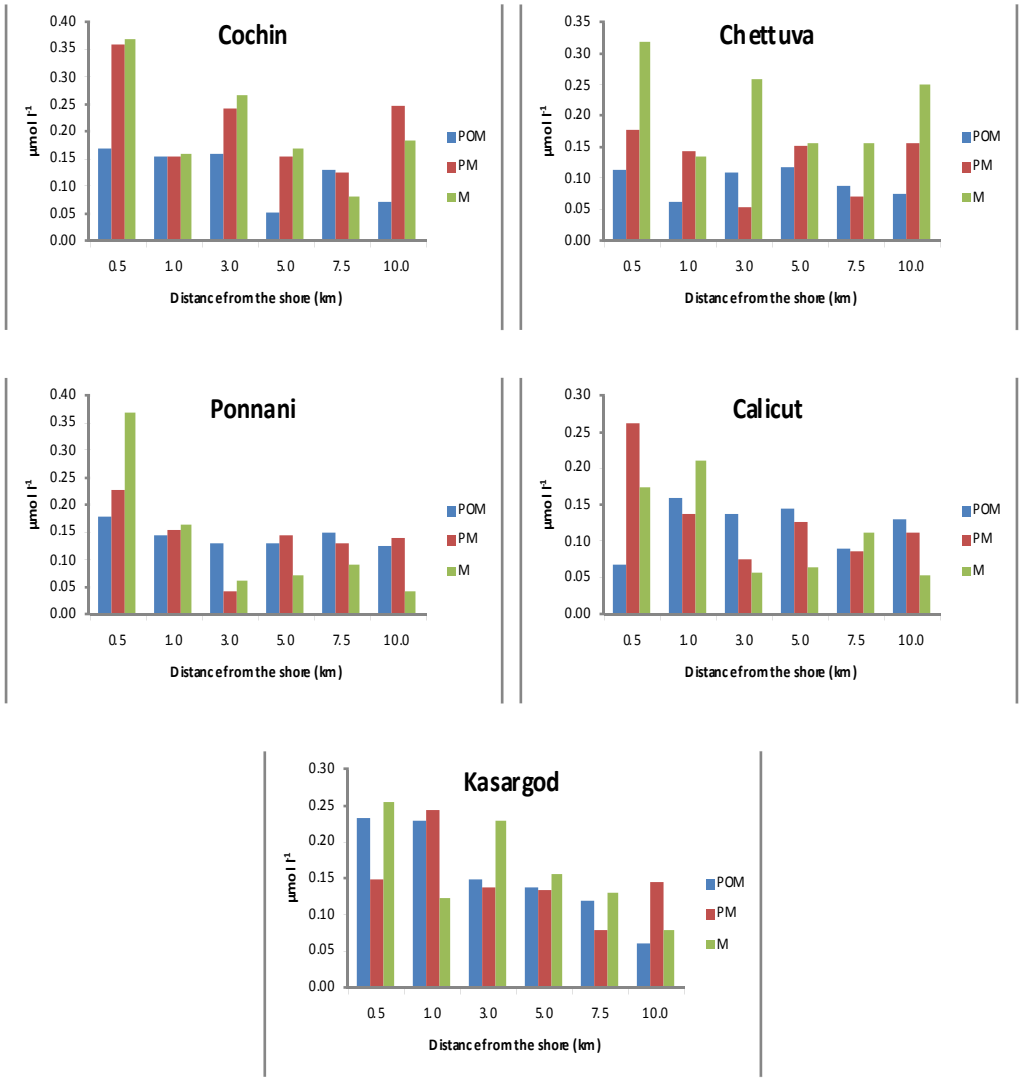


Figure 3N. Seasonal variation of ammonium-Nin bottom water among different transects.

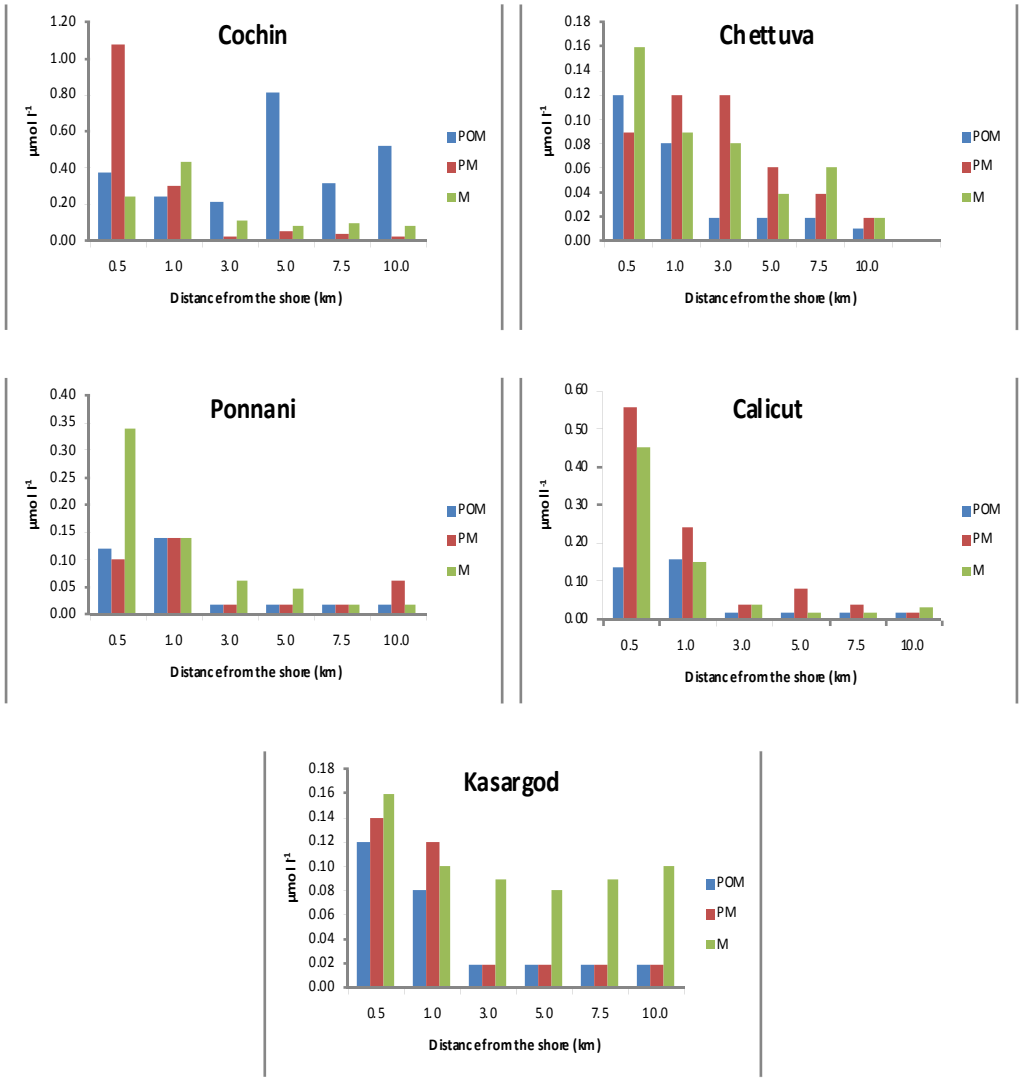


Figure 3O. Seasonal variation of nitrite -N in surface water among different transects.

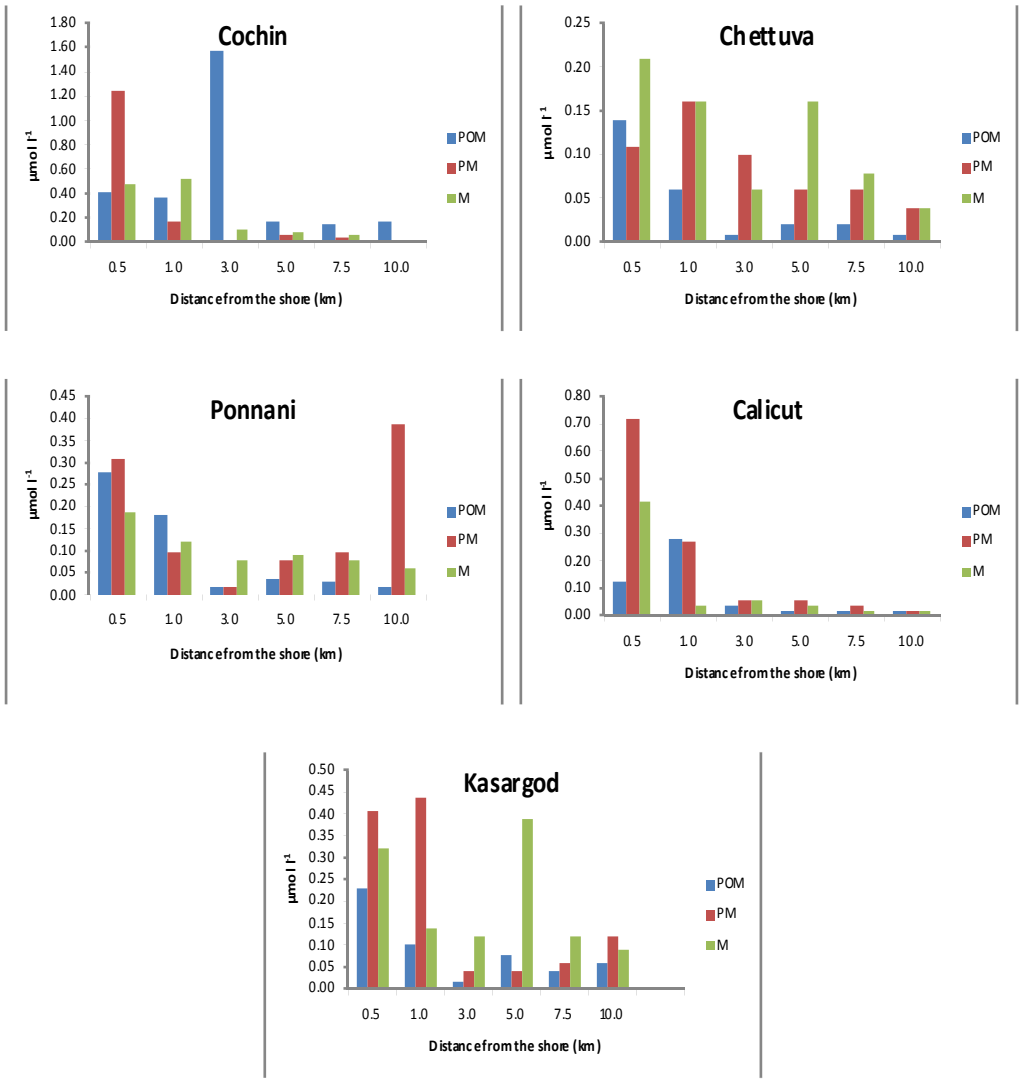


Figure 3P. Seasonal variation of nitrite -N in bottom water among different transects.

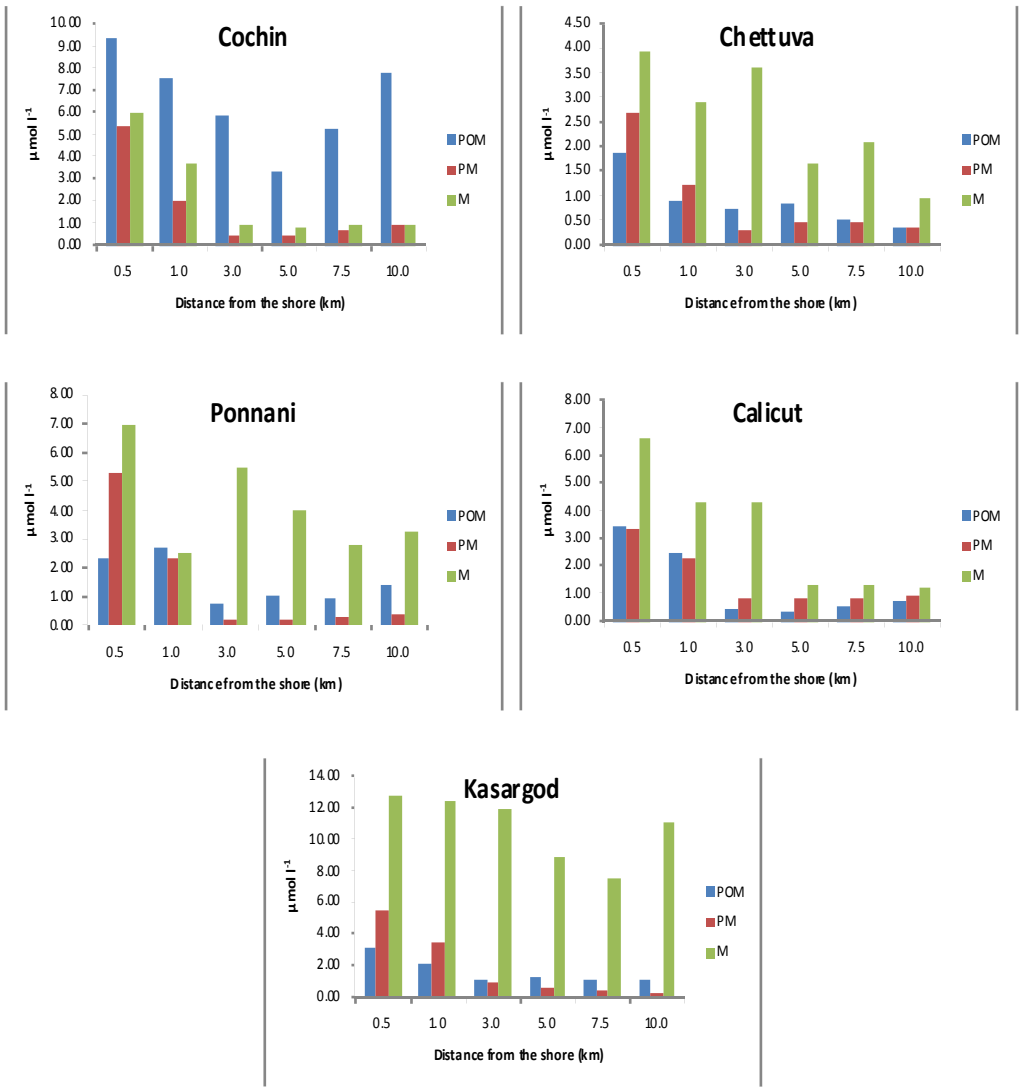


Figure 3Q. Seasonal variation of nitrate-N in surface water among different transects.

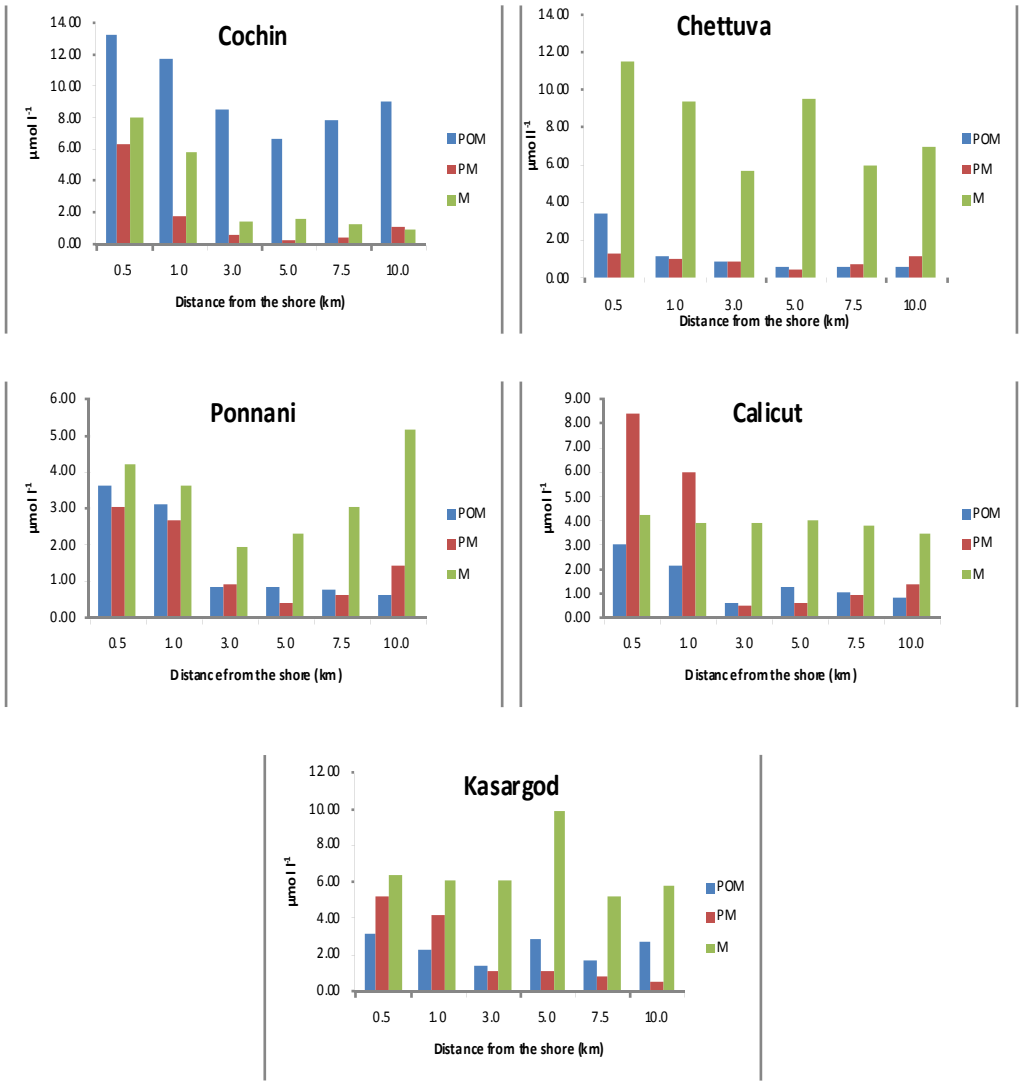


Figure 3R. Seasonal variation of nitrate-N in bottom water among different transects.

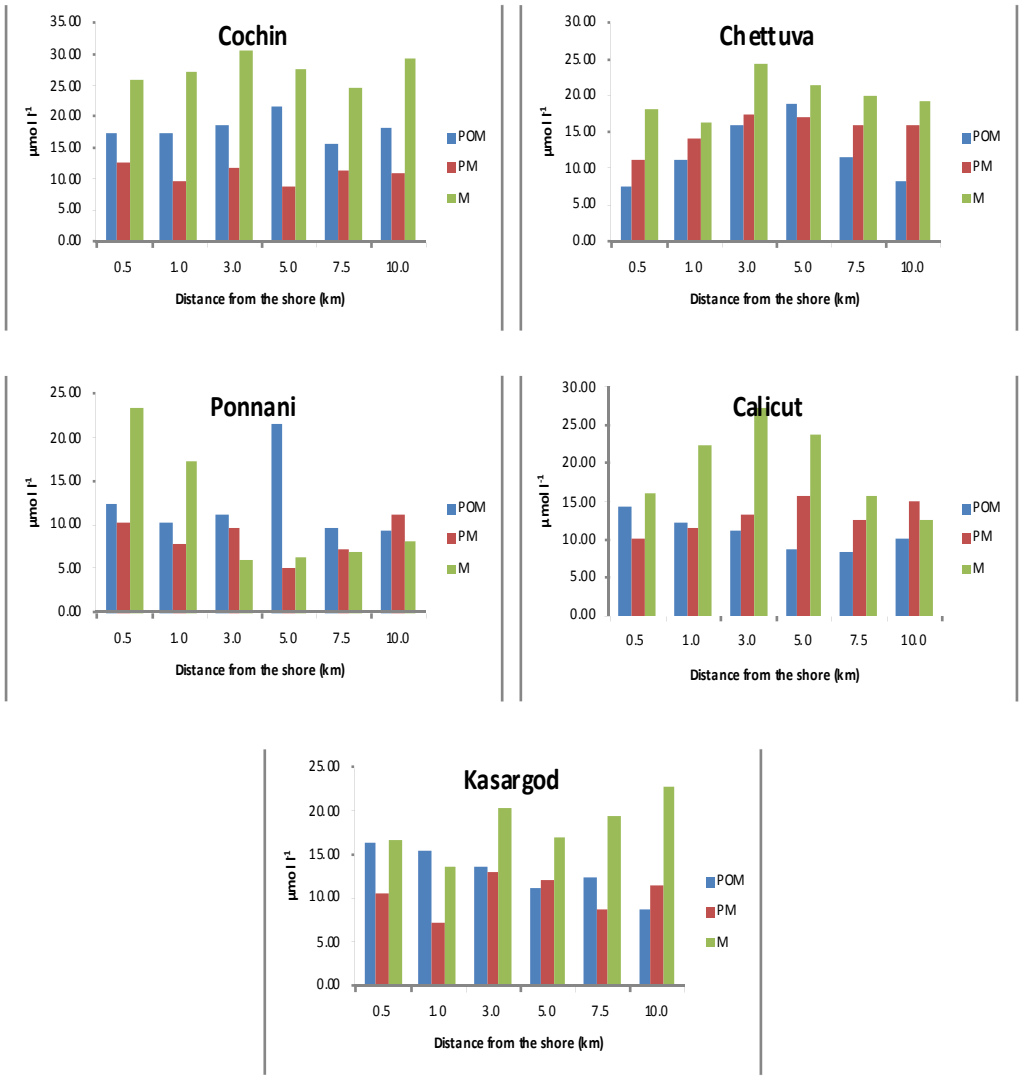


Figure 3S. Seasonal variation of Total Nitrogen in surface water among different transects.

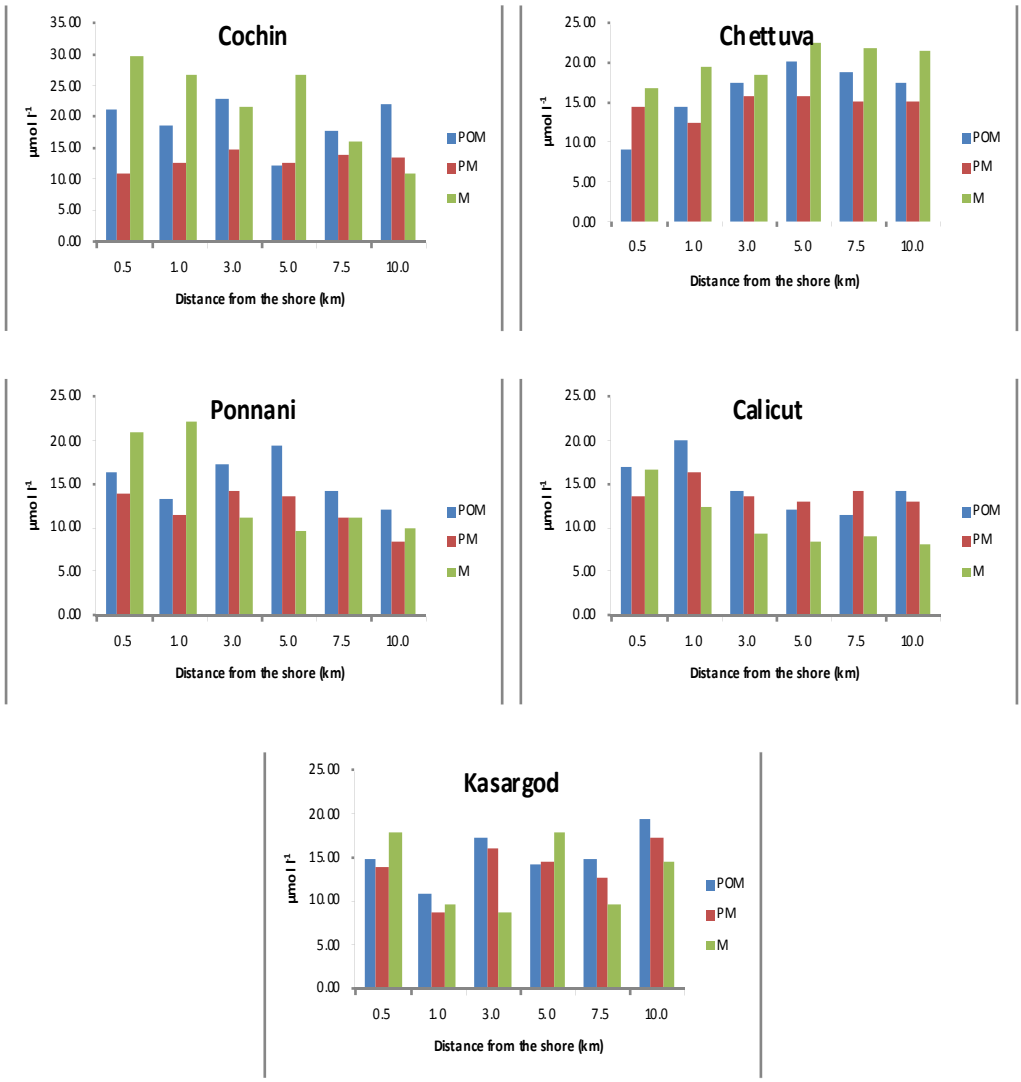


Figure 3T. Seasonal variation of Total Nitrogen in bottom water among different transects.

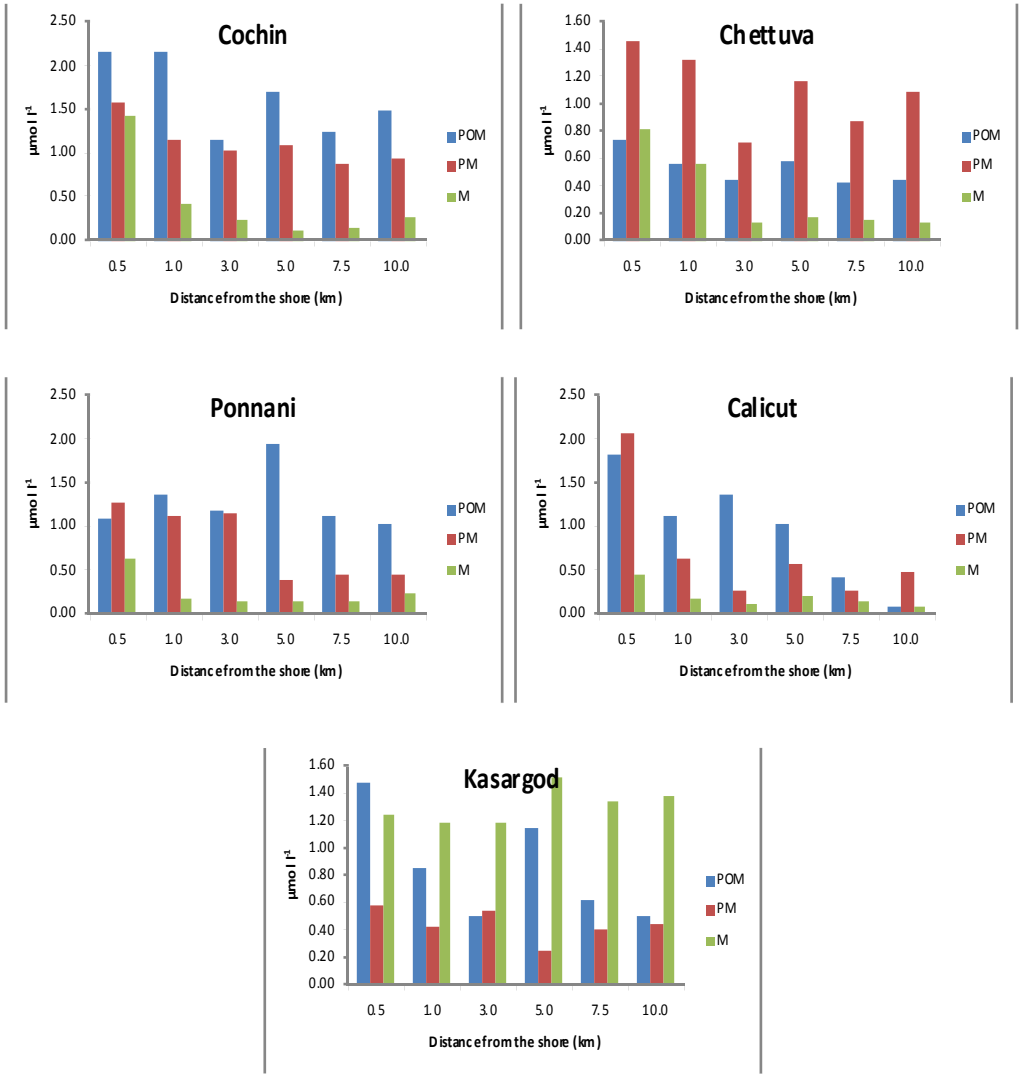


Figure 3U. Seasonal variation of Inorganic phosphate in surface water among different transects.

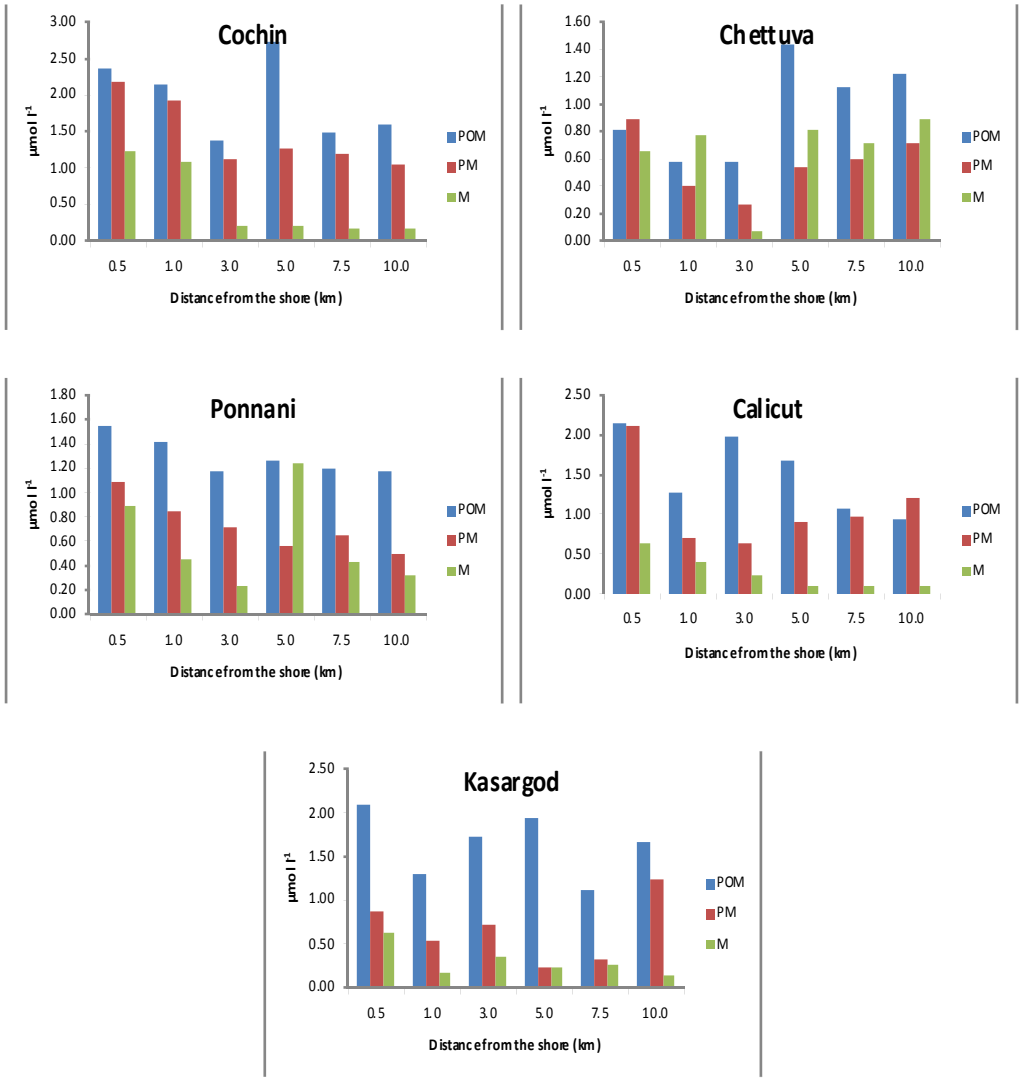


Figure 3V. Seasonal variation of Inorganic phosphate in bottom water among different transects.

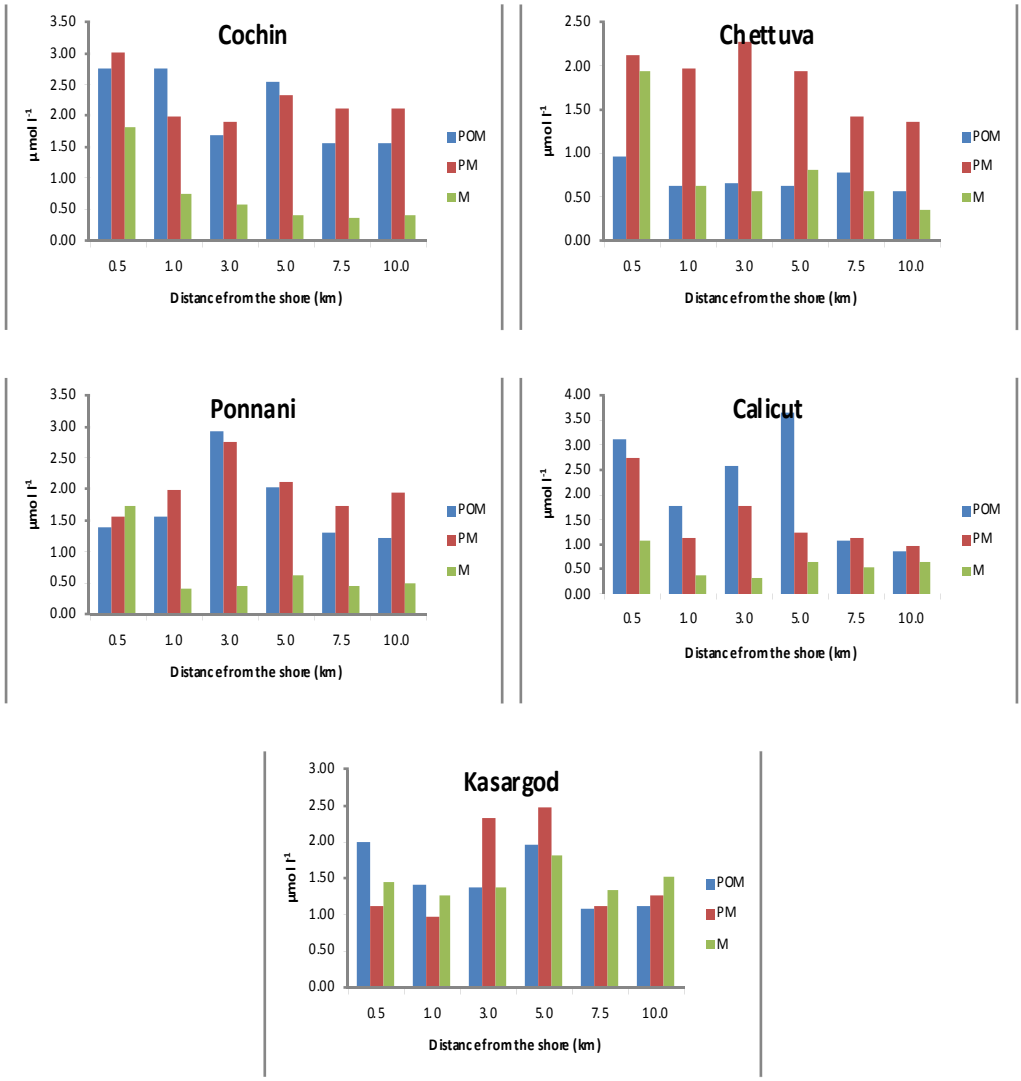


Figure 3W. Seasonal variation of Total Phosphorus in surface water among different transects.

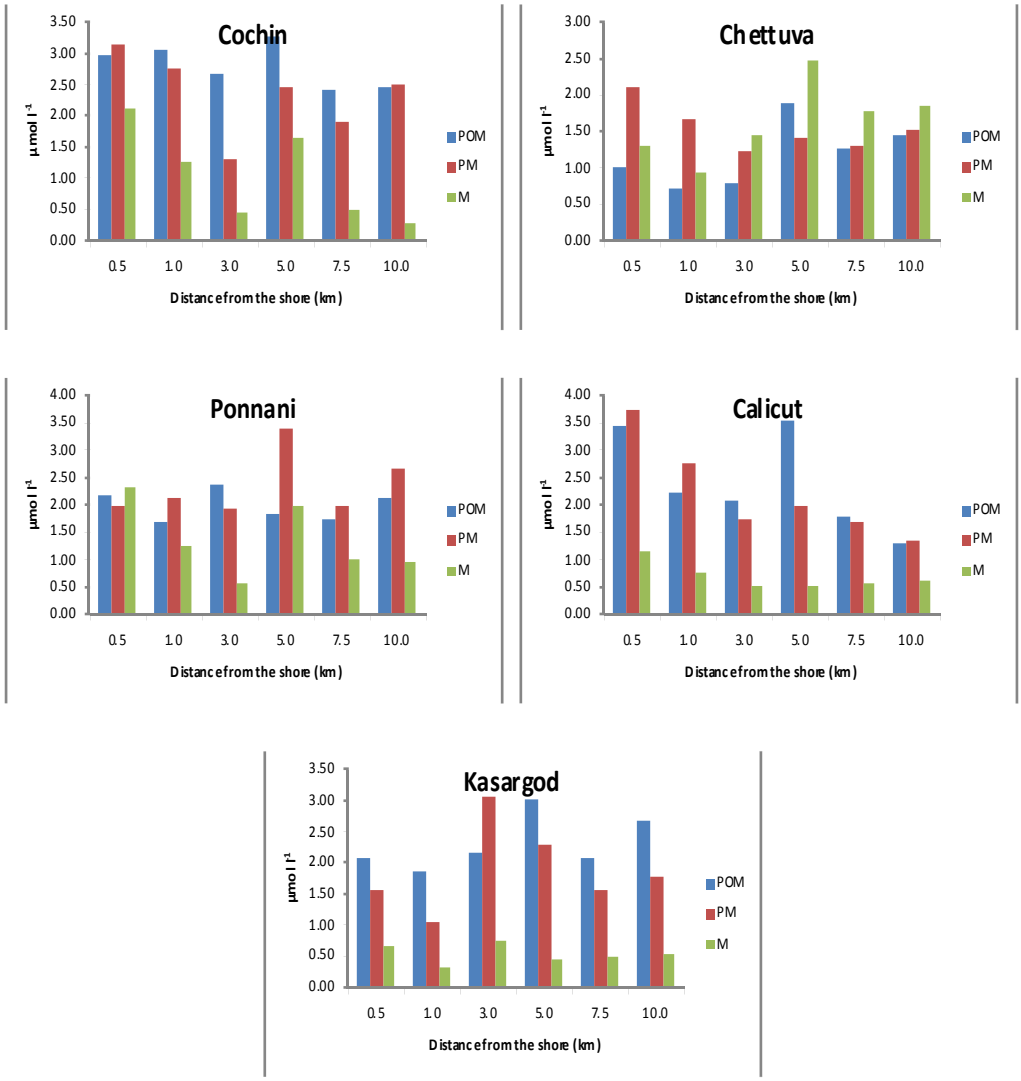


Figure 3X. Seasonal variation of Total Phosphorus in bottom water among different transects.

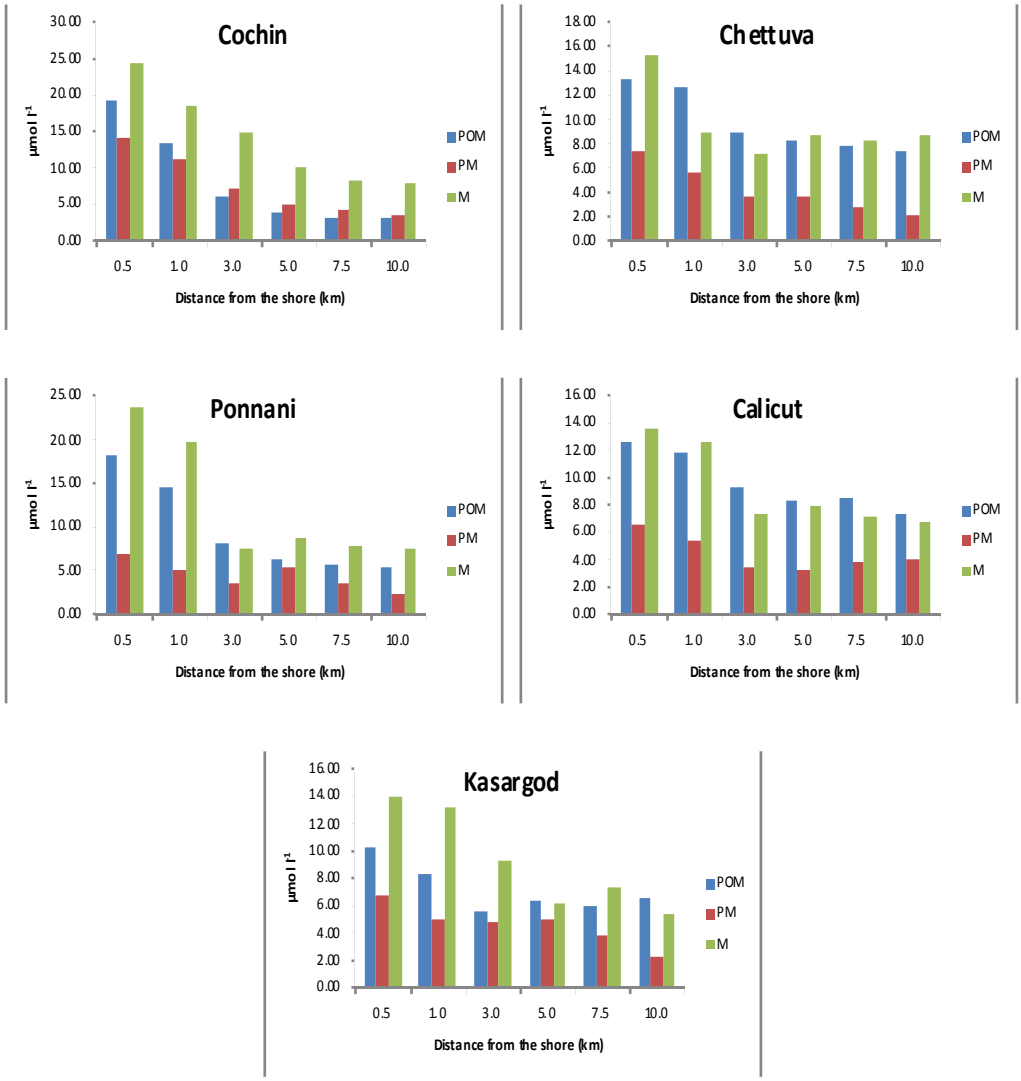


Figure 3Y. Seasonal variation of Inorganic silicate in surface water among different transects.

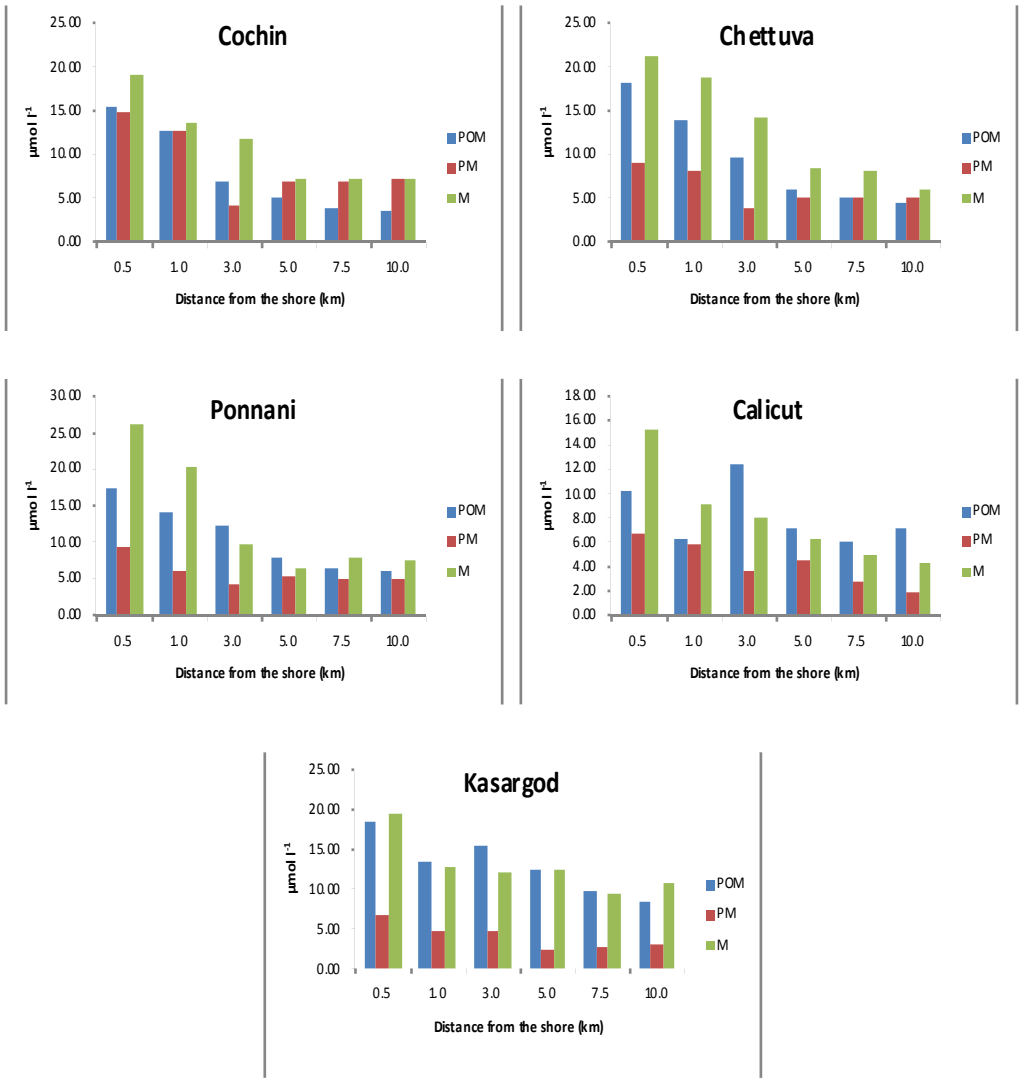


Figure 3Z. Seasonal variation of Inorganic silicate in bottom water among different transects.

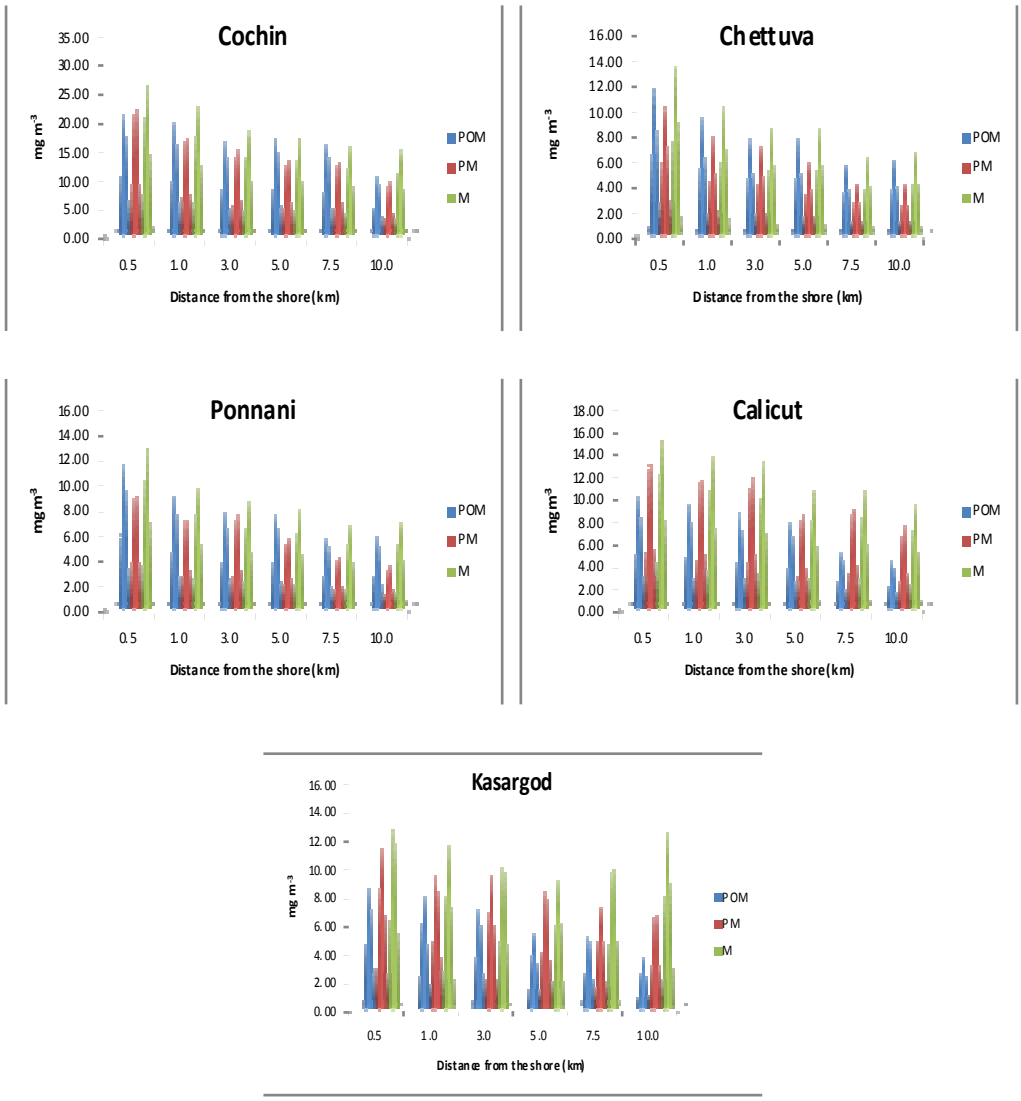


Figure 3A1. Seasonal variation of chlorophyll *a* concentration among different transects of the central and northern coast of Kerala.

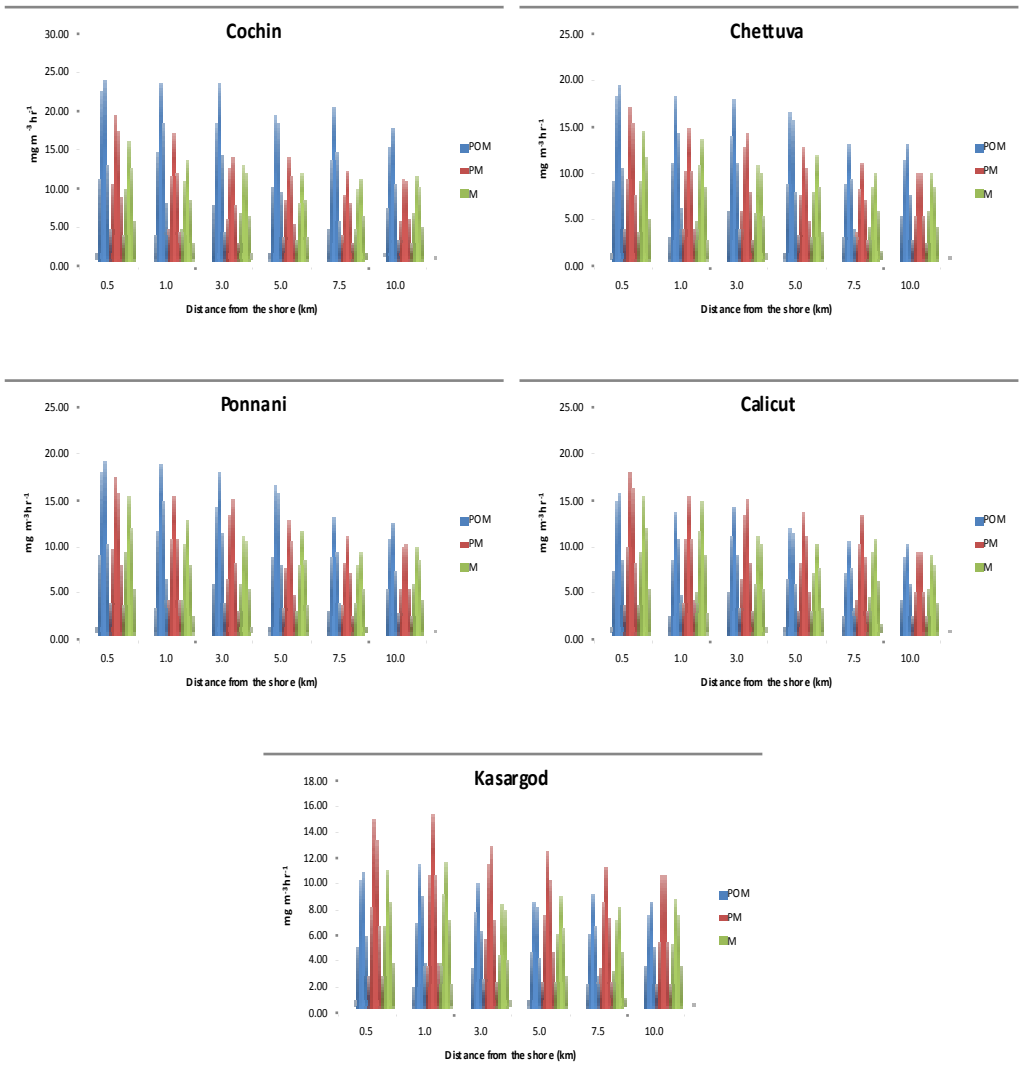


Figure 3A2. Seasonal variation of primary productivity among different transects of the central and northern coast of Kerala.

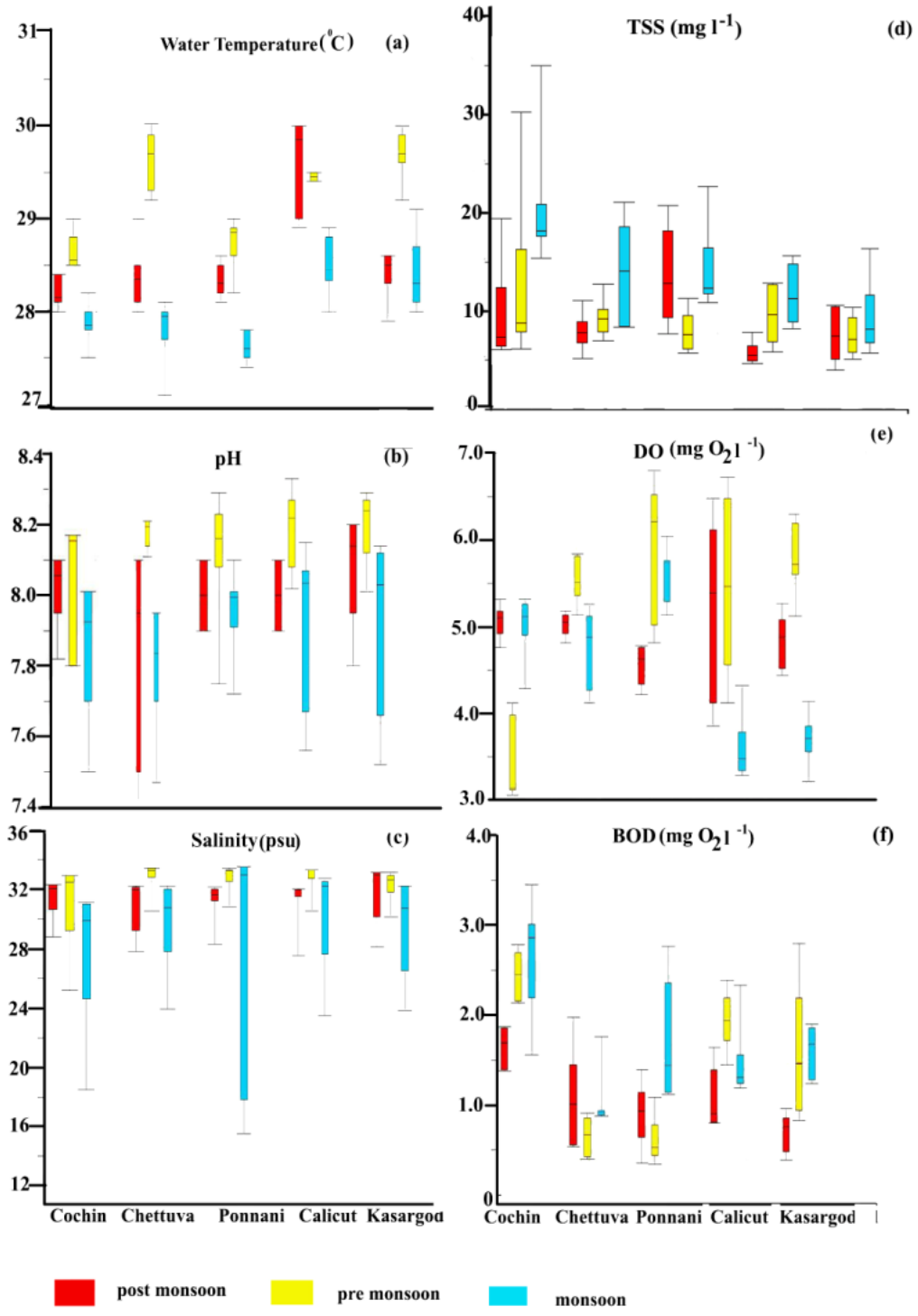


Figure 3A3. Seasonal variation of hydrographic parameters of the surface coastal water at sampling transects along the central and northern coast of Kerala shown through box-whisker plot.

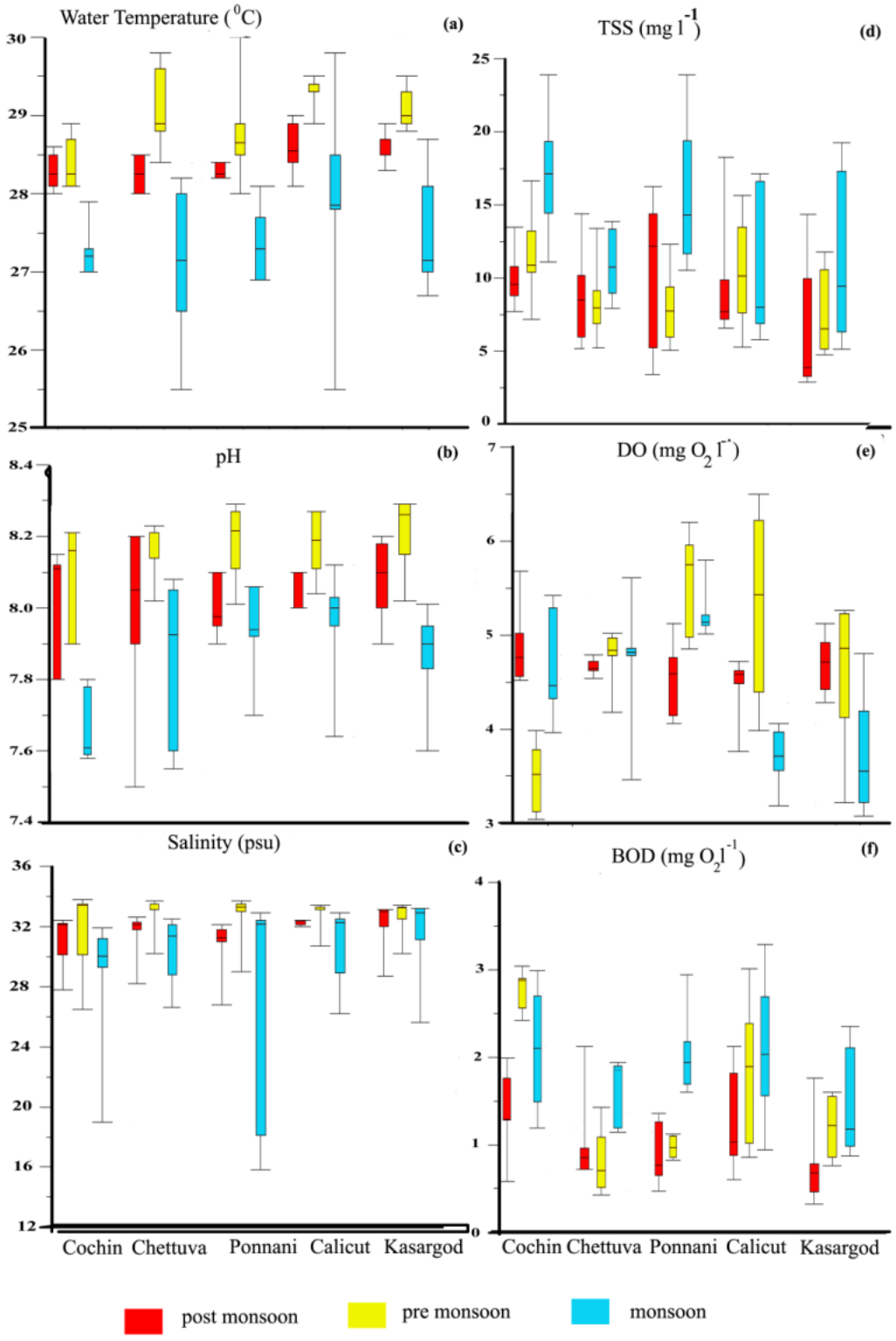


Figure 3A4. Seasonal variation of hydrographic parameters of the bottom water at sampling transects along the central and northern coast of Kerala shown through box-whisker plot.

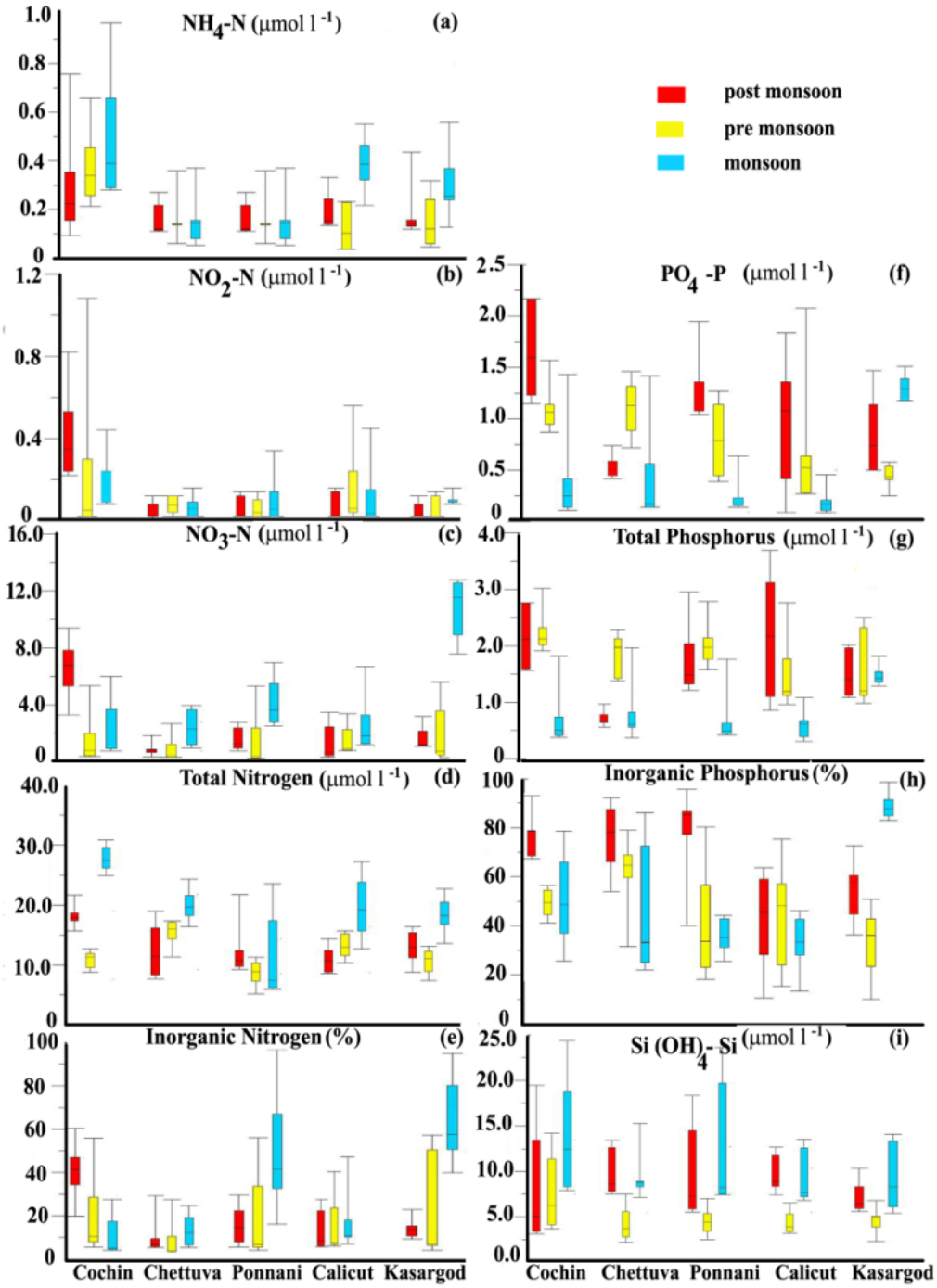


Figure 3A5. Seasonal variation of nutrients of the surface coastal water at sampling transects along the central and northern coast of Kerala shown through box-whisker plot.

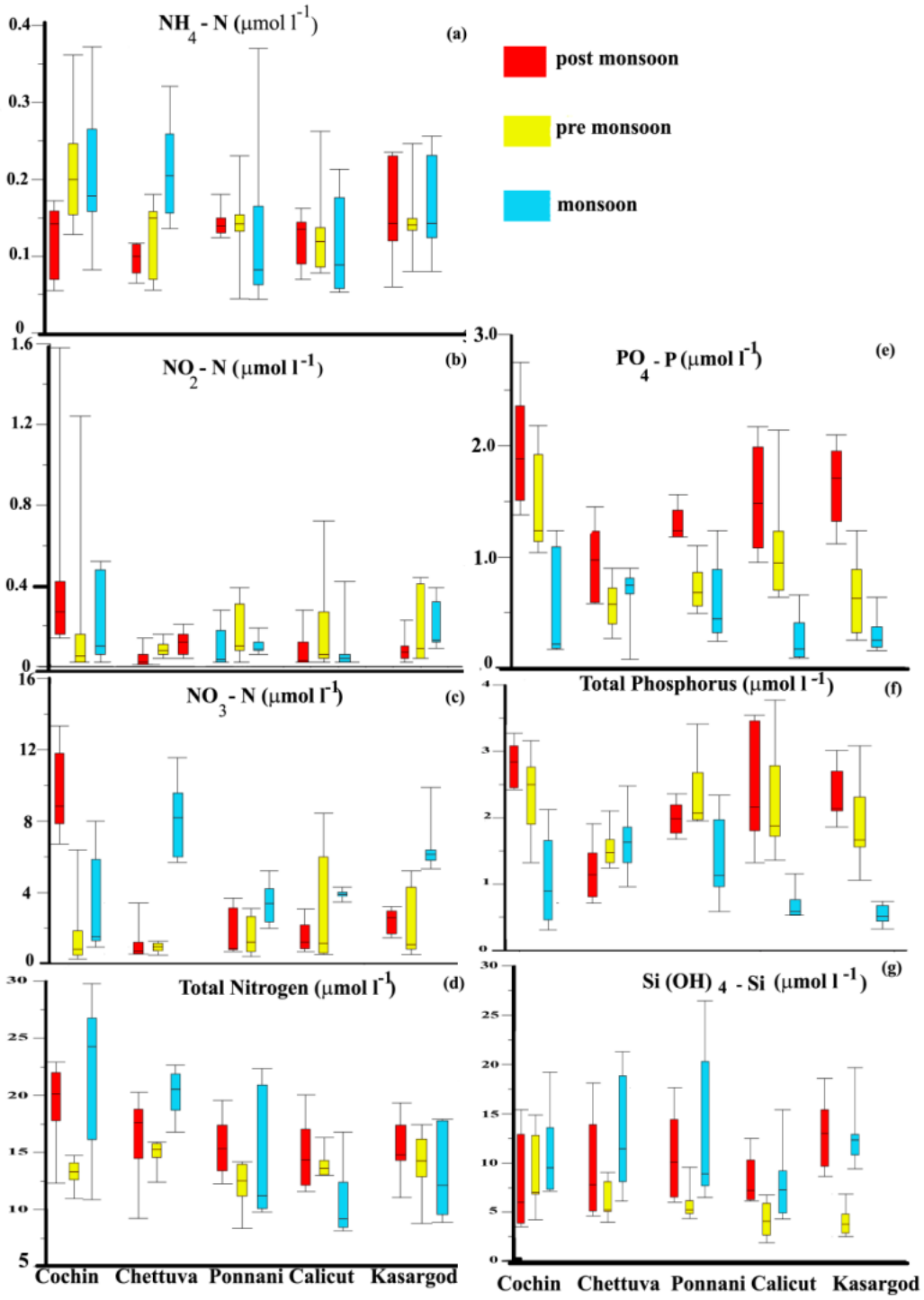


Figure 3A6. Seasonal variation of nutrients of the bottom water at sampling transects along the central and northern coast of Kerala shown through box-whisker plot.

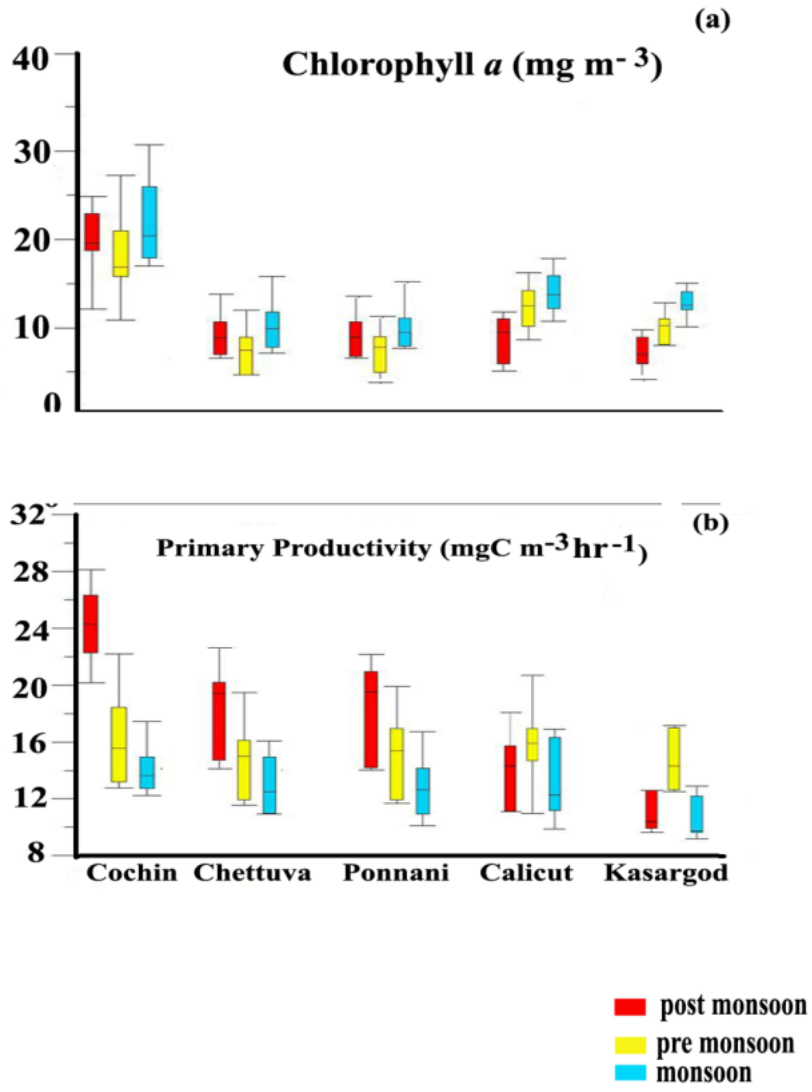
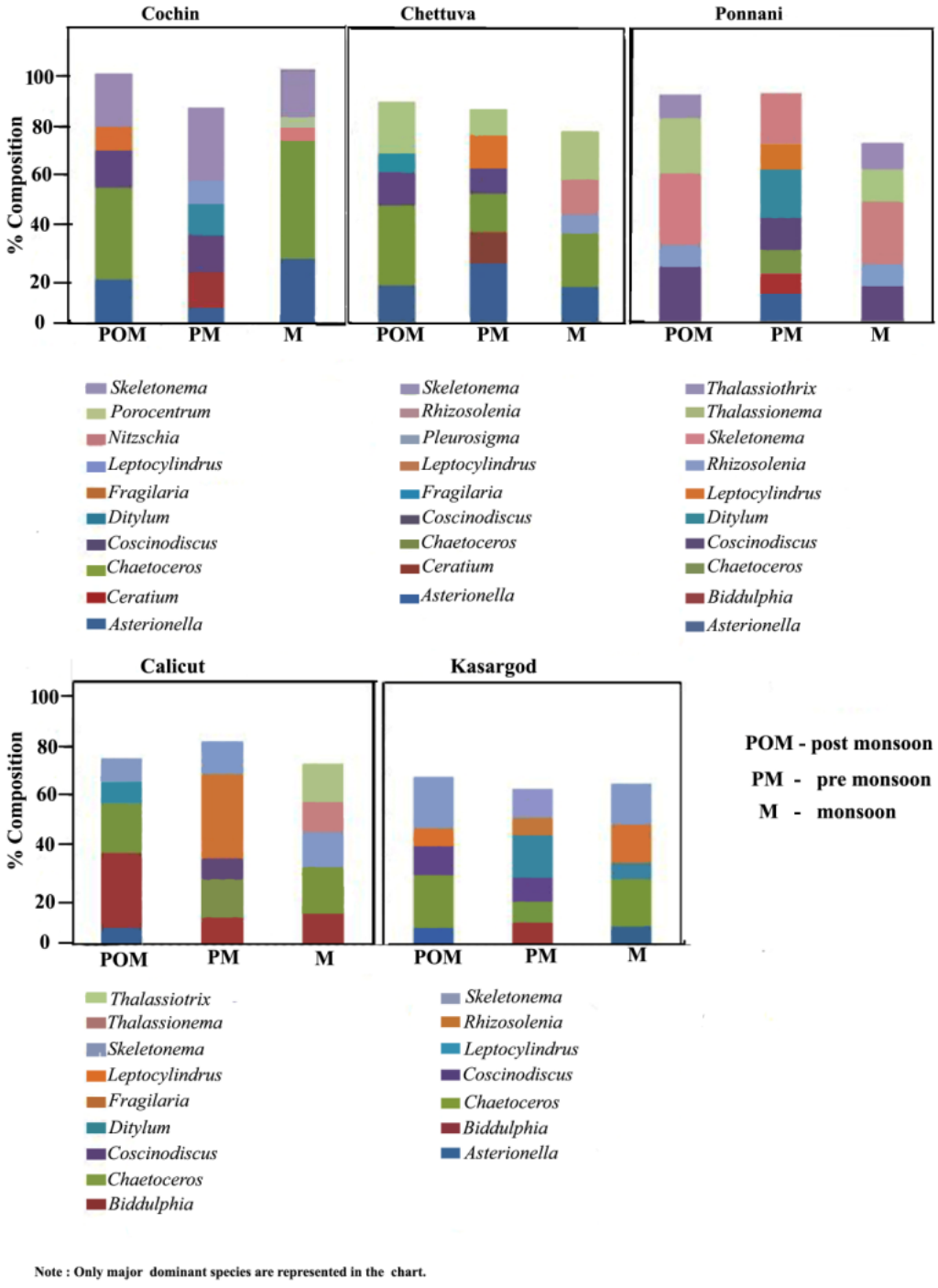


Figure 3A7. Seasonal variation of biological characteristics of the surface coastal water at sampling transects along the central and northern coast of Kerala shown through box-whisker plot.



Note : Only major dominant species are represented in the chart.

Figure 3A8. Seasonal distribution of major phytoplankton in the surface coastal water along the central and northern coast of Kerala.

3.3 Discussion

Physico chemical characteristics

The physico- chemical variables of the present study area are subjected to wide spatial temporal variation. Rainfall is the most important cyclic phenomenon in tropical countries as it brings important changes in the hydrographical characteristics of the marine environments (Damotharan *et al.*, 2010). The average surface water temperature of coastal stations varied between 28.20 - 29.60, 28.65 - 29.68 and 27.60 - 28.50 ^{0}C during post monsoon, pre monsoon and monsoon respectively. A slight increase in surface water temperature was observed moving towards northward coast. Generally, surface water temperature is influenced by the intensity of solar radiation, evaporation, fresh water influx and cooling and mix up with ebb and flow from adjoining neritic waters. Temperature of the surface water followed seasonal changes at different regions of the present study. An increase in water temperature during pre monsoon and decrease in monsoon season was observed, except at Kasargod transect. In response to the rising of atmospheric temperature in pre monsoon (27.00 – 30.67^{0}C) an increase in sea water temperature could have occurred and decrease in monsoon, could be due to the minimum atmospheric temperature (26.15 – 30. 25^{0}C) and increased influx of fresh water, precipitation and upwelling phenomenon predominant in the study area during southwest monsoon (Das *et al.*, 1997; Govindasamy *et al.*, 2000; Hanninen *et al.*, 2000). The average bottom water temperature of coastal stations varied between 28.28 – 28.58, 28.38 – 29.45, 27.08 – 27.88 ^{0}C during post monsoon, pre monsoon and monsoon respectively. As a result of mixing and the shallow nature of the water body, bottom water temperature showed similar changes as that of the overlying surface water. However, a small variation between the surface and bottom layer was conspicuous in monsoon due to stratification of the water column. Regional (between transects) distribution of water temperature indicated very small variation between transects due to the discrepancy in atmospheric temperature at each transect.

pH is an important hydrochemical feature indicating the level of dissolved carbon dioxide in water which in turn can reflect phytoplankton activity and DO level in the sea (Skirrow, 1975). The pH distribution exhibited significant seasonal and spatial variation. Spatially pH followed seasonal fluctuations between high in pre monsoon and low in monsoon at all stations. The average surface values ranged from 7.83 - 8.07, 8.04 - 8.20, 7.79 - 7.96 and bottom values ranged between 7.98 – 8.08, 8.09 – 8.21, 7.66 – 7.96 during post monsoon, pre monsoon and monsoon respectively. Generally, the average pH values of surface and bottom water among seasons exhibited smaller variations due to the shallowness of the study area and turbulence of the water column. In addition the extensive buffering capacity of the sea water causes the change of pH within only a very narrow limit (Riley and Chester, 1971). The slightly lower pH recorded in the monsoon may be due to the biochemical decomposition of organic matter brought to these shallow coastal waters by monsoonal flushing of land runoff, fresh water mixing brought by rivers and increased precipitation. Very limited regional variations in pH were observed during the period of study.

Salinity plays an important role in sustaining aquatic life. Average surface salinity fluctuated seasonally, between 30.87 – 31.72, 30.85 -32.77, 27.48 – 30.12 psu and in bottom water between 30.70-32.27, 31.78 – 32.92, 27.25 – 31.48 psu during post monsoon, pre monsoon and monsoon respectively at all stations. The generally high values of salinity noted in the study region during pre monsoon may be due to less river inflow, high evaporation; movement of water from offshore as reported by earlier workers in other areas (Gowda *et al.*, 2001; Rajasegar, 2003). In monsoon, the reduced salinity is due to the heavy influx of river runoff and precipitation, when compared to other seasons, as reported by Mitra *et al.*, (1990) in the Bay of Bengal and coastal waters of Kalpakkam (Satpathy *et al.*, 1996). Salinity of the coastal waters in the study region showed its maximum value in the bottom waters as compared to the surface due to density gradient. Noticeable variations were observed in salinity

between transects due to the inflow of surface waters of lower salinity brought by rivers finally mixing with the coastal water.

Dissolved oxygen values of surface waters exhibited significant spatial and seasonal variations. An average concentration for surface water varied between 4.56 – 5.23, 5.53 – 5.93, 3.62 – 5.62 mg O_2 l^{-1} and in bottom waters it was in the range 4.46 – 4.88, 3.49 – 5.33, 3.70- 5.23 mg O_2 l^{-1} during post monsoon, pre monsoon and monsoon respectively. In aquatic systems, oxygenation is the result of an imbalance between the process of photosynthesis, degradation of organic matter and reaeration (Gamier *et al.*, 2000). In this study, DO recorded higher values in surface waters and decreased with depth. Similar observations were also reported by Panigrahy *et al.*, (1999); Shriadah and Saif (1999) in their study on coastal waters. This observation agrees with the concept of high concentration of DO in the surface water due to the effect of photosynthetic activities of the phytoplankton, air -sea exchange of gases and higher solubility of oxygen in low saline water. The low values of dissolved oxygen in bottom water are due to high salinity water and consumption of oxygen due to decomposition of organic matter and respiration of bottom fauna (Mitra *et al.*, 1990; Das *et al.*, 1997).

In general, the distribution of DO in the study area displayed high average values in surface, signifying well oxygenated waters, however there were slight fluctuations at certain stations especially at Calicut and Kasargod region during monsoon and at Cochin during pre monsoon. At Cochin the average concentration during pre monsoon was 3.43 mg O_2 l^{-1}. The amount of oxygen dissolved is governed by a number of factors such as temperature, organic matter degradation, primary productivity, respiration etc. DO maximum in the surface layer especially during the pre monsoon period (February–May) was reported earlier (Sen Gupta *et al.*, 1976; Shirodkar and Jayakumar, 1990). The intensity of incident solar radiation is very high during this period, which causes the maximum primary productivity to occur a few meters below the sea surface together with the high vertical stability, which result in the observed oxygen maximum. With the exception of Cochin transect all other transect exhibited

maximum DO. Low DO noticed at Cochin stations may be due to the excessive phytoplankton production which should have augmented the concentration of organic matter in the water column, excess inflow of organic rich sewage from the urban agglomeration and thereby consuming the oxygen for its degradation. During the monsoon season low DO value both in surface and bottom water was reflected in the coastal waters at Calicut and Kasargod, this may be due to the upwelling phenomenon. This region along the southwest coast of India is one of the major upwelling systems of the world (Bakun *et al.*, 1998). It was established that upwelling takes place along this coast during monsoon (May to September) thus ensuing productivity and low DO (Krishnakumar and Bhat, 2008).

The average magnitude of BOD values in the study area was less than 3.0 mg O_2 l^{-1} in most of the stations during all season. Waters with BOD less than 3.0 mg O_2 l^{-1} are known to have received no significant pollution discharges (Martin, 1970). Albeit, these transects receives large influx of domestic effluents, it was not reflected in its BOD values. A plausible explanation for such low BOD values can be due to the strong dispersive effect of coastal water; the degradable organic matter may get diluted. Vertical distribution of BOD, showed more or less similar values due to shallowness of the area and turbulence of the water column. The seasonal average values in monsoon are comparatively higher than non monsoon season; this is could mainly be due to the increased influx of organic wastes from land into the coastal water brought by monsoonal flushing.

An average values of TSS for surface water in the study area varied between 5.70 – 13.60, 7.47 – 13.02, 9.48 – 20.86 mg l^{-1} and in bottom waters it was in the range of 6.38 – 10.61, 7.56 – 11.54, 10.41– 17.18 mg l^{-1} during post monsoon, pre monsoon and monsoon respectively. The regional variations did not show wide variation between transects and indicated the presence of relatively clear water or less TSS towards offshore. The amount of suspended matter is mainly controlled by pollution, prevailing wind, influx of silt born surface runoff, resuspension of surficial sediments by stirring action and high density of phytoplanktons (Cloern, 1987). These factors can indirectly act as one

of the key factors for productivity potential of coastal waters by regulating light penetration (Qasim *et al.*, 1968; Kalimurthy, 1973). Generally, TSS was higher in monsoon, presumed to be due to the increased inflow of terrestrial inputs brought by monsoonal flushing in which rivers acts as vectors in bringing suspended particles into coastal water. Vertical distribution generally showed high TSS value in surface layer compared to bottom layer could be due to high plankton density in surface and high levels of sewage pollution. Similar observations were reported for the coastal waters of Arabian Gulf (Shriadah and Saif, 1999).

Nutrient Stoichiometry

Within phytoplankton, bioelements such as carbon, nitrogen, and phosphorus are present in a proportion, that is, if not costant at least bonded. The elemental composition of marine phytoplankton is remarkably stable at a molar ratio of about 106:16:1:16 for carbon, nitrogen, phosphorus and silicate, respectively (Redfield *et al.*, 1963). During photosynthesis, phytoplankton takes up CO_2, water and nutrients (i.e nitrite, nitrate, ammonium, phosphate) in such proportions that the resulting organic matter follows the Redfield ratio. Wide departures of concentration ratios of these elements from their ratios of uptake by phytoplankton results in one of the elements eventually becoming limiting, affecting biogeochemical fluxes and ecosystem functioning. An obvious case of such a departure in coastal waters is differential supply of these elements from land.

Dissolved inorganic nitrogen concentrations did not show much spatial variation, although seasonal variation was observed with increased concentration during monsoon at all transects except Cochin region which showed an increase in post monsoon and low concentration in pre monsoon. The concentration of DIN was quiet low; this is evident from the average values of NH_4 - N, which ranged from 0.16– 0.30, 0.13- 0.38, 0.16 – 0.50 µmol l^{-1} in surface water and 0.10 – 0.16, 0.13 – 0.22 and 0.11 – 0.21 µmol l^{-1} in bottom water in post monsoon, pre monsoon and monsoon respectively. The NO_2-N concentrations were less than 0.5 µmol l^{-1} in surface and bottom water and NO_3-N concentrations showed a variation of 0.89 – 6.55, 0.90 – 1.89, 2.20 –

10.80 µmol l^{-1} in surface water and 1.18 – 9.55, 0.92 – 2.97, 3.18 – 8.20 µmol l^{-1} in bottom water during post monsoon, pre monsoon and monsoon respectively. The recorded high value of dissolved nitrogen values in monsoon season could be mainly due to the organic materials received from the catchment areas during ebb tide (Das *et al.*, 1997). The recorded low values in pre monsoon may be due to its utilization by phytoplankton as evidenced by high photosynthetic activity and also due to the neritic water dominance, which contained only negligible amount of nitrogenous compounds (Rajashree and Panigrahy, 1996; Das *et al.*, 1997; Govindasamy *et al.*, 2000). Vertical distribution of ammonia in the water column showed increased concentration in surface water compared to bottom water. Ammonia, the chief excretory product of the marine invertebrates, is well known as a nutrient, which is preferred over nitrate by the phytoplankton community in certain environmental conditions. The aforesaid two factors significantly affect the concentration of ammonia (Olson, 1980; Gilbert *et al.*, 1982) in the marine environment. This increased concentration of ammonia in monsoon could be due to sewage pollution brought by riverine influx. The increased concentration of ammonia in surface layer compared to bottom layer could be due to the release of ammonia as the excretory product by marine biota inhabiting the euphotic layer. A comparison between concentrations of ammonia in the nearshore and offshore indicated a general tendency for ammonia to decrease in a sea ward direction due to dilution. A wide regional difference in values was not noticed among the transects, however, high concentration was noticed at Cochin due to the increased quantities of wastes both domestic and industrial from several outlets impinging in to its coastal water.

In general, nitrite – N did not show any broad variation, the average values were more or less similar at the surface and bottom waters. Nitrite- N is the intermediate oxidation state between ammonia and nitrate, and as such it can appear as a transient species by the oxidation of ammonia or by the reduction of nitrate-N. Nitrite- N is also released into the water as an extracellular product of the planktonic organisms (Santschi *et al.*, 1990, Chandran and Ramamurthy, 1984). Regional variations, displayed high concentration at Cochin coastal

waters compared to other transects, could be due to human interference through dumping of untreated domestic sewage from urban sources. The highest nitrite-N value could also be as a result of the oxidation of organic materials emanating from these domestic waste waters with a concomitant high concentrations of BOD (1.66 to 2.65 mg O_2 l^{-1}) compared to other transects.

Variations in nitrate-N and its reduced inorganic compounds are predominantly the results of biologically activated reactions. Quick assimilation by phytoplankton and enhancement by surface runoff results in large-scale spatio temporal variation of nitrate-N in coastal milieu (Qasim, 1977; De Souza, 1983; Zepp, 1997). The average concentrations of nitrate-N showed generally higher values at the surface compared to bottom waters due to nitrification processes (Riley and Chester, 1971). Low concentration in pre monsoon could be due to intense consumption of nitrate during growth period by phytoplanktons which corroborates observations of Prasannakumar *et al.*, 2002 along the southwest coast of India. In monsoon, increased concentration of nitrate-N could be due to nitrogenous waste brought by riverine inputs and the occurrence of extensive upwelling in the area during southwest monsoon which carries sub-surface nutrient rich waters to surface. Similar temporal pattern was observed in the lagoon waters of Brazil, Italy and southwest coast of India (Da Cunha and Wasserman, 2003; Sfriso *et al.*, 1987; Rajagopalan *et al.*, 1992). The high concentration of nitrate-N at Kasargod in monsoon could be due to increased inflow of nitrogenous compounds in to the coastal water, through rivers acting as vectors from a variety of sources, including domestic and fertilizer laden agriculture run off reinforced with upwelling. The concentration of nitrate-N in surface and bottom water at Cochin was high in post monsoon compared to other transects. This increase in nitrate-N could be due to variety of sources including riverine, domestic, industrial, agriculture and urban agglomeration and its subsequent regeneration from organic material in the bottom water. Human activities have markedly altered the earth's nitrogen cycle by doubling the natural rate of nitrogen fixation and causing atmospheric

nitrogen decomposition to increase from three fold to more than tenfold compared to pre industrial time (Kronvang *et al.*, 1993; Bonsdorff *et al.*, 1997).

Based on the average values, the concentrations of dissolved inorganic nitrogen forms followed the order NO_3-N > NH_4-N > NO_2-N. The combined inorganic nitrogen which is added to the coastal waters by terrestrial drainage and river water systems contain substantially greater amounts of combined nitrogen than that occur in open sea water. Biological processes result in interconversion of various forms of nitrogen. NO_3–N is the dominant form of combined inorganic nitrogen in well-oxygenated waters (Gopinath *et al.*, 2002).

The levels of TN displayed marked variation and its concentration in surface water varied from 10.93 – 18.20 , 8.62 –15.37, 11.34 –27.74 µmol l^{-1} and in bottom water it varied from 14.92 –19.21,12.13 – 14.88 and 10.70 – 22.01 µmol l^{-1} in post monsoon, pre monsoon and monsoon respectively. Based on the mean values during each season, dissolved inorganic nitrogen (DIN) accounted for less than 20% of TN in surface waters at all transects (Fig. 3A5 (e)). However, exception was noticed at Cochin, which accounted for nearly 40.70 % during post monsoon, 49.20% at Ponnani during pre monsoon, 22.03% and 63.46% at Kasargod during pre monsoon and monsoon respectively. An average DIN values accounted for less than 30% in bottom waters except at Cochin in post monsoon and at Chettuva, Calicut and Kasargod in monsoon. The large difference between TN and DIN concentrations suggest that nitrogen is found in the coastal waters mostly in organic forms. This result is in agreement with the general view of microbial food web and phytoplankton dynamics, in which NH_4-N, NO_2-N and NO_3-N are rapidly processed by phytoplankton and other microbial components. Meanwhile, the organic nitrogen is assimilated by aquatic organisms in a much slower rate (Riley and Chester, 1971). In the eutrophic Bay of Koper (North Adriatic), the relative composition of total nitrogen comprised of 11.3% for particulate, 68.8% for dissolved organic and 20.1% for the inorganic forms (Faganeli, 1983). DIN levels obtained in this study are remarkably similar than those mentioned above, and suggest limited effect of land based sources on the coastal waters.

As per the above observations a limited effect of land based sources on the coastal water cannot be established as pollution problems following the release of untreated domestic wastes, urban drainage and agricultural effluents are well documented in the investigated area. It is possible that denitrifying bacteria are present in these shallow environments utilizing the nitrates for their energy requirement and progressively reduced to gaseous nitrogen. Recent studies suggested that coastal system of the Arabian Sea (west coast of India) have undergone an ecological change due to enhanced nutrient loading from land in which low concentration of nitrite-N indicates net production of N_2O by denitrifiers (Naqvi *et al.*, 2006). This study endorses with the above findings, as the concentration of nitrite was noted low in the present area of investigation which comes under coastal system of the Arabian Sea.

On tracing the distributional characteristics of dissolved reactive phosphate the average surface concentration varied from 0.85 – 1.65, 0.44 – 1.11, 0.43 – 1.31 µmol l^{-1} and average bottom concentration varied in the range 0 .97 – 1.65, 0.57 – 1.04, 0.17 – 0.66 µmol l^{-1} in post monsoon, pre monsoon and monsoon respectively. The main source of inorganic phosphate in to the coastal water column results from weathering of rocks, anthropogenic inputs of fertilizers (superphosphate), domestic sewage and detergents (alkyl phosphates) which are carried by many sources. In surface and bottom waters, inorganic phosphate level showed wide variation in monsoon compared to other season in which similar levels were observed in both the layers. The difference in monsoon could be due to the stratification of the water column due to low dense water forming a thin lens over the high dense water thus averting the mixing of water. The concentration was also high in post monsoon and lower in monsoon season in all transects except at Kasargod which showed high values in both seasons. Even though the study area comes under extensive upwelling during southwest monsoon, it is not reflected in the phosphate concentration.The concentrations of dissolved phosphate reported in this study more or less coincide with those of the earlier studies conducted by several workers (Shirodkar and Jayakumar, 1990; Anand and Jayaraman, 1972; Sastry and

D'Souza, 1972) in the nearby regions of the Arabian Sea. In all transects PO_4-P concentrations were high in surface waters, consequently N: P ratios were low, reaching an average of less than 10 at most of transects. This tends to suggest nitrogen is the limiting nutrient for phytoplankton growth in these coastal waters. High N:P ratios was spotted at Ponnani and Calicut during the monsoon season suggesting that phosphate could be the limiting nutrient for phytoplankton growth during this season at this transect. Studies have shown that PO_4-P can also be a limiting nutrient in coastal areas associated with periods of high river runoff with high N: P loading ratios (Harrison *et al.*, 1990). Low PO_4-P contents could also be related mostly to their sorption and deposition upon to the suspended particles conveyed to the coastal waters from the surrounding mainland by monsoonal flushing. Suzumura *et al.*, (2000) reported the effect of composition and physicochemical characteristics of natural particles on phosphate adsorption-desorption processes under various aquatic environment. Mamdouh (2003) pointed out that, generally, the typical concentrations of PO_4-P for eutrophic coastal waters are above 0.15 µmol l^{-1} and for highly eutrophic system will be beyond 0.30 µmol l^{-1}. Further, the theoretical half saturation constant (Ks) for uptake of PO4 – P is 0.2 µmol l^{-1} (Gallegos and Jordon, 1997). In this study, results imply that the high PO_4 – P concentrations reflected that there were large excess of PO_4-P, most likely from recycling of P-rich marine sediments. The monsoon rainfall enhance river run off with high N: P loading ratios combined with the sorption of phosphorus by suspended particles, thus fast removal it to the sediments is causing PO_4 – P limitation in the coastal waters at Ponnani and Calicut during monsoon. This could also be the reason for low values encountered in monsoon at all transects except at Kasargod, where it might be due to some point discharges. Moreover, the weatherings of rocks soluble alkali metal phosphate, the bulk of which are carried into the estuaries are also responsible for the variation of inorganic phosphates in coastal waters (Gowda *et al.*, 2001).

The spatial and temporal distribution pattern of TP displayed a large variability during the investigation period. In surface water it varied from

0.71 – 2.18, 1.50 -2.25, 0.62 -1.48 µmol l^{-1} and in bottom water it varied in the range 1.20 –2.82, 1.86 –2.36 and 0.54 –1.35 µmol l^{-1}during post monsoon, pre monsoon and monsoon respectively. Based on the seasonal values, PO_4 – P constituted > 30 % of TP (Fig. 3A5(h)), and large difference between TP and DIP concentrations was not discerned implying that phosphate, in the coastal waters is principally accounted by inorganic forms. The contribution of inorganic phosphorus percentage towards TP reveals short pulses of high and low phosphorus among different seasons. This raises the possibility of organic phosphorus being decomposed into inorganic forms at deeper layers (PO_4 – P constituted 33.27 % - 80.58% of TP) of the study area where the water remains stagnant which gradually moves up to the surface. These data also suggested that the coastal waters are moderately polluted. Such conclusion is consistent with indications provided by Nalewajko and Lean (1980) who pointed out that in moderately polluted coastal waters, the relative importance of phosphorus forms is: 28.5– 98% for particulate, 1.2 – 4% for colloidal, 0.1– 22% for reactive phosphate and 0.1– 6% for dissolved organic P. The respective levels of TP and TN in oligotrophic waters are 0.27 and 47.2 µmol l^{-1}, whereas in mesotrophic waters it reaches 0.89 and 53.8 µmol l^{-1} and in eutrophic seawaters its value are 2.81 and 133.9 µmol l^{-1} respectively (Mamdouh, 2003). These levels when compared with those reported in this study indicate that coastal waters are within the mesotrophic to eutrophic conditions in terms of TP. Considering TN it falls under oligotrophic waters. This is caused due to increased denitrification happening in the coastal waters which is discussed earlier. A wide regional difference in TP values was not noticed among the transects.

The distribution pattern of $Si(OH)_4$-Si concentrations displayed only small spatial and seasonal variations. The study revealed the average surface concentration of SiO_4-Si in the range 7.19 – 9.80, 4.25 – 7.63, and 9.26 – 14.06 µmol l^{-1}, and in bottom water 7.96 – 13.04, 4.11–8.79, 8.05 – 13.11 µmol l^{-1} in post monsoon, pre monsoon and monsoon respectively. The seasonal range was found to follow the order monsoon > post monsoon > pre monsoon. Continental weathering is the primary source for the usually high Si levels in river discharges

(Falkowski *et al.*, 1998). Silicate concentration in coastal waters is also influenced by several factors, more importantly the proportional physical mixing of sea water with fresh water (Purushothaman and Venugopalan, 1972), adsorption of reactive silicate into suspended sedimentary particles (Lal, 1978) and biological removal by phytoplankton especially by diatoms and silicoflagellates (Rao, 1969; Aston, 1980; Liss and Spencer, 1970). In this study seasonal variation indicated higher concentration during monsoon could be due to increased precipitation, land drainage and river discharge from the SW monsoon carrying silicate leached out from rocks and lowest in pre monsoon when the river discharge is at its lowest (Rajasegar, 2003; Govindasamy and Kannan, 1996, Ramakrishnan, 1999). Silicate concentration in the bottom layer remained high except in monsoon due to stratification of the water column caused by increased inflow of fresh water which forms a thin lens over high dense saline layer. The supply of dissolved silica from land usually makes large cell diatoms generally the most dominant phytoplankton group. This results in (a) shorter food chains, with only three trophic levels in the upwelling zones compared to up to six trophic levels in the oligotrophic open ocean; (b) lesser respiration of Primary Productivity and a larger amount reaching the uppermost trophic level (fish); and (c) larger downward export of carbon from the surface layer in coastal compared to open – ocean areas (Naqvi and Unnikrishnan, 2010). A wide regional difference in inorganic silicate levels was not noticed among the transects

Ratios between concentrations of major nutrients, nitrogen, phosphorus, and silicon, in surface coastal water exert a key control on plankton composition. Wide departures of concentration ratios of these elements from their ratios of uptake by phytoplankton (106C: 16N: 1P: 16 Si) result in one of the elements eventually becoming limiting, affecting biogeochemical fluxes and ecosystem functioning. An obvious cause of such departure in coastal waters is differential supply of these elements from land. Plots of the atomic Si:P against N:P ratios in the surface waters of central and northern coast of Kerala revealed nitrogen as the nutrient which is potentially limiting for phytoplankton biomass growth (Fig. 3A9). The data points in the left quadrant (N: P < 16:1) are

indicative of N (nitrogen) limitation, in the right quadrant are indicative of P (phosphorus) limitation and of Si (silicon) limitation in the lower quadrant. In this study the quadrant with the most data points is the upper left quadrant, which indicates more frequent occurrences of potential limitation of a nitrogen nutrient. A decrease in Si: N ratio below 1 leads to a functional group shift from diatoms to coccolithophores and flagellates (causing HABs) which could potentially affect for food web structure, and affecting fisheries and biogeochemical fluxes (Turner, 2002). The near shore coastal region of the investigated area has not reported any incidence of harmful algal blooms in spite of increased domestic discharges. A plausible reason can be the consistency of Si: N ratio maintaining the value greater than 1 for all seasons. In this study, phytoplankton samples examined above 50 µm centric size, diatoms were the most abundant group contributing to nearly 100% of the phytoplankton biomass. Arrigo (2005) has characterized the dominance of different algal groups based on stoichiometric ratio. If N: P ratios exceed 30 then proliferation of dinoflagellates will take place and if it descends to 10 then plankton domination will be mainly of diatoms. This characterization corroborates with the stoichiometric ratios established in this study.

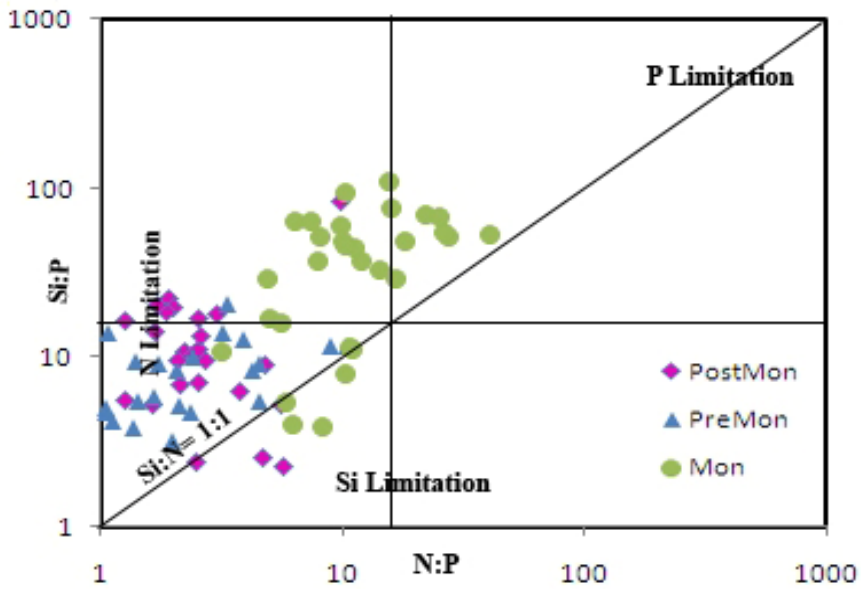


Figure 3A9. Scatter diagrams of atomic nutrient ratios for the surface water along the investigated area. N, P and Si represent dissolved inorganic nitrogen, phosphate and silicate.

Biological Characteristics

In all the stations studied, the chlorophyll concentration was found at its maximum during monsoon season. This could be due to the fresh water input, heavy rainfall and upwelling routed by southwest monsoon. However the full strength of the chlorophyll *a* concentration and productivity was observed in the shore waters which include 0.5 and 1.0 km at all transects. The strong under water currents and tidal effects engage in the drifting of the phytoplankton biomass to offshore waters making it also productive. The mean concentration of Chlorophyll *a* in surface waters varied from 7.11 – 19.62, 7.45 – 18.08, 10.12 – 22.07 mg m^{-3} and primary productivity from 10.94 – 24.25, 14.66 – 16.28, 10.57 -14.11 mgC m^{-3} hr^{-1} during post monsoon, pre monsoon and monsoon respectively along the study area. High concentrations of Chlorophyll *a* ranging from 18.08 to 22.07 mg/m^3 were observed at Cochin during the study period. Primary productivity in the region was found to be in the range of 14.11 – 24.25 mgC m^{-3} hr^{-1}. In general, biological productivity of a region is determined by three factors such as light, nutrients and primary production. At Cochin the increase in plant pigment is largely due to the river runoff and also sewage inflow rich in nutrient content from the urban agglomerations, thus enhanced productivity. Balachandran *et al.*, (1989) has pointed out the role of photosynthetic pigments as indices of biological productivity along the southwest coast of India. The maximum production of chlorophyll *a* along southwest coast was found to take place during monsoon due to upwelling after which there is a decline in its production.

Primary productivity was found high during post monsoon season at all transect, perhaps light penetration may be playing a vital part. Imeri *et al.*, (2008) in the evaluation of trophic state of a lagoon stated that the levels of Chlorophyll *a* in the oligotrophic waters are < 2.5 mg m^{-3}, whereas in mesotrophic waters reach between 2.5 – 8.0 mg m^{-3} and in eutrophic seawaters 8.0 – 25.0 mg m^{-3}. The foregoing trophic state evaluation when compared with those in this study showed that the coastal waters of Cochin are within eutrophic conditions (8.0 – 25.0 mg m^{-3}) in terms of Chlorophyll *a*

concentration, and at other transects are within mesotrophic to eutrophic conditions; which signifies high biological productivity. Most plankton variability appears to be driven by diatom blooms, thus its growth and bloom formation is commonly controlled by both N and Si input in the coastal environment. Factors such as light availability, mixing depth and water temperature can play interactive controlling roles. Diatoms are important for several reasons that with their mineralized siliceous structure they sink faster; their cells being large they support growth of larger zooplankton (produce fast sinking pellets). All these process can enhance the biological pump in which the production of carbon in surface water is exported to the sediments.

3.4 Statistical Analyses

Factor Analysis of Surface water

The varimax rotated results along with eigen values and percent of variance obtained for surface water are summarized in Table 3.6. The PCA of surface water quality extracted four factors (principal component) with eigen values >1. These composite variables captured 74.81% of the variation in the original data. Factor 1 explained 42.20% of the total variance and is associated with strong positive loadings of ammonia, silicate, Chlorophyll *a*; strong negative loading of salinity and pH. In this case ammonia, silicate and Chlorophyll *a* are correlated significantly with each other, suggesting an increase in the concentration of silicate and ammonia is enhancing the phytoplankton biomass. These variables have significant inverse correlation with salinity and pH establishing the diluting effect of river water, which acts as a local surface source of silicates and terrestrial input such as wastes from agricultural run-off, domestic sewage as the source for ammonia (Table 3.7). Ammonia is known to be the preferred form of inorganic nitrogen for phytoplankton and silicate for cells having silicified structures (eg. diatoms) indicating influence of riverine nutrients leading to photosynthesis maxima. Hence, Factor 1 can be termed as the *Riverine Factor*. The second factor showed 15.91% of the total variance and is associated with strong positive loadings of phosphate and TP. A significant correlation was observed between

the above two variables. This suggests there is increased concentration of phosphate in the coastal waters whose source can be traced to anthropogenic nutrient inputs. Factor 2 can be termed as *Phosphorus Factor*. The third factor accounts for 8.82% of the total variance and contains no loading of variables which signifies some "latent" processes other than physico-chemical and biological variables affecting the system. It is deciphered, in this case, considering the high abundance of phytoplankton biomass and one of the important factors which exacerbate the production of plankton is upwelling which takes place along this coast during the monsoon. Factor 3 can be termed as *Upwelling Factor*. Factor 4 accounts for 7.88% of the total variance and contains independent strong positive loading of Dissolved Oxygen. The DO condition can correctly characterize waste loads, natural factors such as degree of stratification, water temperature and circulation patterns and finally anthropogenic factors (such as nutrient loading) can also contribute to its event. It is presumed that strong seasonal currents, high photosynthetic activity and winds keeping the coastal water well aerated. Factor 4 can be termed as *Aeration factor.*

Table 3.6 Varimax factor analysis using PCA and identified principal components of the surface coastal waters along central and northern coast of Kerala.

	PC1	PC2	PC3	PC4
NH_4-N	0.832	0.132	0.107	-
NO_2-N	0.599	0.432	-	0.222
NO_3-N	0.582	0.211	-	-0.48
TN	0.521	-0.33	0.403	-
PO_4-P	0.316	0.817	-0.121	-0.268
TP	-	0.896	-0.105	-
$Si(OH)_4$-Si	0.833	-0.186	-0.354	-
WaterTemperature	-0.503	0.496	-	0.382
TSS	-0.203	0.256	0.476	-
Salinity	-0.828	0.133	0.336	-0.13
pH	-0.765	0.207	0.405	0.14
DO	-0.423	-	-0.444	0.601
BOD	0.578	-	0.554	0.28
Chlorophyll *a*	0.846	0.167	0.319	0.208
Eigen	5.91	2.23	1.23	1.1
%Variance	42.2	15.91	8.82	7.88
%Cumulative Variance	42.2	58.11	66.93	74.81

Table 3.7 Correlation matrix among the hydrographic – nutrient – biological parameters of the surface waters along the central and northern coast of Kerala.

	NH_4-N	NO_2-N	NO_3-N	TN	PO_4-P	TP	SiO_4-Si	Water Temperature .	Salinity	pH	DO	BOD	Chlorophyll *a*
NH_4-N	1												
NO_2-N	.457**	1											
NO_3-N	.434**	.393**	1										
TN	.394**	-	.221*	1									
PO_4-P	.290**	.428**	.421**	-	1								
TP	-	.310**	-	-.257*	.740**	1							
$Si(OH)_4$-Si	.649**	.321**	.387**	.328**	-	-	1						
Water Temperature	-.226*	-	-.279**	-.390**	-	.354**	-.449**	1					
Salinity	-.616**	-.411**	-.435**	-.358**	-	-	-.857**	.388**	1				
pH	-.552**	-.319**	-.431**	-.275**	-	-	-.769**	.489**	.738**	1			
DO	-.408**		-.330**	-.226*	-.249*	-	-	.272**	-	.261*	1		
BOD	.476**	.325**	-	.343**	-	-	.341**	-.219*	-.404**	-	-.313**	1	
Chlorophyll *a*	.773**	.649**	.415**	.481**	.305**	-	.564**	-.276**	-.521**	-.480**	-.355**	.668**	1

** Correlation is significant at the 0.01 level 2-tailed.

* Correlation is significant at the 0.05 level 2-tailed.

Factor Analysis of bottom water

The varimax rotated results along with eigen values and percent of variance obtained for bottom water are summarized in Table 3.8. The PCA of bottom water quality extracted five factors (principal component) with eigen values >1. These composite variables captured 72.71% of the variation in the original data. Factor 1 explained 29.75% of the total variance and is associated with strong positive loadings of ammonia-N,nitrate-N, silicate, TSS and strong negative loading of salinity. The ammonia-N,nitrate-N, silicate, TSS are correlated significantly with each other, but the correlations of salinity with ammonia-N,nitrate-N, silicate, TSS are negative and highly significant (Table 3.9). This suggests that the contribution of nutrients to the coastal water is mostly from riverine sources. This factor being similar to that observed in surface water could therefore be termed as the riverine Factor. Hence, Factor 1 can be termed as the *Riverine Factor*. The second factor showed 17.18% of the total variance and is associated with strong positive loadings of phosphate and TP. A significant correlation was observed between the above two variables. This suggests there is increased concentration of phosphate in the coastal waters whose source can be traced to anthropogenic nutrient inputs. This factor being similar to that observed in surface water could therefore be termed as the phosphorus factor. Factor 2 can be termed as *Phosphorus Factor*. The third factor accounts for 9.69% of the total variance and contains independent strong positive loading of DO. The DO condition can correctly characterize waste loads, natural factors such as degree of stratification, water temperature and circulation patterns and finally anthropogenic factors (such as nutrient loading) can also contribute to its event. It is presumed that due to shallowness of the coastal water, strong vertical mixing is keeping the bottom water well aerated. Factor 3 can be termed as *Aeration Factor*.

Factor 4 and Factor 5 accounts for 8.25% and 7.84% of the total variance respectively and contains no loading of variables which signifies some “latent” processes other than physico-chemical and biological variables affecting the system. It is deciphered, in this case, considering the high abundance of

phytoplankton biomass and one of the important factors which exacerbate the production of plankton along this coast is upwelling. The other most likely process that can take place in bottom water is the diagentic processes in the sediment, which can influence the nutrient flux in sediment water interface. Inorganic and organic nutrients in varying amounts and forms are almost continually transported to bottom by sedimentation. Nutrients can accumulate in sediments in either the solid phase or in the dissolved phase in the pore water between sediment grains. Once they have accumulated in the coastal sediments they may undergo a number of changes or processes that are modified by chemical and microbial activities (diagenesis). This can serve as an alternate source of nutrients in bottom water and thus can be characterized as diagenetic factor. Thus Factor 4 and Factor 5 can be termed as *Upwelling* and *Diagenetic Factor* respectively.

Table 3.8 Varimax factor analysis using PCA and identified principal components of the bottom waters along central and northern coast of Kerala.

	PC1	PC2	PC3	PC4	PC5
NH_4-N	0.754	4.48E-02	-1.88E-02	-0.256	-1.34E-02
NO_2-N	0.538	0.374	-0.269	9.12E-02	0.233
NO_3-N	0.618	3.36E-02	-0.331	0.473	8.20E-02
TN	0.513	0.147	0.132	0.489	-0.36
PO_4-P	0.224	0.806	-0.157	6.06E-02	4.48E-02
TP	0.12	0.876	-9.57E-02	2.64E-03	7.39E-02
$Si(OH)_4$-Si	0.785	-0.118	0.21	-8.33E-02	-6.32E-02
Water Temperature	-0.208	0.64	0.236	-0.497	0.132
TSS	0.772	-0.161	0.311	-0.191	9.16E-02
Salinity	-0.856	8.97E-02	-0.331	0.103	5.82E-02
pH	-6.29E-02	-0.185	0.212	0.278	0.863
DO	-0.184	0.284	0.777	0.278	-3.65E-03
BOD	0.525	-0.284	-0.268	-0.279	0.208
Eigen	3.87	2.23	1.26	1.07	1.02
%Variance	29.75	17.18	9.69	8.25	7.84
% Cumulative Variance	29.75	46.92	56.62	64.87	72.71

Table 3.9 Correlation matrix among the hydrographic – nutrient parameters of the bottom waters along the central and northern coast of Kerala.

	AMMONIA	NITRITE	NITRATE	TN	IP	TP	SIL	WT	TSS	SALINITY	PH	DO	BOD
Ammonia-N	1												
Nitrite -N	.403(**)	1											
Nitrate-N	.310(**)	.505(**)	1										
Total Nitrogen	.282(**)	0.206	.305(**)	1									
Inorganic Phosphate	0.126	.284(**)	0.176	0.19	1								
Total Phosphorus	0.141	.275(**)	0.078	0.186	.741(**)	1							
Inorganic Silicate	.536(**)	.228(*)	.413(**)	.277(**)	0.139	-0.075	1						
Water Temp.	-0.059	0.135	-.287(**)	-0.191	.289(**)	.405(**)	-0.147	1					
TSS	.522(**)	.293(**)	.289(**)	.289(**)	-0.004	-0.042	.582(**)	-0.118	1				
Salinity	-.596(**)	-.297(**)	-.348(**)	-.415(**)	-0.091	0.003	-.780(**)	0.126	-.727(**)	1			
pH	-0.089	-0.037	-0.012	-0.097	-0.09	-0.093	-0.027	-0.091	0.027	0.029	1		
DO	-0.189	-0.098	-0.136	0.074	0.029	0.146	-0.116	.234(*)	0.005	0.002	0.086	1	
BOD	.338(**)	0.135	.247(*)	0.125	-0.048	-0.037	.252(*)	-.213(*)	.458(**)	-.376(**)	0.034	-.322(**)	1

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

Correlation matrix of bottom waters

3.5 Conclusion

The present findings have demonstrated that both natural and anthropogenic sources creating an anomaly in the coastal waters. Addition of nutrient load in which rivers act as vectors reinforced by seasonal upwelling is augmenting the productivity in terms of phytoplankton biomass. The consistency in Chlorophyll *a* concentration maintaining its mesotrophic to eutrophic state regardless of seasonal trends suggests that coastal region along the central and northern Kerala is a biologically active zone. Periodic N limitation played a role in determining phytoplankton community biomass and productivity. Most plankton variability along the coast appears to be driven by species of diatoms; Si supply being a driving force. A definite gradient was conspicuous between the surface and bottom waters for the physico chemical variables highlighting the dynamic environment of the study area. Principal component analysis of the datasets revealed riverine, phosphorus, upwelling, aeration processes in surface water and in addition diagenetic process in bottom water as the factors influencing or creating an ecological change in the waters of central and northern coast of Kerala.

Chapter 4

DISSOLVED METALS IN SEAWATER

4.1 Introduction
4.2 Results
4.3 Discussion
4.4 Conclusion

4.1 Introduction

Coastal waters are highly affected by pollution because they are shallow water bodies, heavily used, close to pollution sources and not well circulated as the open ocean. The demands of an increasing world population in combination with technical advasnces of mankind, particularly since industrialization from the nineteenth century onwards, are challenging the natural performance of system earth. A significant quantity of the environmental contaminant impinges into coastal waters mainly due to by-products of anthropogenic activities in the watershed, including urban, industrial effluents and agricultural runoff (Accorneroa *et al.*, 2004). The ubiquitous presence of metals in the environment, toxicity, persistence, ability to bioaccumulate in the aquatic food web and occurrence of many catastrophic events of human health significance in the past has made its determination meaningful in marine pollution studies. Further, knowledge of the distribution and concentration of heavy metals in coastal water can assist in identifying the sources of pollution in the system. This is particularly true for central and northern coast of Kerala, where untreated domestic sewages and industrial effluents are disposed in to the coastal waters routed through fresh water bodies. It is estimated that about 17,104 m^3/ day of treated and untreated effluents from both medium as well as large scale industries are being discharged, thus impairing the quality of coastal waters drastically. Moreover, metals introduced into the sea through fluvial waters, the atmosphere, or advective water transport, form a balance between sedimentation processes, incorporation by organisms, and advection/diffusion. The dynamics of the metals in the water, in terms of advection/diffusion, and the transfer of dissolved or particulate metals to different matrices are rapid, making it difficult to investigate aquatic pollution problems and can only be possible to appreciate these changes on small spatial scales with some type of gradient. There has been a dearth of information on the concentration of dissolved metals in the coastal waters of Kerala coast. In this chapter the spatial and temporal variability in the distribution of dissolved metals *viz*. Cu, Pb, Cr, Ni, Zn, Cd and Hg along the central and northern coast of Kerala are discussed.

4.2 Results

Distribution of dissolved heavy metals in the water column

4.2.1 Copper (Cu)

Among the transects, wide fluctuation was observed in the distribution of dissolved Cu in the water column (Table 4.1, Table 4.2, Fig. 4A).Concentration of dissolved Cu (average ± SD) in surface water at Cochin varied in the range 4.20 to 10.20 (6.17 ± 2.20), 2.55 to 9.14 (6.82± 2.40) and 4.20 to 18.10 (11.58 ± 5.10) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. A definite seasonal trend was conspicuous with concentration increasing from post monsoon to monsoon. An increase in concentration gradient was discerned in its distribution from shore (0.5 km) towards offshore (10.0 km) or seaward while the gradient reversed in the other two seasons. The concentration of dissolved Cu in bottom water varied in the range 3.90 to 9.45 (5.67 ± 2.01), 4.20 to 10.12 (7.39 ± 2.17) and 1.50 to 11.60 (6.02 ± 3.70) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration in bottom water was slightly lower than that observed in surface water and followed similar seasonal variation as that of the surface water.

At Chettuva, concentration of dissolved Cu (average ± SD) in the surface water varied in the range 4.60 to 6.60 (5.45 ± 0.79), 1.65 to 7.15 (5.57 ± 1.98) and 3.60 to 11.40 (6.78 ± 3.54) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. Seasonal fluctuation was evident with increase in concentration in pre monsoon and low in post monsoon. A decrease in concentration gradient was discerned in its distribution from shore (0.5 km) towards offshore (10.0 km) or seaward in post monsoon and monsoon while its distribution remained comparable in pre monsoon. The concentration of dissolved Cu in bottom water varied in the range 3.30 to 4.70 (4.01 ± 0.53), 4.65 to 8.18(6.39 ± 1.16) and 3.20 to 7.90 (4.94 ± 1.74) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration was slightly lower than that observed in surface water except in pre monsoon where its concentration was comparable and slightly higher than the surface water.

Seasonal variation of dissolved Cu in bottom water followed similar trend as that of the surface water.

Concentration of dissolved Cu (average ± SD) in the surface water at Ponnani varied in the range 3.30 to 5.10 (14.21 ± 0.67), 2.20 to 4.60 (3.88 ± 0.84) and 8.40 to 19.10 (13.06 ± 4.64) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. A definite seasonal trend was conspicuous with concentration increasing from post monsoon to monsoon. A decrease in concentration gradient was discerned in its distribution from shore (0.5 km) towards offshore (10.0 km) or seaward in monsoon while the gradient was comparable in the other two seasons. The concentration of dissolved Cu in bottom water varied in the range 2.10 to 4.90 (3.65 ± 1.03), 2.90 to 5.90 (4.28 ± 1.21) and 6.00 to 16.40 (11.02 ± 3.46) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration in bottom water was slightly higher than that observed in surface water in pre monsoon, while it was lower than that of the levels in surface water for other two seasons. Seasonal variation of dissolved Cu in bottom water followed similar trend as that of the surface water.

At Calicut, concentration of dissolved Cu (average ± SD) in surface water varied in the range 3.75 to 5.40 (4.49 ± 0.70), 3.60 to 10.70 (7.13± 3.17) and 4.50 to 11.60 (8.48± 2.62) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. A definite seasonal trend was conspicuous with concentration increasing from post monsoon to monsoon. A decrease in concentration gradient was discerned in its distribution from shore (0.5 km) towards offshore (10.0 km) or seaward in all season. The concentration of dissolved Cu in bottom water varied in the range 1.05 to 6.30 (3.61± 1.80), 2.10 to 6.40 (4.20 ± 1.83) and 2.15 to 8.90 (5.64 ± 2.56) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively

At Kasargod concentration of dissolved Cu (average ± SD) in surface water varied in the range 4.10 to 8.10 (6.32 ± 1.41), 3.75 to 9.90 (7.53± 2.29) and 6.00 to 16.05 (9.09± 3.55) µg l^{-1} in post monsoon, pre monsoon and

monsoon respectively. A definite seasonal trend was conspicuous with concentration increasing from post monsoon to monsoon. A decrease in concentration gradient was discerned in its distribution from shore (0.5 km) towards offshore (10.0 km) or seaward in all season. The concentration of dissolved Cu in bottom water varied in the range 2.40 to 6.90 (4.58 ± 1.91), 2.30 to 7.20 (5.23 ± 2.17) and 4.13 to 20.80 (9.06± 6.00) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration was lower than that observed in surface water and followed similar seasonal fluctuations as that of the surface water.

The maximum concentration of dissolved Cu of 19.10 µg l^{-1} in surface water was recorded at Ponnani in monsoon and the minimum value of 1.65 µg l^{-1} at Chettuva in pre monsoon. The maximum concentration of dissolved Cu of 20.80 µg l^{-1} in bottom water was reported at Kasargod in monsoon, while the minimum value of 1.05 µg l^{-1} was reported at Calicut in post monsoon.

4.2.2 Lead (Pb)

Concentration of Pb in the water column was found to be detectable and showed wide variation in its distribution among the transects (Table 4.1, Table 4.2, Fig. 4B). At Cochin, concentration of dissolved Pb (average ± SD) in surface water varied in the range 3.62 to 6.70 (4.58 ± 1.17), 4.14 to 7.80 (5.33 ± 1.43) and BDL to 0.80 (0.13± 0.33) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. A decrease in concentration gradient was conspicuous in its distribution from shore (0.5 km) towards offshore (10.0 km) in post monsoon and pre monsoon. The concentration of dissolved Pb in bottom water varied in the range 3.40 to 5.20 (4.47± 0.66) and 2.60 to 4.90 (4.07± 0.82) µg l^{-1} in post monsoon and pre monsoon respectively. Lead was not detectable in the water column (both surface and bottom) in monsoon except in the shore region (0.5 km), where it showed the presence of 0.80 µg l^{-1}. Seasonal fluctuation showed an erratic pattern in the surface and bottom water. The levels of dissolved lead in surface water was high in pre monsoon, while in the bottom water high values was observed in post monsoon. In monsoon the concentration of Pb was not detectable in the water column.

At Chettuva, concentration of dissolved Pb (average ± SD) in the surface water varied in the range 1.72 to 2.24 (1.93 ± 0.20), 1.89 to 2.16 (1.99 ± 0.12) and BDL to 0.60 (0.10 ± 0.10) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration of dissolved Pb in bottom water varied in the range 1.58 to 2.29 (2.00± 0.26), 2.00 to 2.39 (2.09± 0.15) and BDL to 2.40 (0.66± 1.06) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. Its level in the water column and it's distribution from shore (0.5 km) towards offshore (10.0 km) or seaward in post monsoon and pre monsoon remained comparable. In monsoon the concentration of dissolved Pb in the water column was almost low and was not detectable in the offshore region (3.0 km – 10.0 km).

Concentration of dissolved Pb (average ± SD) in the surface water at Ponnani varied in the range 1.74 to 2.02 (1.84 ± 0.10), 2.01 to 2.16 (2.06± 0.05) and BDL to 0.80 (0.23 ± 0.37) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. A definite seasonal trend was not conspicuous with its level low in monsoon. The concentration of dissolved Pb in bottom water varied in the range 1.91 to 2.26 (2.04 ± 0.15), 2.16 to 2.28 (2.22 ± 0.04) and BDL to 1.10 (0.22 ± 0.44) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively (Fig). The concentration of dissolved Pb in bottom water was generally higher than that observed in surface water in post monsoon and pre monsoon. Variation in the concentration gradient from shore (0.5 km) towards offshore (10.0 km) or seaward in post monsoon was comparable in both surface and bottom water. In pre monsoon the concentration gradient from shore to offshore in the surface water column showed a decrease, while in bottom water it showed a reverse trend.

At Calicut, concentration of dissolved Pb (average ± SD) in surface water varied in the range 1.87 to 3.02 (2.37 ± 0.46), 1.95 to 2.16 (2.07± 0.07) and BDL to 0.90 (0.18± 0.36) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration of dissolved Pb in bottom water varied in the range 0.23 to 3.27 (1.68 ± 1.20), 1.99 to 2.29 (2.10 ± 0.12) and BDL to 0.40 (0.12 ± 0.18) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively.

Seasonal variation as well as distribution in the water column generally showed an erratic pattern. The concentration of Pb was almost low in monsoon in the water column.

At Kasargod, concentration of dissolved Pb (average ± SD) in surface water varied in the range 1.88 to 2.24 (1.99 ± 0.13), 1.86 to 2.17 (2.04 ± 0.11) and BDL to 0.20 (0.05± 0.08) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration of dissolved Pb in bottom water varied in the range 2.04 to 2.52 (2.21 ± 0.17), 1.95 to 2.32 (2.13 ± 0.14) and BDL to 0.20 (0.053 ±0.09) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. Its distribution from shore (0.5 km) towards offshore (10.0 km) or seaward in post monsoon and pre monsoon remained comparable. In monsoon the concentration of dissolved Pb in the water column was almost low and was not detectable in the offshore region (3.0 km – 10.0 km). The concentration of dissolved Pb in bottom water was generally higher than the levels in surface water in post monsoon and pre monsoon.

The maximum concentration of dissolved Pb of 7.80 µg l^{-1} in surface water in pre monsoon and in bottom water of 5.20 µg l^{-1} in post monsoon was recorded at Cochin. The minimum value (BDL) was recorded at all transects in monsoon.

4.2.3 Chromium (Cr)

Dissolved chromium was below the detectable limit in surface water for all season in majority of the studied transects (Table 4.1, Table 4.2, Fig. 4C). At Cochin a low concentration of 1.30 and 1.90 µg l^{-1} was detected in nearshore (0.5 km) surface and bottom water respectively in post monsoon, while its concentration was 0.70 and 0.78 µg l^{-1} respectively in pre monsoon. In monsoon the levels was not detectable. At Chettuva and Ponnani dissolved Cr was not detected in the water column in all seasons. At Calicut, in post monsoon dissolved Cr in surface water showed a level of 1.20 µg l^{-1} and 1.60 µg l^{-1} at 0.5 km and 3.0 km from the shore respectively. In bottom water Cr was discerned only at 0.5 km and showed a level of 1.80 µg l^{-1}. In pre monsoon a concentration

of 1.80 µg l^{-1} and 1.32 µg l^{-1} was distributed in the surface and bottom water at 0.5 km respectively. In monsoon the levels was not detectable. At Kasargod a low concentration of 0.62 µg l^{-1} was detected in surface water at 10.0 km in post monsoon. In monsoon a concentration of 0.62 µg l^{-1} was detected in surface water at 10.0 km and 1.81 µg l^{-1} in bottom water at 5.0 km.

The maximum concentration of dissolved Cr of 1.80 µg l^{-1} in surface water was discerned at Calicut in pre monsoon. The maximum concentration in bottom water of 1.81 µg l^{-1} was recorded at Kasargod in monsoon. The minimum value (BDL) was recorded at all transect in all seasons.

Table 4.1 Concentration of heavy metals (Cu, Pb and Cr) in coastal water among transects in different season.

Station Name	Distance from the shore (km)	Source	Cu			Pb			Cr		
			POM	PM	M	POM	PM	M	POM	PM	M
Cochin	0.5	S	5.80	8.70	18.10	6.70	7.80	0.80	1.30	0.67	BDL
		B	5.20	9.30	11.60	5.20	4.90	BDL	1.90	0.78	BDL
	1	S	4.20	9.14	15.20	5.10	6.20	BDL	0.65	BDL	BDL
		B	4.10	10.12	8.40	4.66	4.20	BDL	BDL	BDL	BDL
	3	S	4.50	7.88	14.10	4.37	5.01	BDL	BDL	BDL	BDL
		B	3.90	7.80	6.33	4.68	4.45	BDL	BDL	BDL	BDL
	5	S	6.90	2.55	4.20	3.82	4.60	BDL	BDL	BDL	BDL
		B	5.55	6.00	1.50	3.98	3.51	BDL	BDL	BDL	BDL
	7.5	S	5.40	6.20	8.90	3.86	4.20	BDL	BDL	BDL	BDL
		B	5.80	6.90	2.70	3.40	2.60	BDL	BDL	BDL	BDL
	10	S	10.20	6.45	9.00	3.62	4.14	BDL	BDL	BDL	BDL
		B	9.45	4.20	5.60	4.90	4.37	BDL	BDL	BDL	BDL
Chettuva	0.5	S	6.60	6.10	11.40	2.12	1.90	0.60	BDL	BDL	BDL
		B	4.70	6.50	7.90	2.29	2.01	2.40	BDL	BDL	BDL
	1	S	6.20	6.58	10.10	1.88	1.89	BDL	BDL	BDL	BDL
		B	4.30	6.90	6.30	2.12	2.00	1.60	BDL	BDL	BDL
	3	S	5.10	1.65	8.10	1.82	2.16	BDL	BDL	BDL	BDL
		B	3.60	4.65	4.20	1.58	2.39	BDL	BDL	BDL	BDL
	5	S	4.80	7.15	3.60	2.24	2.13	BDL	BDL	BDL	BDL
		B	3.30	8.18	3.75	2.06	2.06	BDL	BDL	BDL	BDL
	7.5	S	4.60	6.10	3.89	1.82	1.90	BDL	BDL	BDL	BDL
		B	3.80	5.98	3.20	1.80	2.05	BDL	BDL	BDL	BDL
	10	S	5.55	5.85	3.60	1.72	1.99	BDL	BDL	BDL	BDL
		B	4.35	6.10	4.30	2.17	2.05	BDL	BDL	BDL	BDL

Ponnani	0.5	S	3.80	4.10	11.10	1.75	2.16	0.80	BDL	BDL	BDL
		B	4.60	2.90	16.40	1.92	2.26	0.20	BDL	BDL	BDL
	1	S	5.10	4.60	19.10	1.87	2.05	0.60	BDL	BDL	BDL
		B	4.90	3.50	11.30	2.14	2.21	BDL	BDL	BDL	BDL
	3	S	4.80	2.20	18.75	1.74	2.05	BDL	BDL	BDL	BDL
		B	3.90	3.30	11.70	1.91	2.16	1.10	BDL	BDL	BDL
	5	S	4.35	4.10	10.80	2.02	2.04	BDL	BDL	BDL	BDL
		B	3.30	5.20	11.85	2.26	2.19	BDL	BDL	BDL	BDL
	7.5	S	3.90	4.15	10.20	1.80	2.01	BDL	BDL	BDL	BDL
		B	3.10	4.90	8.90	2.10	2.28	BDL	BDL	BDL	BDL
	10	S	3.30	4.10	8.40	1.86	2.05	BDL	BDL	BDL	BDL
		B	2.10	5.90	6.00	1.93	2.22	BDL	BDL	BDL	BDL
Calicut	0.5	S	5.10	9.30	11.20	1.92	2.11	0.90	1.20	1.80	BDL
		B	4.30	6.40	7.90	2.05	2.04	0.30	1.80	1.32	BDL
	1	S	4.80	10.70	11.60	1.87	2.04	0.20	BDL	BDL	BDL
		B	4.10	6.40	8.90	1.84	2.01	0.40	BDL	BDL	BDL
	3	S	3.75	9.90	4.50	2.21	2.16	BDL	1.60	BDL	BDL
		B	6.30	4.20	3.90	0.30	1.99	BDL	BDL	BDL	BDL
	5	S	5.40	5.10	8.10	2.48	1.95	BDL	BDL	BDL	BDL
		B	3.60	3.20	2.15	0.23	2.07	BDL	BDL	BDL	BDL
	7.5	S	4.10	4.20	7.80	2.75	2.06	BDL	BDL	BDL	BDL
		B	2.30	2.90	4.56	2.42	2.29	BDL	BDL	BDL	BDL
	10	S	3.80	3.60	7.65	3.02	2.09	BDL	BDL	BDL	BDL
		B	1.05	2.10	6.45	3.27	2.19	BDL	BDL	BDL	BDL
Kasargod	0.5	S	8.10	9.90	8.80	1.88	2.17	0.20	BDL	BDL	BDL
		B	6.90	7.20	7.90	2.24	2.01	0.12	BDL	BDL	BDL
	1	S	7.00	9.60	8.60	1.91	2.01	0.10	BDL	BDL	BDL
		B	6.60	7.10	9.20	2.04	2.11	0.20	BDL	BDL	BDL
	3	S	6.30	7.60	7.80	2.24	1.86	BDL	BDL	BDL	BDL
		B	5.10	6.90	20.80	2.52	1.95	BDL	BDL	BDL	BDL
	5	S	4.10	3.75	6.00	1.94	2.01	BDL	BDL	BDL	BDL
		B	2.40	2.30	4.13	2.12	2.15	BDL	BDL	BDL	1.81
	7.5	S	5.40	6.20	7.30	2.01	2.10	BDL	BDL	BDL	BDL
		B	2.90	3.10	6.20	2.10	2.32	BDL	BDL	BDL	BDL
	10	S	7.05	8.10	16.05	2.02	2.13	BDL	0.62	BDL	0.62
		B	3.60	4.80	6.15	2.24	2.24	BDL	BDL	BDL	BDL

NOTE: S- surface water, B - bottom water, POM - post monsoon, PM - pre monsoon, M - monsoon

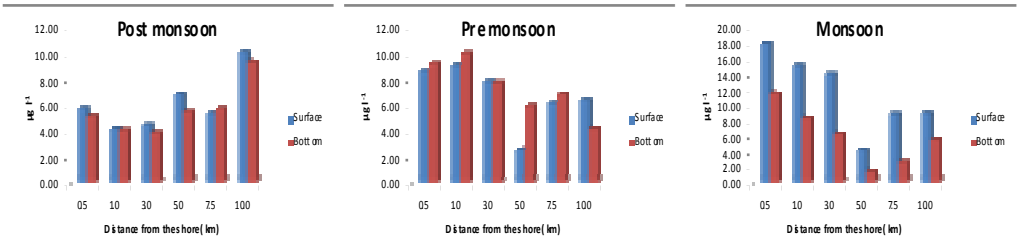
BDL - below detectable limit

Table 4.2 Average concentration ± Standard Deviation (SD) of heavy metals (Cu,Pb,Cr) in coastal water among transects in different season.

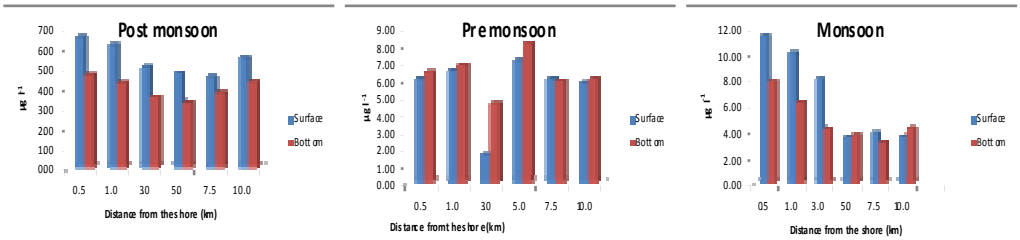
Station Name	Source	POM	Cu			Pb			Cr	
			PM	M	POM	PM	M	POM	PM	M
Cochin										
	S	6.17	6.82	11.58	4.58	5.33	0.13	0.33	0.11	BDL
		± 2.20	± 2.40	± 5.10	± 1.17	± 1.43	± 0.33			
	B	5.67	7.39	6.02	4.47	4.07	BDL	0.32	0.13	BDL
		± 2.01	± 2.17	± 3.70	± 0.66	± 0.82				
Chettuva										
	S	5.45	5.57	6.78	1.93	1.99	0.10	BDL	BDL	BDL
		± 0.79	± 1.98	± 3.54	± 0.20	± 0.12	± 0.10			
	B	4.01	6.39	4.94	2.00	2.09	0.66	BDL	BDL	BDL
		± 0.53	± 1.16	± 1.74	± 0.26	± 0.15	± 1.06			
Ponnani										
	S	14.21	3.88	13.06	1.84	2.06	0.23	BDL	BDL	BDL
		± 0.67	±0.84	± 4.64	± 0.10	± 0.05	± 0.37			
	B	3.65	4.28	11.02	2.04	2.22	0.22	BDL	BDL	BDL
		± 1.03	± 1.21	± 3.46	± 0.15	± 0.04	± 0.44			
Calicut										
	S	4.49	7.13	8.48	2.37	2.07	0.18	0.47	0.30	BDL
		± 0.70	± 3.17	± 2.62	± 0.46	± 0.07	± 0.36			
	B	3.61	4.2	5.64	1.68	2.10	0.12	0.3	0.22	BDL
		± 1.80	± 1.83	± 2.56	± 1.20	± 0.12	± 0.18			
Kasargod										
	S	6.32	7.53	9.09	1.99	2.04	0.05	0.10	BDL	0.10
		± 1.41	± 2.29	± 3.55	± 0.13	±0.11	± 0.08			
	B	4.58	5.23	9.06	2.21	2.13	0.053	BDL	BDL	0.30
		± 1.91	± 2.17	± 6.00	± 0.17	± 0.14	± 0.09			

NOTE: S- surface water, B - bottom water, POM - post monsoon, PM - pre monsoon, M - monsoon,BDL- below detectable limit

Cochin



Chettuva



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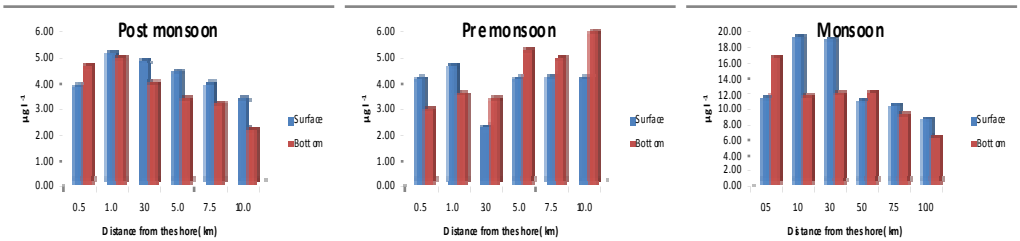

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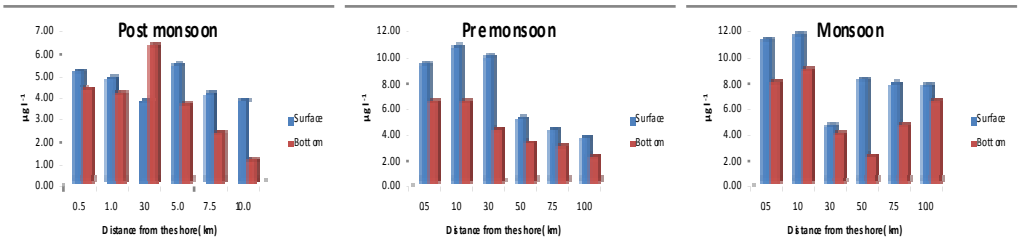

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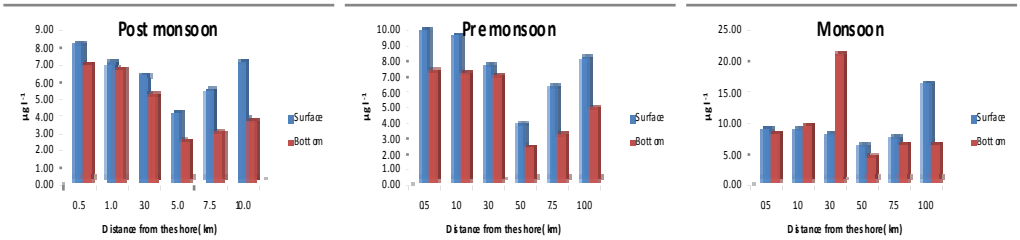
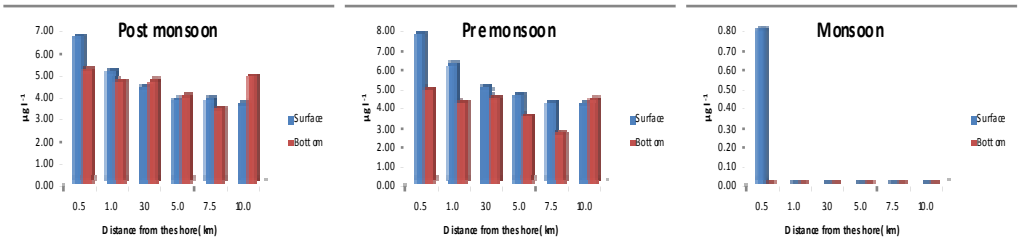


Figure 4A. Seasonal variation of dissolved Copper (Cu) in coastal water among different transects.

Cochin



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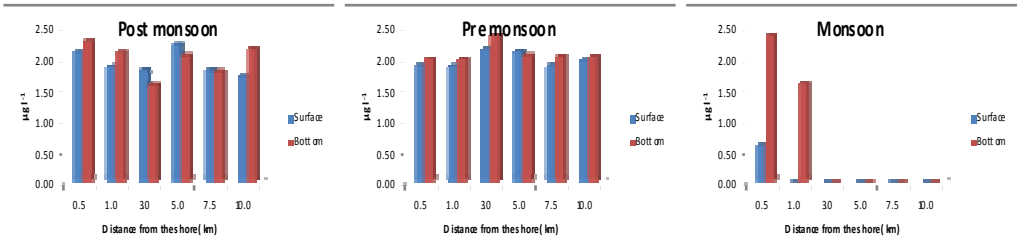
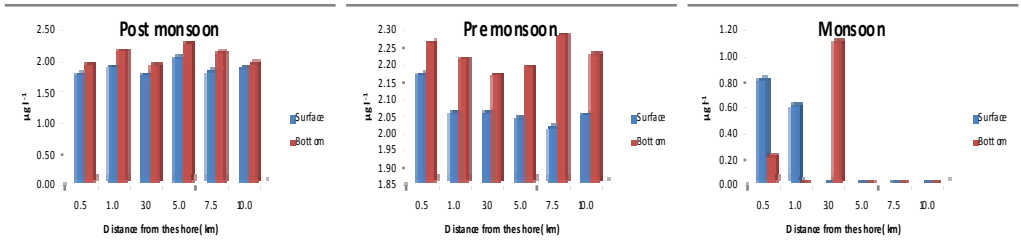


Ponnani



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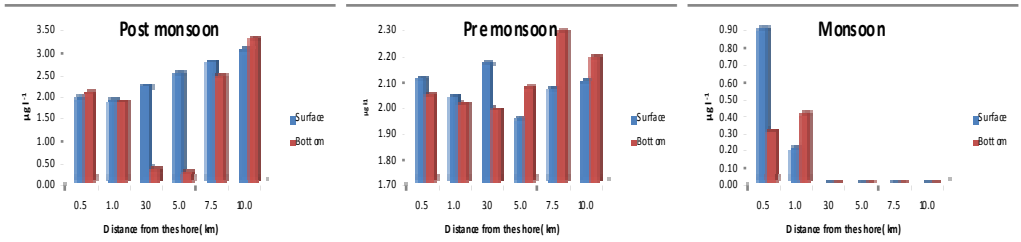

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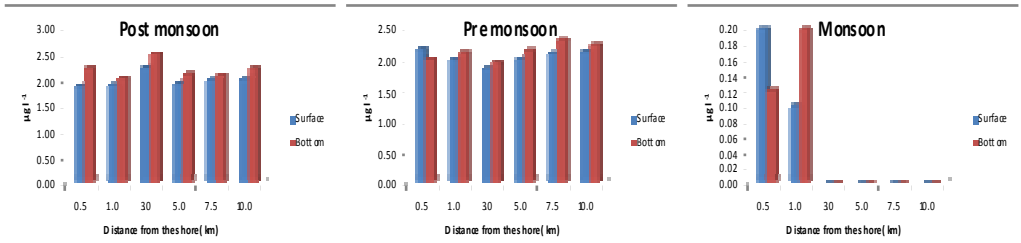
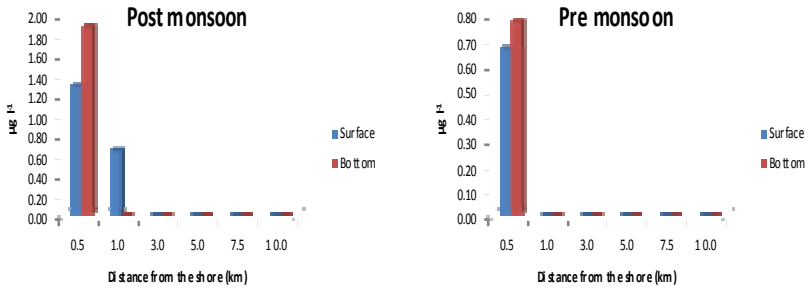


Figure 4B. Seasonal variation of dissolved Lead (Pb) in coastal water among different transects.

Cochin



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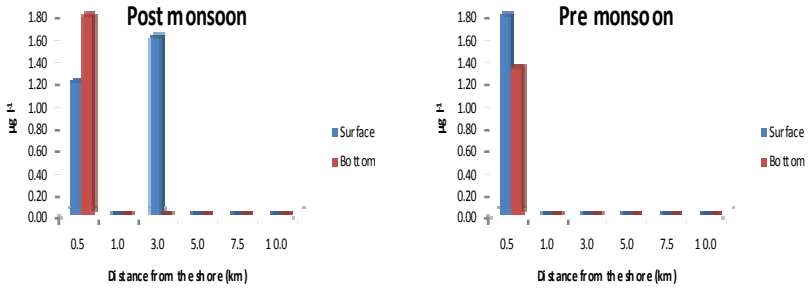

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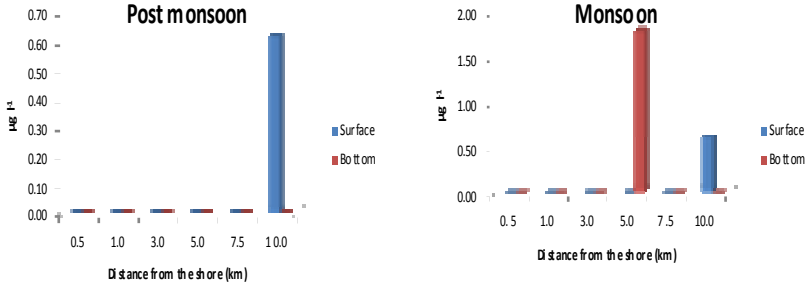


Figure 4C. Seasonal variation of dissolved Chromium (Cr) in coastal water among different transects.

4.2.4 Nickel (Ni)

Wide variation was observed in the distribution of dissolved Ni in the water column among the transects (Table 4.3, Table 4.4, Fig. 4D). Concentration of dissolved Ni (average ± SD) in surface water at Cochin varied in the range 3.21 to 10.95 (6.35 ± 2.75), BDL to 19.50 (8.19± 6.70) and BDL to 14.23 (4.49± 5.08) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration of dissolved Ni in bottom water varied in the range BDL to 16.81 (3.51± 6.60), 4.12 to 11.17 (6.90± 2.57) and BDL to 8.96 (5.85 ± 3.56) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. A decrease in concentration gradient was discerned in its distribution from shore (0.5 km) towards offshore (10.0 km) or seaward in all season. In monsoon bottom water detected higher level of dissolved Ni compared to surface water, while in other seasons higher concentration was reported in surface layer. Both bottom and surface water showed an erratic seasonal trend in its distribution.

At Chettuva, concentration of dissolved Ni (average ± SD) in the surface water varied in the range 3.56 to 8.12 (5.29 ± 2.03), BDL to 6.32 (3.96± 1.83) and 3.36 to 7.15 (5.92 ± 1.37) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration of dissolved Ni in bottom water varied in the range BDL to 8.54 (5.20 ± 3.27), 11.60 to 16.00 (14.05 ± 1.90) and BDL to 2.10 (0.35 ± 0.86) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. Seasonal variation showed an erratic pattern in the distribution of Ni in the water column. In post monsoon, the concentration of Ni in surface and bottom water generally showed an offshore decrease. The level of Ni in bottom water was higher compared to the surface layer. In pre monsoon levels of dissolved Ni in surface water showed an offshore decrease while in bottom water the trend towards offshore was comparable between the stations and bottom water reported higher concentration of Ni compared to surface water. In monsoon concentration of dissolved Ni showed an offshore increase in surface water, while it was not detectable in the bottom water.

At Ponnani, concentration of dissolved Ni (average ± SD) in the surface water varied in the range 0.80 to 2.12 (1.45 ± 0.54), 2.34 to 5.21 (3.37± 1.14)

and BDL to 2.60 (0.56 ± 1.02) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration of dissolved Ni in bottom water varied in the range BDL to 1.40 (0.60± 0.68), 1.00 to 4.16 (2.02± 1.14) and BDL to 1.40 (0.23 ± 0.57) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. Seasonal trend in the distribution of Ni in water column showed an increase in pre monsoon and a decline in monsoon. In post monsoon, the concentration of Ni in surface and bottom water generally showed a decrease in the concentration gradient from shore to offshore. The level of Ni in bottom water was lower compared to the surface layer and in majority of stations it was below the detectable limit. In pre monsoon levels of dissolved Ni in surface water and bottom water showed an offshore decrease in the concentration gradient. In monsoon concentration of dissolved Ni showed an offshore decrease in surface water, while it showed an erratic pattern in its distribution in the bottom water.

At Calicut, concentration of dissolved Ni (average ± SD) in the surface water varied in the range BDL to 10.25 (5.28 ± 4.53), 5.21 to 25.77 (13.83 ± 6.69) and BDL to 3.25 (1.70 ± 1.51) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration of dissolved Ni in bottom water varied in the range 6.30 to 19.38 (10.58 ± 4.65), 2.35 to 4.53 (2.98 ± 0.80) and BDL to 10.70 (2.56 ± 4.20) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. Seasonal trend in the distribution of Ni in surface water showed an increase in pre monsoon and a decline in monsoon and in bottom water showed an increase in post monsoon and a decline in monsoon. In post monsoon, the concentration of Ni in surface and bottom water showed a dissimilar concentration gradient from shore to offshore. The level of Ni in surface water showed an offshore decrease while its level increased in bottom water. A vertical concentration gradient was distinct with high concentration in bottom water compared to that in surface layer. In pre monsoon the concentration gradient of dissolved Ni in surface water and bottom water from shore to offshore was comparable. The average concentration of Ni in the bottom water was low compared to surface water. In monsoon concentration of dissolved Ni

showed an offshore decrease in surface water, while it was not detectable in the bottom water for most of the stations. However, at 5.0 and 7.5 km offshore, increased levels of Ni was detected in bottom water.

At Kasargod, concentration of dissolved Ni (average ± SD) in the surface water varied in the range 2.13 to 9.62 (5.40 ± 2.62), 3.64 to 11.25 (7.65 ± 3.48) and BDL to 6.42 (2.57 ± 2.44) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration of dissolved Ni in bottom water varied in the range 4.10 to 13.62 (7.22 ± 3.44), 2.54 to 14.21 (5.71 ± 4.46) and BDL to 1.54 (0.26 ± 0.63) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. Seasonal trend in the distribution of Ni in surface water showed an increase in pre monsoon and a decline in monsoon and in bottom water showed an increase in post monsoon and a decline in monsoon. In post monsoon, the concentration of Ni in surface and bottom water showed an erratic concentration gradient from shore to offshore. The level of Ni in bottom water was higher than the surface water towards offshore (3.0 – 10.0 km). In pre monsoon the concentration gradient of dissolved Ni in surface water and bottom water from shore to offshore showed a decrease. In monsoon, concentration of Ni in the bottom water was not detectable except a low value at near shore (0.5 km), while its distribution in surface water was comparable from shore to offshore.

The maximum concentration of dissolved Ni of 25.77 µg l^{-1} in surface water and 19.38 µg l^{-1} in bottom water was discerned at Calicut in pre monsoon and post monsoon respectively. The minimum value (BDL) was recorded at all transects in monsoon season.

4.2.5 Zinc (Zn)

Among the transects, wide variation was observed in the distribution of dissolved Zn in the water column (Table 4.3, Table 4.4, Fig. 4E). At Cochin, concentration of dissolved Zn (average ± SD) in the surface water varied in the range 3.10 to 11.80 (6.25 ± 3.11), 2.45 to 10.53 (6.69 ± 2.70) and 14.80 to 31.60 (22.57 ± 6.65) µg l^{-1} in post monsoon, pre monsoon and monsoon

respectively. The concentration of dissolved Zn in bottom water varied in the range 2.45 to 9.07 (4.77 ± 2.30), 4.30 to 8.14 (5.78 ± 1.35) and 16.16 to 31.20 (22.04 ± 6.92) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. Seasonal trend in the distribution of Zn in surface water showed an increase in monsoon and a decline in post monsoon and in bottom water, it showed an increase in monsoon and a decline in pre monsoon. In post monsoon and pre monsoon, the concentration of Zn in surface and bottom water showed an increase in concentration gradient from shore to offshore, while in monsoon concentration gradient showed an offshore decrease. In monsoon, most of the stations showed an increased level of dissolved Zn in bottom water relative to surface water, while it was not discerned in the other two seasons.

At Chettuva, concentration of dissolved Zn (average ± SD) in the surface water varied in the range 3.10 to 5.03 (3.95 ± 0.72), 4.32 to 10.00 (7.16± 2.22) and 19.88 to 30.60 (22.66 ± 3.96) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration of dissolved Zn in bottom water varied in the range 1.92 to 3.90 (2.95± 0.80), 2.70 to 6.89 (4.32 ± 1.70) and 18.06 to 28.80 (21.01± 4.13) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. Seasonal variation of dissolved Zn in the water column generally showed a steady increase from post monsoon to monsoon. In post monsoon, the concentration of Zn in surface and bottom water generally showed an offshore increase and in the other two seasons it showed an offshore decrease. The level of Zn in bottom water was low relative to the surface layer throughout the seasons.

At Ponnani, concentration of dissolved Zn (average ± SD) in the surface water varied in the range 3.18 to 4.70 (3.93 ± 0.53), 2.40 to 6.10 (4.65 ± 1.62) and 18.15 to 44.58 (25.89 ± 9.83) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration of dissolved Zn in bottom water varied in the range 2.90 to 4.70 (3.65 ± 0.73), 1.90 to 5.60 (4.03± 1.43) and 11.52 to 34.60 (21.22 ± 8.89) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. Seasonal trend in the distribution of Zn in surface and bottom water showed an increase in monsoon and a decline in post monsoon.

In post monsoon and pre monsoon, the concentration of Zn in surface and bottom water showed a decrease in concentration gradient from shore to offshore. In monsoon, concentration gradient of surface water showed an offshore increase while the bottom water showed a decrease. The level of Zn in bottom water was low relative to the surface layer throughout the seasons.

At Calicut, concentration of dissolved Zn (average ± SD) in the surface water varied in the range 2.38 to 6.10 (4.27 ± 1.35), 9.30 to 12.06 (10.88± 1.11) and 16.89 to 29.60 (22.63 ± 5.02) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration of dissolved Zn in bottom water varied in the range 3.70 to 7.88 (5.56± 1.52), 5.10 to 9.60 (6.38 ± 1.64) and 14.90 to 19.40 (16.76± 1.77) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. Seasonal variation of dissolved Zn in the water column generally showed a steady increase from post monsoon to monsoon. In post monsoon, the concentration gradient of Zn in surface water from shore to offshore was comparable, and in bottom water it generally showed an offshore increase. In pre monsoon concentration gradient of surface water increased off shore and in monsoon it showed a decrease. In bottom water the concentration gradient was comparable for the two seasons. The level of Zn in bottom water was high relative to the surface layer in post monsoon, while the reverse was noted in the distribution for other two seasons.

At Kasargod, concentration of dissolved Zn (average ± SD) in the surface water varied in the range 4.10 to 5.10 (4.62 ± 0.39), 3.29 to 5.80 (4.58 ± 0.88) and 30.67 to 42.40 (35.58 ± 4.98) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration of dissolved Zn in bottom water varied in the range 3.20 to 5.90 (4.86± 1.02), 2.90 to 6.82 (4.13 ± 1.42) and 23.78 to 36.25 (29.76± 4.59) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. Seasonal variation of dissolved Zn in the water column generally showed an erratic distribution, however its level was high in monsoon. The concentration gradient of Zn in surface and bottom water from shore to offshore was comparable in all season. The level of Zn in bottom water was high relative

to the surface layer in post monsoon, while the reverse was noted in the distribution for other two seasons.

The maximum concentration of dissolved Zn of 44.58 µg l^{-1} in surface water was recorded at Ponnani in monsoon and the minimum value of 2.45 µg l^{-1} at Cochin in pre monsoon. The maximum concentration of dissolved Zn of 34.60 µg l^{-1} in bottom water and the minimum value of 1.90 µg l^{-1} was reported at Ponnani in monsoon and pre monsoon respectively.

4.2.6 Cadmium (Cd)

Marked variation was discerned in the distribution of Cd in the water column among the studied transects (Table 4.3, Table 4.4, Fig. 4F). At Cochin, concentration of dissolved Cd (average ± SD) in the surface water varied in the range 1.40 to 2.20 (1.90 ± 0.28), BDL to 1.30 (0.67 ± 0.57) and 2.90 to 6.20 (4.60 ± 1.33) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration of dissolved Cd in bottom water varied in the range 0.20 to 3.30 (1.45 ± 1.24), BDL to 1.30 (0.97 ± 0.48) and 1.60 to 5.70 (3.08 ± 1.47) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. Seasonal trend in the distribution of Cd in water column showed an increase in monsoon and a decline in pre monsoon. In all season the concentration of Cd in surface water showed a decrease in concentration gradient from shore to offshore, while in bottom water it showed an increase towards offshore. The concentration of dissolved Cd in bottom waters of offshore region showed (5.0 – 10.0 km) high concentration relative to the surface layer in post monsoon and pre monsoon.

At Chettuva, concentration of dissolved Cd (average ± SD) in the surface water varied in the range BDL to 0.30 (0.10 ± 0.13), 1.10 to 5.20 (2.50± 1.43) and 0.30 to 0.80 (0.50 ± 0.18) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration of dissolved Cd in bottom water varied in the range 0.81 to 3.40 (1.66± 0.93), 2.68 to 5.50 (3.77 ± 1.18) and 0.10 to 0.20 (0.18 ± 0.04) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. Seasonal variation of dissolved Cd in the surface water showed an increase in pre monsoon and declined in post monsoon while in bottom water it

also showed an increase akin to surface water in pre monsoon and declined in monsoon. In post monsoon, the concentration of Cd in surface water was detected only in nearshore (0.5 – 3.0 km) while it was absent in offshore. In pre monsoon the concentration gradient of the water column generally showed an increase towards offshore while in monsoon it was comparable. The bottom water showed high levels relative to the surface water except in monsoon.

At Ponnani, concentration of dissolved Cd (average ± SD) in the surface water varied in the range 0.10 to 0.40 (0.27 ± 0.10), 0.10 to 1.20 (0.59 ± 0.44) and 0.50 to 6.90 (3.67 ± 2.75) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration of dissolved Cd in bottom water varied in the range BDL to 0.60 (0.18 ± 0.29), 0.20 to 0.60 (0.42 ± 0.16) and 0.10 to 7.60 (2.88 ± 3.28) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. Seasonal trend in the distribution of Cd in surface and bottom water showed an increase in monsoon and a decline in post monsoon. In all seasons the concentration gradient generally showed an offshore decrease in surface and bottom water. In post monsoon, dissolved Cd in offshore water (3.0 km – 10.0 km) was not detectable and the levels detected in near shore bottom water were high relative to surface water.

At Calicut, concentration of dissolved Cd (average ± SD) in the surface water varied in the range 0.20 to 0.70 (0.43 ± 0.19), 2.10 to 6.30 (4.27 ± 1.95) and 0.10 to 4.90 (2.75 ± 2.14) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration of dissolved Cd in bottom water varied in the range BDL to 0.20 (0.08± 0.08), 1.80 to 6.10 (3.43 ± 1.81) and 0.10 to 6.90 (3.45 ± 2.70) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. Seasonal variation of dissolved Cd in water column generally showed an erratic pattern in its distribution. In post monsoon, the concentration gradient of Zn in surface water from shore to offshore was comparable, and in bottom water it generally showed an offshore increase. The concentration gradient of the water column generally showed an offshore decrease for all seasons. In monsoon the levels of Cd in bottom water was high relative to the surface layer.

At Kasargod, concentration of dissolved Cd (average ± SD) in the surface water varied in the range 0.90 to 1.50 (1.25 ± 0.20), 1.19 to 2.31 (2.02 ± 0.42) and BDL to 2.30 (0.75 ± 0.98) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration of dissolved Cd in bottom water varied in the range BDL to 0.60 (0.28 ± 0.20), 0.60 to 6.10 (2.06 ± 2.06) and BDL to 3.60 (0.80 ± 1.41) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. Seasonal variation of dissolved Cd in the water column showed an increase in pre monsoon and decline in monsoon. In post monsoon concentration gradient of surface water towards offshore showed an increase while bottom water showed a decline. The concentration gradient in pre monsoon for surface water was comparable towards offshore, while in the case of bottom water it showed an increase. In monsoon it showed an offshore increase in both surface and bottom water. The level of Cd in bottom water was low relative to the surface layer in most of the station for all seasons. The maximum concentration of dissolved Cd of 6.90 µg l^{-1} in surface water was reported at Ponnani while in bottom water it was discerned at Calicut of a concentration of 6.10 µg l^{-1} in monsoon.

4.2.7 Mercury (Hg)

Wide spatio temporal variation was observed in the distribution of dissolved Hg in the water column in the studied transects (Table 4.3, Table 4.4, Fig. 4G). At Cochin, concentration of dissolved Hg (average ± SD) in the surface water varied in the range 0.21 to 0.35 (0.26 ± 0.06), 0.13 to 0.24 (0.18± 0.04) and 0.18 to 0.36 (0.25 ± 0.06) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration of dissolved Hg in bottom water varied in the range 0.16 to 0.36 (0.26 ± 0.07), 0.11 to 0.21 (0.16 ± 0.04) and 0.12 to 0.34 (0.19 ± 0.08) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The level of Hg in the water column was found to be comparable between stations for all seasons.

At Chettuva, concentration of dissolved Hg (average ± SD) in the surface water varied in the range 0.02 to 0.26 (0.10 ± 0.09), 0.02 to 0.13 (0.08± 0.05) and 0.05 to 0.18 (0.09± 0.05) µg l^{-1} in post monsoon, pre monsoon and

monsoon respectively. The concentration of dissolved Hg in bottom water varied in the range 0.01 to 0.26 (0.07± 0.10), 0.01 to 0.26 (0.07± 0.10) and 0.02 to 0.28 (0.08 ± 0.10) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The distribution of Hg in water column showed a comparable pattern in its distribution among season. The concentration gradient generally showed an offshore decrease in all season. The levels of Hg in bottom water were low relative to the surface layer.

At Ponnani, concentration of dissolved Hg (average ± SD) in the surface water varied in the range 0.03 to 0.28 (0.12 ± 0.10), 0.01 to 0.09 (0.05 ± 0.03) and 0.01 to 0.12 (0.05 ± 0.04) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration of dissolved Hg in bottom water varied in the range 0.02 to 0.11 (0.07± 0.03), 0.06 to 0.11 (0.08 ± 0.02) and 0.01 to 0.12 (0.08 ± 0.04) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. Seasonal trend in the distribution of Hg in surface water showed an increase in post monsoon and a decline in monsoon while in bottom water it showed a reverse trend with an increase in monsoon and a decline in post monsoon. In post monsoon the concentration gradient in surface water showed an offshore increase while in bottom water it was comparable. In pre monsoon the concentration gradient in the water column showed an offshore increase, with a vertical gradient having high concentration in bottom water relative to the surface layer. In monsoon the concentration gradient in the water column showed an offshore decrease, with a vertical gradient having high concentration in bottom water relative to the surface layer.

At Calicut, concentration of dissolved Hg (average ± SD) in the surface water varied in the range 0.07 to 0.27 (0.20 ± 0.08), 0.08 to 0.16 (0.11± 0.03) and 0.05 to 0.13 (0.09± 0.04) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration of dissolved Hg in bottom water varied in the range 0.08 to 0.33 (0.16± 0.09), 0.06 to 0.14 (0.08± 0.03) and 0.05 to 0.11 (0.07 ± 0.03) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. Seasonal trend in the distribution of Hg in water column showed an increase in post monsoon and a decline in monsoon. In post monsoon the

concentration gradient of the water column showed an offshore increase while in monsoon it was comparable. In pre monsoon the concentration gradient in the water column showed an offshore decrease. The levels of Hg in bottom water were low relative to the surface layer in all season.

At Kasargod, concentration of dissolved Hg (average ± SD) in the surface water varied in the range 0.03 to 0.17 (0.07 ± 0.05), 0.03 to 0.19 (0.10± 0.07) and 0.01 to 0.08 (0.06± 0.03) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. The concentration of dissolved Hg in bottom water varied in the range 0.03 to 0.13 (0.07± 0.04), 0.03 to 0.15 (0.07± 0.06) and 0.03 to 0.05 (0.03 ± 0.01) µg l^{-1} in post monsoon, pre monsoon and monsoon respectively. Seasonal trend in the distribution of Hg in surface water showed an increase in pre monsoon and a decline in post monsoon. In bottom water the distribution of Hg in surface water showed an increase in post monsoon and a decline in monsoon. In post monsoon the concentration gradient of the water column showed an offshore decrease while in pre monsoon it showed an increase. In monsoon the concentration gradient in the water column showed an offshore decrease. The levels of Hg in bottom water were low relative to the surface layer in all seasons.

The maximum concentration of dissolved Hg of 0.36 µg l^{-1} in surface water was recorded at Cochin in monsoon and the minimum value of 0.01µg l^{-1} at Ponnani in pre monsoon and monsoon and also at Kasargod in monsoon. The maximum concentration of dissolved Hg of 0.36 µg l^{-1} in bottom water was reported at Cochin in monsoon and the minimum value of 0.01 µg l^{-1} was reported at Ponnani in monsoon and also at Chettuva in post monsoon and pre monsoon.

Table 4.3 Concentration of heavy metals (Ni, Zn, Cd, and Hg) in coastal water among transects in different season.

Station Name	Distance from the shore (km)	Source	Ni			Zn			Cd			Hg		
			POM	PM	M	POM	PM	M	POM	PM	M	POM	PM	M
Cochin	0.5	S	7.10	7.41	14.23	4.70	8.20	31.60	2.10	1.30	6.20	0.23	0.16	0.22
		B	2.54	4.12	8.21	3.60	5.20	30.40	0.60	1.10	2.90	0.36	0.21	0.18
	1	S	5.23	8.56	4.56	3.10	6.10	28.80	1.90	1.20	5.50	0.32	0.22	0.26
		B	BDL	6.32	8.74	3.90	4.30	31.20	0.40	1.10	3.10	0.26	0.18	0.19
	3	S	10.95	10.39	BDL	4.17	7.15	20.80	1.40	BDL	4.70	0.35	0.24	0.18
		B	0.00	6.41	8.96	2.45	5.10	19.94	0.20	BDL	1.60	0.28	0.16	0.34
	5	S	7.30	19.50	1.25	7.22	2.45	14.80	2.20	BDL	5.20	0.21	0.16	0.36
		B	BDL	11.17	BDL	5.30	5.49	16.16	3.30	1.10	3.40	0.16	0.13	0.12
	7.5	S	4.30	3.29	2.70	6.50	5.70	16.50	1.90	0.60	3.10	0.21	0.19	0.28
		B	1.70	4.90	3.48	4.28	6.44	17.99	2.10	1.20	1.80	0.20	0.16	0.22
	10	S	3.21	BDL	4.20	11.80	10.53	22.92	1.90	0.90	2.90	0.22	0.13	0.21
		B	16.81	8.50	5.70	9.07	8.14	16.56	2.10	1.30	5.70	0.29	0.11	0.12
Chettuva	0.5	S	7.63	6.32	3.36	3.70	9.10	30.60	0.20	2.70	0.50	0.12	0.12	0.11
		B	8.54	15.60	2.10	3.90	4.70	28.80	1.80	2.90	0.20	0.09	0.09	0.05
	1	S	8.12	5.20	6.89	3.10	8.06	21.90	0.30	1.10	0.60	0.12	0.11	0.08
		B	8.21	11.60	BDL	2.90	5.60	22.30	1.40	2.68	0.20	0.02	0.06	0.03
	3	S	4.21	3.87	5.64	4.38	10.00	21.68	0.10	1.78	0.40	0.26	0.13	0.05
		B	6.63	16.00	0.00	3.31	6.89	19.94	0.81	4.87	0.20	0.26	0.26	0.03
	5	S	3.56	BDL	6.08	3.30	5.89	20.60	0.00	5.20	0.80	0.04	0.04	0.18
		B	0.00	15.56	0.00	1.92	2.90	18.08	1.60	5.50	0.20	0.02	0.02	0.28
	7.5	S	3.90	2.30	6.40	4.18	5.60	21.30	0.00	1.90	0.40	0.04	0.06	0.09
		B	3.24	13.20	0.00	2.10	3.10	18.90	0.98	2.90	0.18	0.04	0.01	0.09
	10	S	4.31	2.10	7.15	5.03	4.32	19.88	0.00	2.31	0.30	0.02	0.02	0.05
		B	4.60	12.36	0.00	3.57	2.70	18.06	3.40	3.80	0.10	0.01	0.01	0.02
Ponnani	0.5	S	2.12	4.31	2.60	4.20	5.90	21.20	0.40	0.80	6.90	0.03	0.02	0.12
		B	1.30	4.16	1.40	3.90	4.80	34.60	0.60	0.60	6.20	0.06	0.11	0.12
	1	S	2.10	5.21	BDL	4.70	6.10	28.40	0.30	0.90	5.30	0.05	0.07	0.08
		B	1.40	1.60	BDL	4.20	5.30	17.90	0.50	0.40	2.70	0.08	0.09	0.11
	3	S	1.20	2.60	BDL	4.10	6.10	18.15	0.10	1.20	6.10	0.12	0.01	0.04
		B	BDL	2.40	BDL	4.70	5.60	21.59	0.00	0.60	7.60	0.07	0.06	0.08
	5	S	1.40	3.12	BDL	3.18	4.20	19.61	0.30	0.31	1.30	0.28	0.06	0.02
		B	BDL	1.56	BDL	2.90	3.40	28.30	0.00	0.20	0.30	0.11	0.07	0.08
	7.5	S	1.10	2.34	0.32	3.80	3.20	23.40	0.30	0.21	1.90	0.19	0.09	0.06
		B	0.90	1.40	BDL	3.10	3.20	13.40	BDL	0.31	0.40	0.11	0.08	0.09
	10	S	0.80	2.66	0.44	3.60	2.40	44.58	0.20	0.10	0.50	0.06	0.05	0.01
		B	0.00	1.00	BDL	3.10	1.90	11.52	BDL	0.40	0.10	0.02	0.07	0.01

Calicut	0.5	S	9.45	5.21	3.25	4.90	9.70	29.60	0.60	5.60	4.60	0.12	0.09	0.13
		B	11.24	2.65	1.23	5.60	5.40	14.90	0.10	3.70	6.90	0.08	0.14	0.11
	1	S	10.25	14.50	3.21	6.10	9.30	27.80	0.40	6.30	4.90	0.07	0.10	0.12
		B	10.23	2.35	BDL	3.70	6.20	19.40	0.20	6.10	5.30	0.11	0.07	0.06
	3	S	8.29	25.77	BDL	2.38	11.53	21.00	0.70	6.10	4.39	0.20	0.16	0.09
		B	8.40	4.53	BDL	6.49	9.60	18.42	BDL	5.00	5.10	0.16	0.07	0.06
	5	S	0.00	13.40	BDL	3.31	11.44	21.59	0.20	3.20	1.80	0.26	0.08	0.06
		B	6.30	2.45	10.70	4.20	6.20	15.37	0.10	2.10	2.20	0.11	0.06	0.11
	7.5	S	1.60	11.80	1.20	3.80	11.22	18.90	0.30	2.30	0.70	0.26	0.09	0.06
		B	7.90	2.90	3.40	5.46	5.80	16.40	0.10	1.80	1.10	0.18	0.07	0.06
	10	S	2.10	12.30	2.54	5.10	12.06	16.89	0.40	2.10	0.10	0.27	0.14	0.05
		B	19.38	2.98	BDL	7.88	5.10	16.09	BDL	1.90	0.10	0.33	0.10	0.05
Kasargod	0.5	S	6.24	11.24	3.24	4.70	5.80	42.40	1.30	2.30	0.60	0.04	0.03	0.04
		B	5.12	6.40	1.54	4.10	2.90	25.30	0.60	1.10	0.40	0.13	0.03	0.03
	1	S	5.26	11.25	2.18	5.10	4.90	36.40	1.20	2.10	BDL	0.04	0.04	0.07
		B	4.10	14.21	BDL	3.20	3.60	29.90	0.40	0.60	BDL	0.10	0.03	0.05
	3	S	9.62	9.62	BDL	4.77	3.29	30.87	1.30	1.19	BDL	0.17	0.19	0.07
		B	13.62	5.42	BDL	5.60	6.82	23.78	0.00	0.81	BDL	0.08	0.15	0.05
	5	S	2.13	3.64	6.42	4.10	4.06	30.67	0.90	2.31	BDL	0.09	0.08	0.08
		B	6.52	2.54	BDL	5.90	3.08	31.14	0.20	1.56	BDL	0.04	0.03	0.03
	7.5	S	3.21	4.20	3.60	4.20	4.32	32.80	1.30	2.06	1.60	0.03	0.10	0.07
		B	5.66	2.54	BDL	5.20	4.12	32.18	0.20	2.20	0.80	0.04	0.04	0.03
	10	S	5.97	5.97	BDL	4.84	5.10	40.34	1.50	2.18	2.30	0.03	0.19	0.01
		B	8.32	3.12	BDL	5.20	4.24	36.25	0.30	6.10	3.60	0.03	0.16	0.03

NOTE: S- surface water, B - bottom water, POM - post monsoon, PM - pre monsoon, M - monsoon

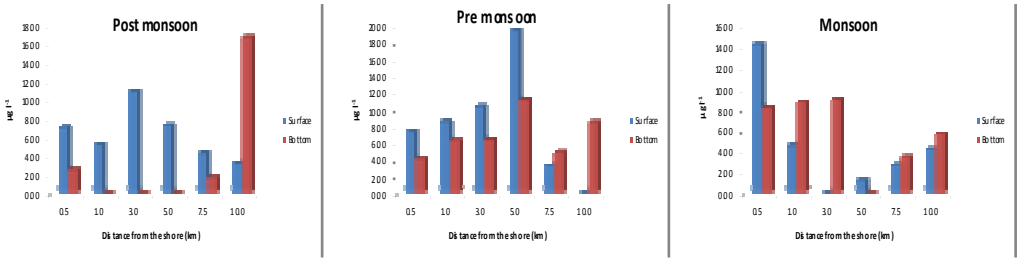
BDL - below detectable limit

Table 4.4 Average concentration ± Standard Deviation (SD) of heavy metals (Ni, Zn, Cd and Hg) in coastal water among transects in different season.

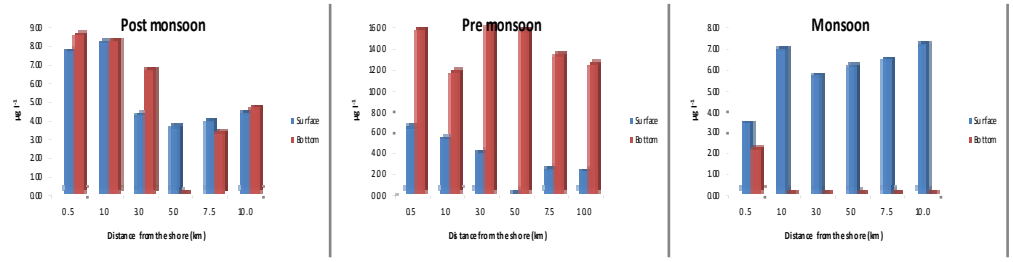
Station Name	Source	Ni			Zn			Cd			Hg		
		POM	PM	M	POM	PM	M	POM	PM	M	POM	PM	M
Cochin													
	S	6.35	8.19	4.49	6.25	6.69	22.57	1.90	0.67	4.60	0.26	0.18	0.25
		±	±	±	±	±	±	±	±	±	±	±	±
		2.75	6.70	5.08	3.11	2.70	6.65	0.28	0.57	1.33	0.06	0.04	0.06
	B	3.51	6.90	5.85	4.77	5.78	22.04	1.45	0.97	3.08	0.26	0.16	0.19
		±	±	±	±	±	±	±	±	±	±	±	±
		6.60	2.57	3.56	2.30	1.35	6.92	1.24	0.48	1.47	0.07	0.04	0.08
Chettuva													
	S	5.29	3.96	5.92	3.95	7.16	22.66	0.10	2.50	0.50	0.10	0.08	0.09
		±	±	±	±	±	±	±	±	±	±	±	±
		2.03	1.83	1.37	0.72	2.22	3.96	0.13	1.43	0.18	0.09	0.05	0.05
	B	5.20	14.05	0.35	2.95	4.32	21.01	1.66	3.77	0.18	0.07	0.07	0.08
		±	±	±	±	±	±	±	±	±	±	±	±
		3.27	1.9	0.86	0.80	1.7	4.13	0.93	1.18	0.04	0.10	0.10	0.10
Ponnani													
	S	1.45	3.37	0.56	3.93	4.65	25.89	0.27	0.59	3.67	0.12	0.05	0.05
		±	±	±	±	±	±	±	±	±	±	±	±
		0.54	1.14	1.02	0.53	1.62	9.83	0.10	0.44	2.75	0.10	0.03	0.04
	B	0.6	2.02	0.23	3.65	4.03	21.22	0.18	0.42	2.88	0.07	0.08	0.08
		±	±	±	±	±	±	±	±	±	±	±	±
		0.68	1.14	0.57	0.73	1.43	8.89	0.29	0.16	3.28	0.03	0.02	0.04
Calicut													
	S	5.28	13.83	1.7	4.27	10.88	22.63	0.43	4.27	2.75	0.20	0.11	0.09
		±	±	±	±	±	±	±	±	±	±	±	±
		4.53	6.69	1.51	1.35	1.11	5.02	0.19	1.95	2.14	0.08	0.03	0.04
	B	10.58	2.98	2.56	5.56	6.38	16.76	0.08	3.43	3.45	0.16	0.08	0.07
		±	±	±	±	±	±	±	±	±	±	±	±
		4.65	0.8	4.2	1.52	1.64	1.77	0.08	1.81	2.70	0.09	0.03	0.03
Kasargod													
	S	5.40	7.65	2.57	4.62	4.58	35.58	1.25	2.02	0.75	0.07	0.10	0.06
		±	±	±	±	±	±	±	±	±	±	±	±
		2.62	3.48	2.44	0.39	0.88	4.98	0.20	0.42	0.98	0.05	0.07	0.03
	B	7.22	5.71	0.26	4.86	4.13	29.76	0.28	2.06	0.80	0.07	0.07	0.04
		±	±	±	±	±	±	±	±	±	±	±	±
		3.44	4.46	0.63	1.02	1.42	4.59	0.20	2.06	1.41	0.04	0.06	0.01

NOTE: S- surface water, B - bottom water, POM - post monsoon, PM - pre monsoon, M - monsoon

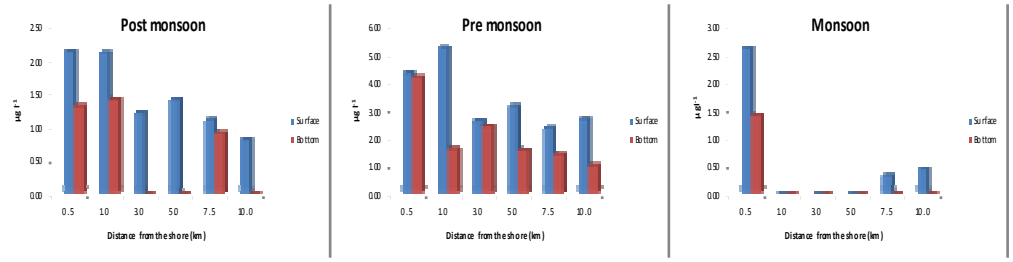
Cochin



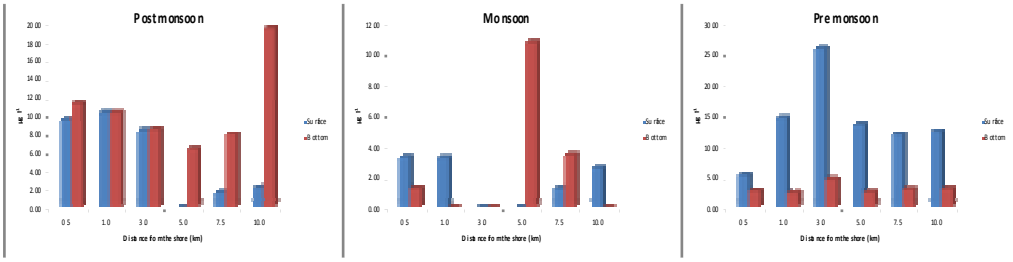
Chettuva



Ponnani



Calicut



Kasargod

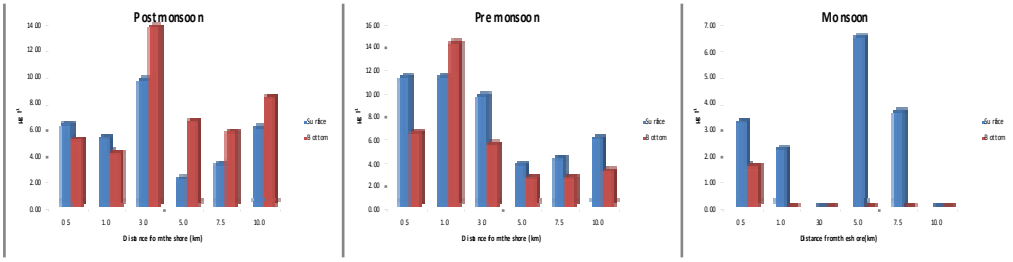
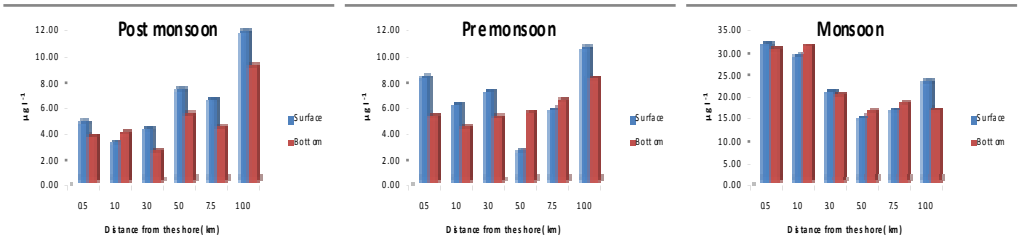


Figure 4D. Seasonal variation of dissolved Nickel (Ni) in coastal water among different transects.

Cochin



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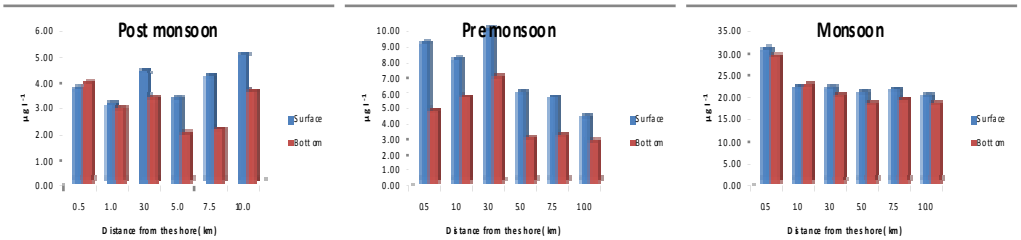
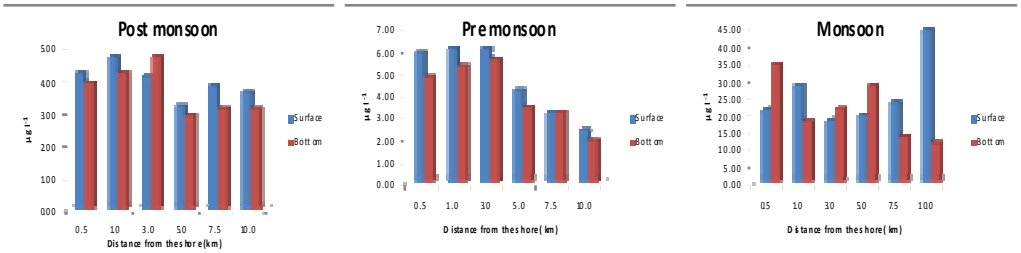
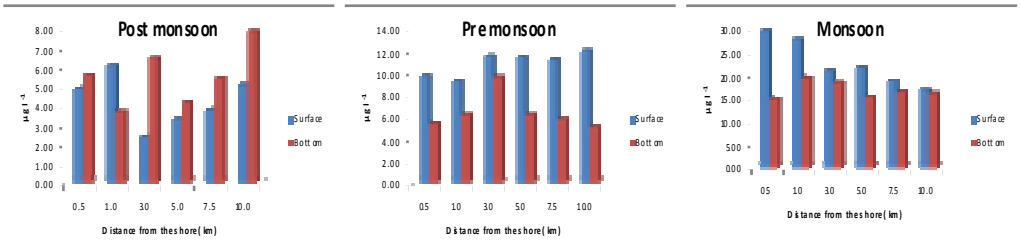


Ponnani



Calicut



Kasargod

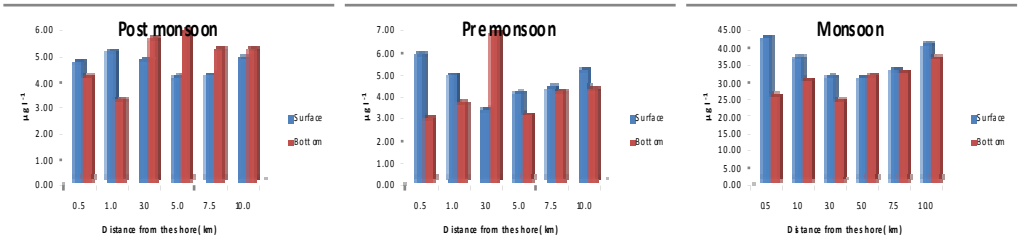
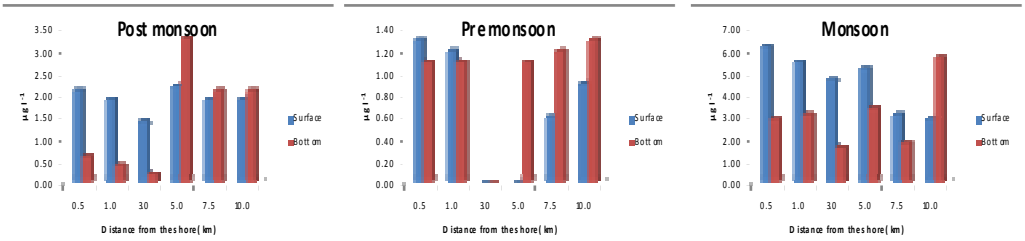
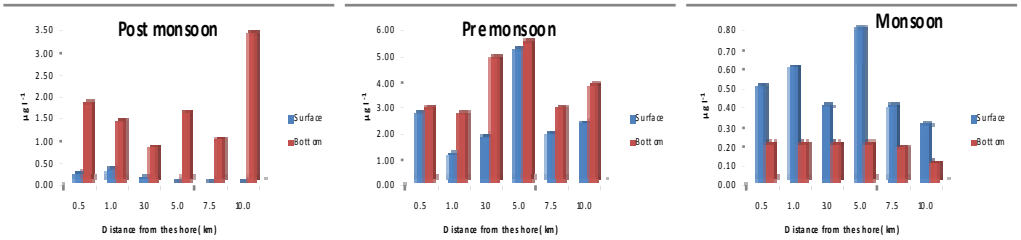


Figure 4E. Seasonal variation of dissolved Zinc (Zn) in coastal water among different transects.

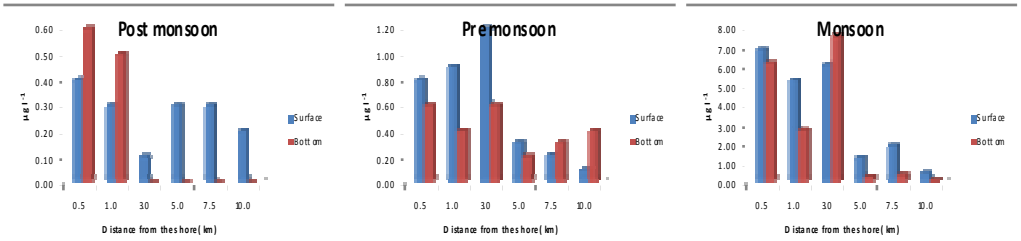
Cochin



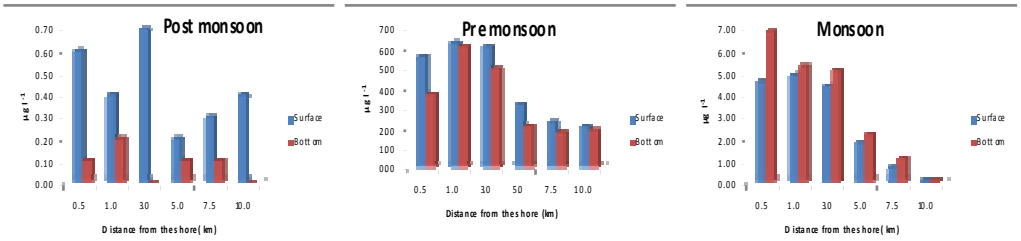
Chettuva



Ponnani



Calicut



Kasargod

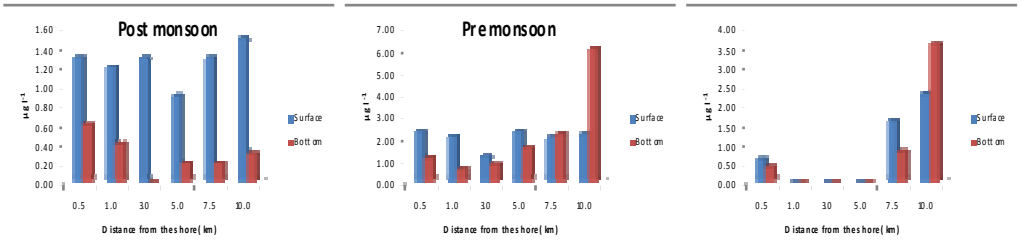
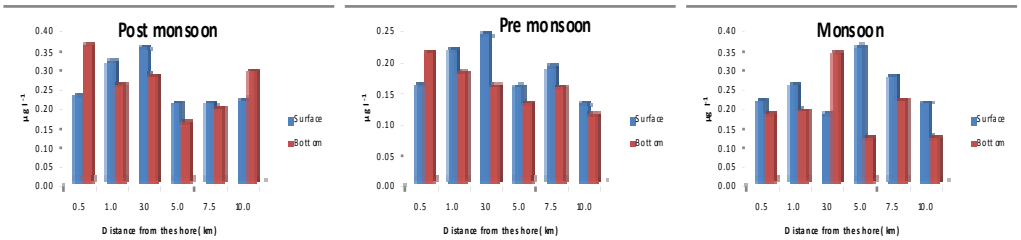
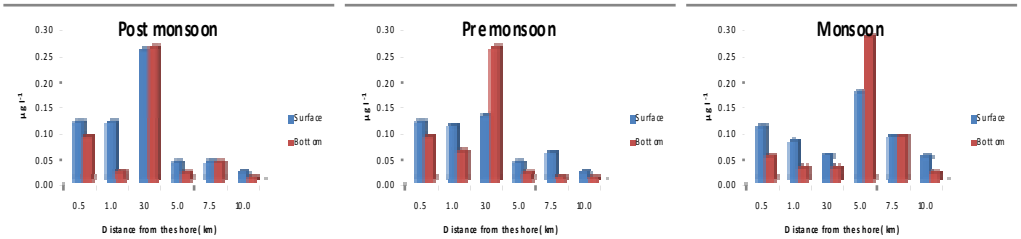


Figure 4F. Seasonal variation of dissolved Cadmium (Cd) in coastal water among different transects.

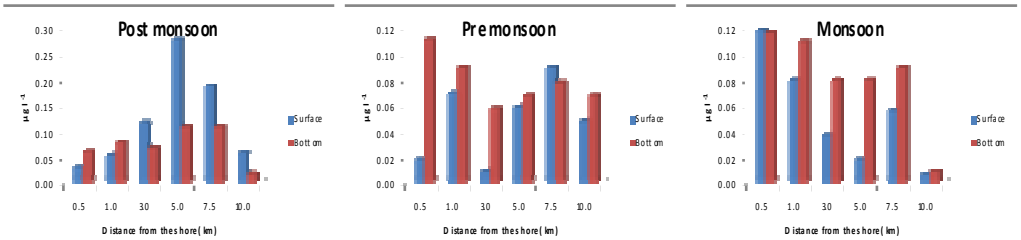
Cochin



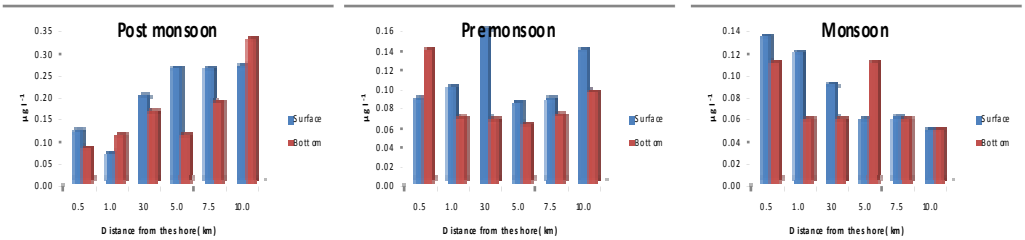
Chettuva



Ponnani



Calicut



Kasargod

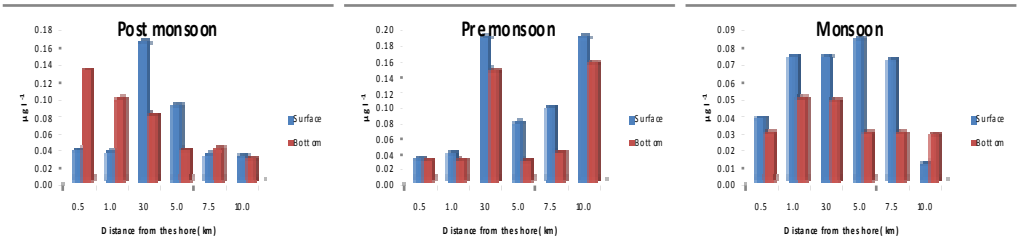


Figure 4G. Seasonal variation of dissolved Mercury (Hg) in coastal water among different transects.

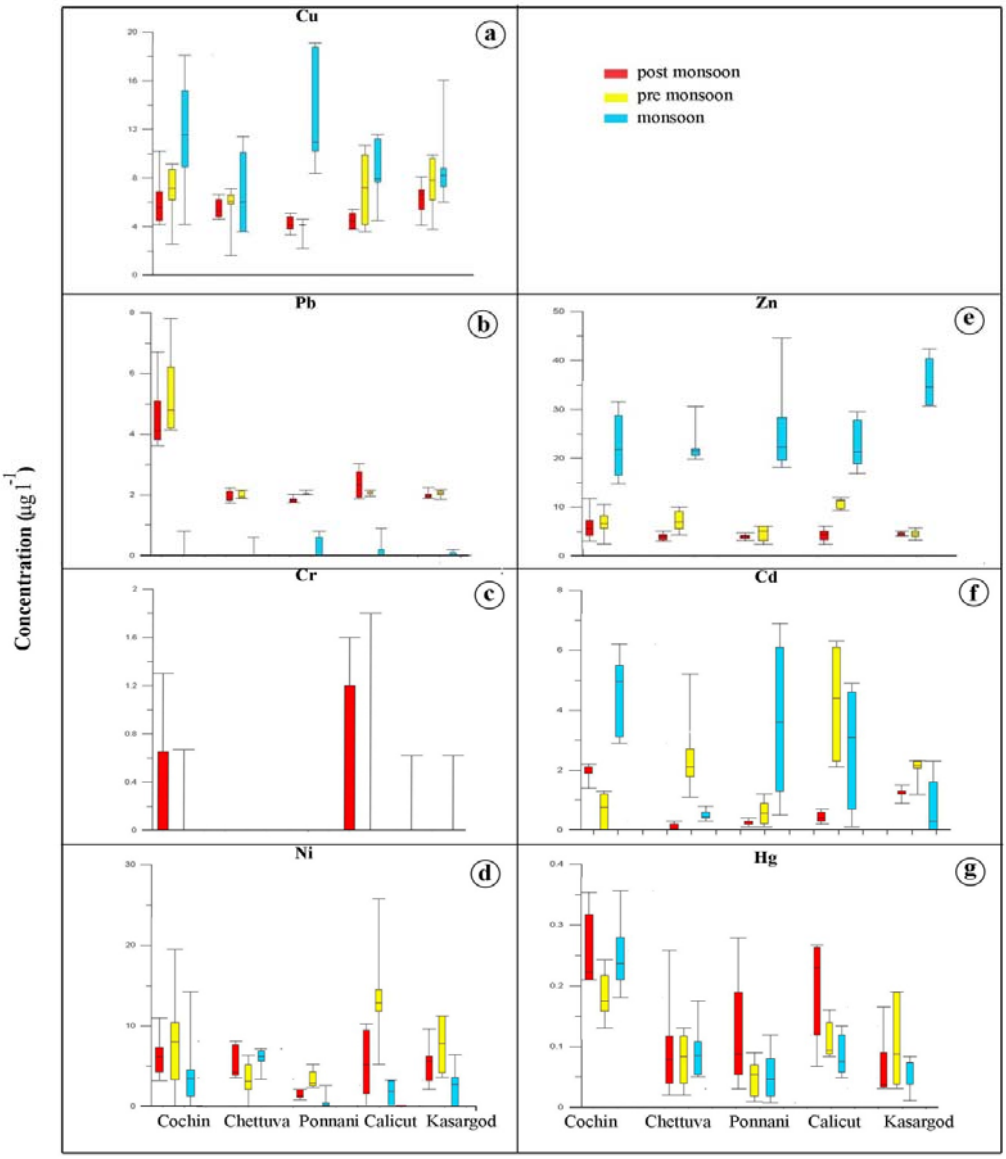


Figure 4H. Dissolved metal concentration (µg l^{-1}) in surface water along the central and northern coast of Kerala shown through box whisker plot.

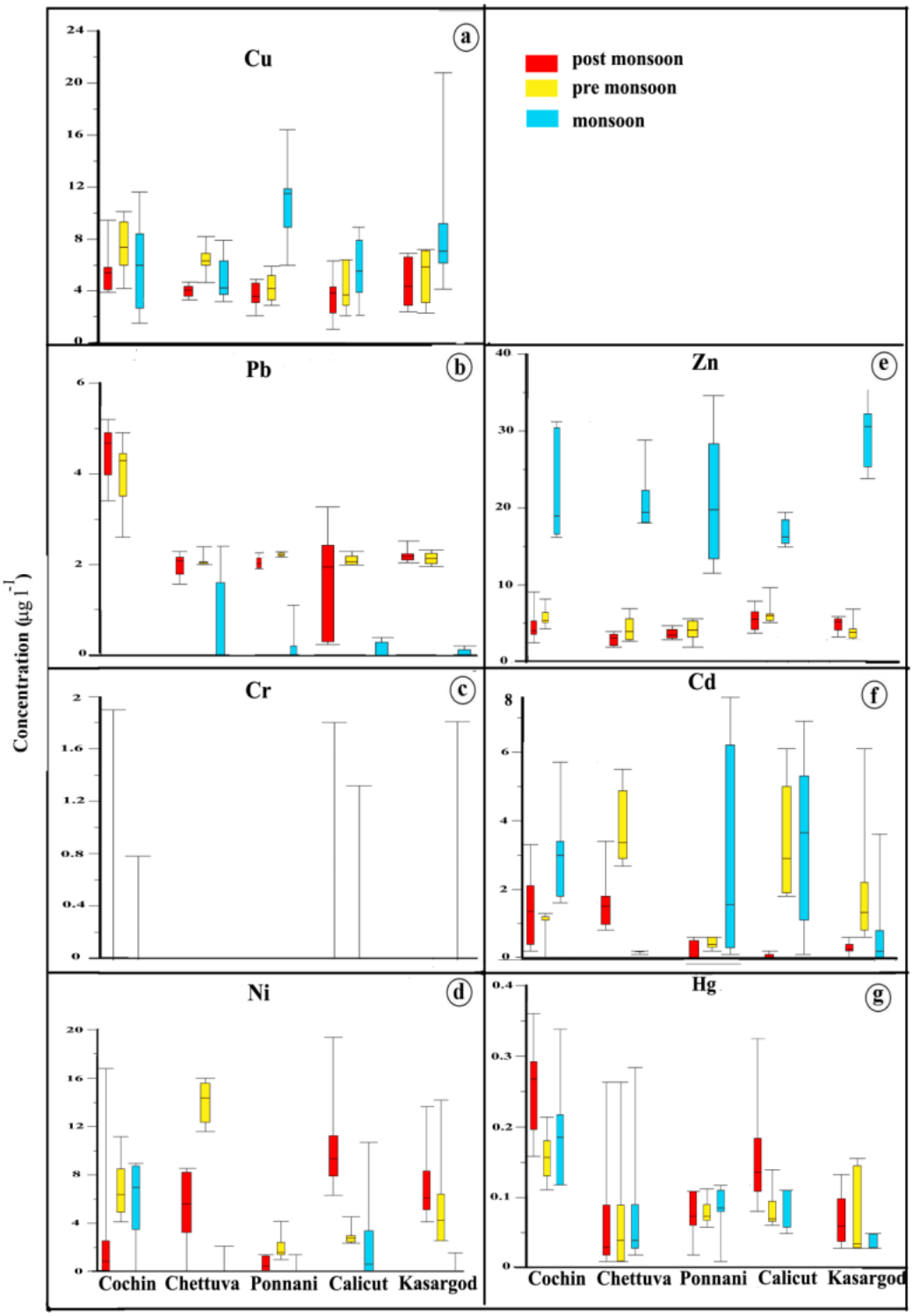


Figure 4I. Dissolved metal concentration (µg l^{-1}) in bottom water along the central and northern coast of Kerala shown through box whisker plot.

4.3 Discussion

Heavy metals such as Cu, Pb, Cr, Ni, Zn, Cd and Hg were found in the coastal waters in detectable levels and at varying concentrations among different seasons. The sources of metals in water and its relation to higher population densities, agricultural wastes, urbanization and industrialization are well documented (Salomons and Fostner, 1984; Furness and Rainbow, 1990). In the whole study area, the seasonal average concentrations of the analyzed heavy metals in surface water followed (in decreasing order) 3.93–35.58 $\mu g\ l^{-1}$ for Zn, 0.56–13.83 $\mu g\ l^{-1}$ for Ni, 3.88–13.06 $\mu g\ l^{-1}$ for Cu, 0.05–5.33 $\mu g\ l^{-1}$ for Pb, 0.10–4.60 $\mu g\ l^{-1}$ for Cd, BDL–0.47 $\mu g\ l^{-1}$ for Cr and 0.05–0.26 $\mu g\ l^{-1}$ for Hg (Fig. 4H). In bottom water it followed 2.95 – 29.76 $\mu g\ l^{-1}$ for Zn, 0.23 – 14.05 $\mu g\ l^{-1}$ for Ni, 3.61 – 11.02 $\mu g\ l^{-1}$ for Cu, BDL – 4.47 for Pb, 0.08 – 3.77 $\mu g\ l^{-1}$ for Cd, BDL – 0.32 $\mu g\ l^{-1}$ for Cr and 0.035 – 0.257 $\mu g\ l^{-1}$ for Hg (Fig. 4I). Concentrations of the dissolved metals measured in the coastal waters of central and northern coast of kerala were within the ranges reported for other areas of the world and the region is not as much polluted as the other coastal waters of India (Table 4.5).

Seasonal variation in the mean concentrations of metals in surface water showed a high trend for Cu (6.78–13.06 $\mu g\ l^{-1}$) at all transects during monsoon and low (4.21–6.32 $\mu g\ l^{-1}$) during post monsoon except at Ponnani. This may be due to the presence of major sources of metal pollution through agricultural runoff and sewage outlets. Phytoplankton activity might also facilitate the seasonal variation in Cu, as this metal is an essential element for their growth (Tada *et al.*, 2001). High concentrations of Cu recorded during monsoon, can be attributed to land run-off carrying the washing of polluted land surface area. In addition the extensive use of antifouling paint residues arising from boat maintenance and vessel repair would have released cuprous oxide which in turn enriches the Cu content in water. Bottom water also exhibited similar variation as that of surface water due to the shallowness and turbulence of the water column.

Table 4.5 Average heavy metal concentration (µg l^{-1}) found in coastal waters from various regions of the world.

Location	Cu	Pb	Cr	Ni	Zn	Cd	Hg	Reference
Kerala coast,India	3.88-13.06	0.05-5.33	BDL -0.47	0.56 - 13.83	3.93 -35.58	0.10 - 4.60	0.05-0.26	Present study
Arabian Sea	2.50 - 7.90	-		BDL - 11.50	5.50 - 42.40	-	-	Sen Gupta *et al.*, 1978
Velsao Bay, India	6.0 - 8.0	BDL	-	BDL	11.0 - 16.0	-	-	Zingde *et al.*, 1979
Andaman sea	1.0 - 5.0	BDL - 6.20		-	2.1- 12.7	0.3 -2.0		Sanzgiri and Braganga, 1981
Bay of Bengal, India	1.20 -17.50	-	-	0.80-30.30	1.90 - 174.0	0.30 -2.90	0.05 - 0.30	Qasim and Sen Gupta, 1983
Mahim Coast, India	12.0 - 15.0	-	-	3.0 - 6.0	103.0 - 121.0			Sabnis, 1984
Pondicherry Coast,India	0.70 -61.50	-	-	ND - 14.80	16.70 - 135.70	3.20 - 69.00	ND - 0.15	Govindasamy *et al.*, 1997
Coromandel coast,India	0.31 -50.70	-	-	ND-14.60	9.00-130.60	0.30 -66.80	ND -0.12	Govindasamy and Azariah,1999
Greek coastal waters	0.03-20.7	0.03-12.2	-	0.06-41.9	0.02-120	0.002-2.3	-	Dassenakis *et al.*, 1996
Coastal Mediterranean Sea	0.01-50	0.016-20.5	-	-	0.20-210	0.002-0.9	-	UNEP, 1996
Northern Indian Ocean	-	0.04 - 0.50	-	-	-	0.04 - 0.26		Sen Gupta and Qasim, 2001
Southern Adriatic Sea (Apulia)	0.50-5.00	0.04-2.93	-	0.11-1.26	0.07-20.94	0.01-0.25	-	Accornero *et al.*, 2004
Basque coast	0.20-15.0	0.30- 68.0	2.0-5.0	0.30-8.50	1.10-454	0.2-11.0	0.30-3.0	Maria *et al.*, 2004
Indian Ocean	3.5	3.0		3.0	9.5	0.17		Nakatsuka *et al.*, 2007

NOTE: BDL:- below detectable limit; ND ; non detectable

The mean concentration of dissolved Cu in bottom water exhibited a high trend (4.94 – 11.02 µg l^{-1}) in monsoon and low (3.61 –5.67 µg l^{-1}) in post monsoon in the study area. In unpolluted coastal waters Cu have levels in the range of 2–5 µg l^{-1}, while its concentration greater than 30 µg l^{-1} are categorized as contamination and a range of 80–160 µg l^{-1} can significantly reduce algal biomass (Hoare *et al.*, 1995; Le jeune *et al.*, 2007). In the present study the coastal region is moderately polluted with Cu and the increased concentration during monsoon cannot produce a direct effect on the primary producer.

Lead (Pb) is an extremely reactive element; it is removed from the water column through its association with particulates and subsequent sedimentation. It is classified as a scavenged element. Mainly dissolved Pb is derived from industrial discharges and a significant input of Pb originates from atmospheric contamination (Maria *et al.*, 2004). Concentration of Pb showed a relatively restricted range of variability and an even distribution throughout the study area. However, the seasonal average value of Pb in surface water was found to be high at Cochin (0.13–5.33 µg l^{-1}) and Calicut (0.18–2.37 µg l^{-1}) due to intense boat trafficking, industrial and harbour activities. During monsoon Pb concentration was low in surface (0.05–0.23 µg l^{-1}) and bottom water (BDL – 0.66 µg l^{-1}) in studied transects where much of it may be removed from the surface water by organic matter through deposition brought by monsoonal flushing. In general, dissolved Pb is highly homogeneous, both spatially and vertically, in the water column of the Kerala coast. Combined effects of atmospheric deposition, which prevents surface depletion, and active vertical mixing, which attenuates surface enrichment may be a plausible explanation. Anthropogenic input of lead into these coastal waters seems to be insignificant, as very high concentrations are not encountered at any transects except at Cochin, where its level is intensified by industrial discharges and port activities.

Chromium was not detectable in all transects, though low concentration was observed in the water column at Cochin and Calicut in the near shore region of 0.5 and 1.0 km from the coast. This can be due to industrial influence. In monsoon Cr was detected in the surface waters at 10.0 km off and in bottom

water at 5.0 km off from the coast of Kasargod. This could be due to some point discharges or diagentic processes in the sediments leading to the release of Cr into the water column. In aquatic environment Cr is found as Cr (III) and Cr (VI) as water soluble complex anions. Information on the geochemical behavior of Cr in seawater is limited. Chromium is known to have no major biochemical function, and it is therefore not surprising that many species of plankton do not concentrate Cr to any greater extent. Chromium is known to decrease rapidly during fresh water– sea water mixing either as particulate Cr or precipitation as chromium hydroxide (Mayer, 1988). The meager presence of Cr in the coastal waters does not mean that it is being absent or not being added to the environment. Enrichment of Cr in the southwest coastal sediments has been well documented (Balachandran *et al.*, 2005). A plausible explanation in the present study can be the removal of Cr by precipitation and deposition in sediments.

The concentration of Ni did not show a seasonal trend, but much variation in its surface layer concentration (3.37–13.83 µg l^{-1}) was observed during pre monsoon and relatively low concentration (0.56–5.92 µg l^{-1}) during monsoon in the study area. A similar seasonal variation was also observed in bottom waters due to the shallowness and vertical mixing of the water column. The mean concentration in bottom waters was discerned to be 2.02 – 14.05 µg l^{-1} and 0.23 – 5.85 µg l^{-1} for pre monsoon and monsoon respectively. The depletion and enrichment of Ni can be attributed to its involvement in the biogeochemical cycling resulting in its removal from surface waters by plankton or biologically produced particulate matter and subsequent regeneration either by oxidation and resolubilisation in the bottom water. This can be the reason for higher mean value of Ni observed in bottom waters in addition to the diagenetic processes occurring at the sediment water interface.

Bottom sediments tend to accumulate metals and affect the near bottom layer due to resuspension and dissolution processes (Khan *et al.*, 1998). The mean concentration in surface water was relatively high at Cochin (4.49–8.19 µg l^{-1}) and Calicut (1.70–13.83 µg l^{-1}) compared to other

transects due to the inflow of untreated effluents from harbor activities, urban agglomeration and various industrial assortments situated along the coastal belt of this region. Nonetheless, laboratory data demonstrate that Ni is necessary for the assimilation of urea for phytoplankton proliferation and should exhibit a surface depletion characteristic of nutrients (Price and Morel, 1991). However, the high surface concentration of Ni in the study area is perplexing. Despite marine phytoplankton need for Ni to assimilate urea, it may be unable to deplete the nickel concentration of surface sea- water simply because of the kinetic inertness of the Ni^{2+} ion (Hudson *et al.*, 1992).

Zinc showed a definite seasonal pattern with low concentration (3.93–6.25 µg l^{-1}) during post monsoon and high concentration (22.57–35.58 µg l^{-1}) during monsoon. Zinc could get strongly depleted from the surface waters as it has a nutrient type distribution in sea water (Govindasamy and Azariah, 1999). The low concentration might have resulted due to the increased utilization by biota including phytoplankton. Diatoms playing an important role in the biogeochemical cycling of Zn have been documented (Bruland *et al.*, 1978). The primary role of Zn acting as metal centre in the transport of $Si(OH)_4$ for silica frustules formation in diatoms is well studied (Hildebrand, 2000). The very large local variations in the diatoms arising due to the increased concentration of silicate during monsoon and its significant contribution to the phytoplankton community throughout the season in the southwest coastal waters has been reported (Venkataraman and Wafar, 2005). The major involvement of diatoms in phytoplankton production and their remineralization might have led to the increased concentration of Zn at all transects in the Kerala coastal waters during monsoon besides land based discharges in this study. A similar seasonal variation was also observed in bottom waters due to the shallowness and vertical mixing of the water column. The mean concentration in bottom waters was discerned to be 2.95 – 5.56 µg l^{-1} and 16.76 – 29.76 µg l^{-1} for post monsoon and monsoon respectively.

The concentration of Cd exhibited a wider variation (0.50–4.60 µg l^{-1}) during monsoon, and pre monsoon (0.59 – 4.27 µg l^{-1}) while its variation was

low (0.10–1.90 µg l^{-1}) in post monsoon. A similar mean variation was observed in bottom water with a range of 0.08 – 1.66, 0.42 – 3.77 and 0.18 – 3.45 µg l^{-1} during post monsoon, pre monsoon and monsoon respectively due to the shallowness and vertical mixing of the water column. The mean value in surface water was high at Cochin during post monsoon (1.90 µg l^{-1}) and monsoon (4.60 ppb). Cadmium is released into the atmosphere by fossil fuel and by the burning of agricultural and municipal wastes including dried sewage sludge and industrial wastes (Mart and Nurnberg, 1986). These activities are relatively prominent at Cochin, facilitating high input of Cd into the coastal waters. In general, a high value of Cd concentration during monsoon season at all transects appear to be related to monsoon flushing bringing agricultural runoff, urban wastes and industrial discharges. An Increase in mean concentration of Cd (4.27 µg l^{-1}) in surface water was observed at Calicut in pre monsoon compared to other transects, this increase can be attributed due to the discharges of urban and metal processing effluents from the hinterland in which rivers act as vectors finally impinging into the coastal water as Calicut represents one of the industrially advanced and urbanized region.

Mercury did not show any seasonal trend; its concentration being relatively identical in surface and bottom waters at all transects except at Cochin where it's mean value was high (0.16–0.26 µg l^{-1}) in the water column during all seasons due to industrial influence. An increase in the mean value of Hg (0.20 µg l^{-1}) in surface water and 0.16 µg l^{-1} in bottom water was noted at Calicut during post monsoon. This may be due to some point discharges.

The concentration gradient of dissolved metals from shore to offshore showed an erratic pattern in its distribution in all transects. Metals introduced into the sea through fluvial waters, the atmosphere, or advective water transport, forming a balance between sedimentation processes, incorporation by organisms and advection/diffusion are documented (Salomons and Fostner, 1984). The dynamics of the metals in the water, in terms of advection/diffusion, and rapid transfer of dissolved or particulate metals to different matrices could be the reason for the metals irregular distribution. Lastly, the sea itself may be a

major source, by accumulating metals from atmospheric fallout over the large area of the coastal shelves and carrying them landward with the tide.

As per the quality criteria (QC) for dissolved metals in coastal waters defined by EPA and values furnished by European directives, a concentration greater than 1 µg l^{-1} for Cu, 2 µg l^{-1} for Pb, 12 µg l^{-1} for Cr, 2 µg l^{-1} for Ni, 20 µg l^{-1} for Zn, 0.5 µg l^{-1} for Cd and 0.3 µg l^{-1} for Hg represents contamination due to metals (Maria *et al.*, 2004). The number of samples and the percentage of samples that exceed the QC for each variable analyzed using the above criteria in each transect for surface water are summarized in Table 4.6. It followed the order Cochin > Kasargod > Chettuva > Calicut >Ponnani. The high percentage 53.97%, observed at Cochin is probably due to industrial influence, urbanization and port activities. While, at other transects it mainly results from the metal residue brought through agricultural runoff and contribution from small scale industries situated in the hinterland which impinges into the coastal water through freshwater bodies. In general, on the basis of the total number of water samples analyzed along the central and northern coast of Kerala, 100% samples exceed the established QC value for Cu; around 77.78% and 67.78% exceeded that for Ni and Cd respectively. A relatively good number of the samples (44.44%) reached the QC established for Pb; Zn and Hg registered low values, while Cr remained without any contribution. The variations obtained in QC for dissolved metals in bottom water were similar to that observed in surface waters due to the shallowness and vertical mixing of the water column (Table 4.7). It also followed the order Cochin > Kasargod > Chettuva > Calicut >Ponnani. In general, on the basis of the total number of bottom water samples analyzed along the central and northern coast of Kerala, 100% samples exceed the established QC value for Cu; around 58.89% exceeded each for Ni and Cd. For Pb 56.67% of samples reached the QC and was the sole metal which exceeded the contribution than that in surface water; Zn and Hg registered low values of 14.44% and 2.22% respectively, while Cr remained without any contribution.

Table 4.6 Number of Surface water samples (N) which exceed the Quality Criteria (QC), for each variable in each of the coastal transects, together with the total percentage of variables that exceed the QC in central and northern coast of Kerala.

Transect	Cu	Pb	Cr	Ni	Zn	Cd	Hg	N	%
Cochin	18(6,6,6)	12(6,6,0)	0	15(6,5,4)	04(0,0,4)	16(6,4,6)	03(2,0,1)	68	53.97
Chettuva	18(6,6,6)	04(2,2,0)	0	17(6,5,6)	05(0,0,5)	09(0,6,3)	00(0,0,0)	53	42.06
Ponnani	18(6,6,6)	07(1,6,0)	0	09(2,6,1)	04(0,0,4)	08(0,2,6)	00(0,0,0)	46	36.51
Calicut	18(6,6,6)	09(4,5,0)	0	13(4,6,3)	04(0,0,4)	13(2,6,5)	00(0,0,0)	57	45.24
Kasargod	18(6,6,6)	08(3,5,0)	0	16(6,6,4)	06(0,0,6)	15(6,6,3)	00(0,0,0)	63	50.00
N	90	40	0	70	23	61	3		
%	100	44.44	0	77.78	25.56	67.78	3.33		

Values given in bracket are samples which exceeded the QC in each season (post monsoon, pre monsoon, monsoon).

Table 4.7 Number of bottom water samples (N) which exceed the Quality Criteria (QC), for each variable in each of the coastal transects, together with the total percentage of variables that exceed the QC in central and northern coast of Kerala.

Transect	Cu	Pb	Cr	Ni	Zn	Cd	Hg	N	%
Cochin	18(6,6,6)	12(6,6,0)	0	13(2,6,5)	02(0,0,2)	15(4,5,6)	02(1,0,1)	62	49.21
Chettuva	18(6,6,6)	11(4,6,1)	0	12(5,6,1)	02(0,0,2)	11(6,6,0)	00(0,0,0)	54	42.86
Ponnani	18(6,6,6)	09(3,6,0)	0	2(0,2,0)	03(0,0,3)	07(2,2,3)	00(0,0,0)	39	30.95
Calicut	18(6,6,6)	08(3,5,0)	0	14(6,6,2)	00(0,0,0)	11(0,6,5)	00(0,0,0)	51	40.48
Kasargod	18(6,6,6)	11(6,5,0)	0	12(6,6,0)	06(0,0,6)	09(1,6,2)	00(0,0,0)	56	44.44
N	90	51	0	53	13	53	2		
%	100	56.67	0	58.89	14.44	58.89	2.22		

Values given in bracket are samples which exceeded the QC in each season (post monsoon,pre monsoon, monsoon).

In order to identify the relative importance of dissolved heavy metals in the study area, the concentrations of dissolved metals of each transect were compared with those considered for minimal risk concentration of metals reported for water quality criteria (WQC, 1972). A concentration of 10 ppb for Cu, 10 ppb for Pb, 50 ppb for Cr, 2 ppb for Ni, 20 ppb for Zn, 10 ppb for Cd, 0.10 ppb for Hg represents minimal risk of deleterious effect. Enrichment

factors (Ef) for each metal was determined by comparing the observed dissolved metal concentration over minimal risk concentration of heavy metals reported for water quality criteria. Ef values greater than 1 indicate the enrichment of the waters with metals, relative to the water quality criteria. Table 4.8 present the percentage of surface water samples showing Ef values greater than one at each transect. Lead, Cd and Cr metals registered low Ef values, while Cu, Ni, Zn and Hg showed enrichment. The surface waters in terms of enrichment of metals along the central and northern coast of Kerala followed the order Cochin > Chettuva > Calicut > Kasargod > Ponnani. The high enrichment at Cochin (32.54%) can be attributed to various industrial assortments situated along the coastal belt. It is not surprising that the essential elements Cu (16.67%) and Zn (25.56%) showing enrichment, while the presence of Ni (77.78%) and Hg (47.78%) may possess some ecotoxicological risks for organism inhabiting these waters. Table 4.9 present the percentage of bottom water samples showing Ef values greater than one at each transect. A different trend was observed in terms of enrichment in bottom water as compared to surface water. It followed the order Cochin > Calicut > Kasargod > Chettuva > Ponnani. This variation may be due to the diagenetic changes taking place at the sediment water interface leading to the sorption and release of metals. The dissolved metals that contributed towards bottom water enrichment were similar to that of the surface. However, there was a decrease in the percentage of samples contributing towards enrichment compared to that of surface water. The essential elements Cu (7.78 %) and Zn (14.44%) showed a low enrichment, while the presence of Ni (58.89%) and Hg (42.22%) may possess some ecotoxicological risks for bottom dwelling organism. A recent study has revealed increased bioaccumulation of Cu, Zn, and Ni in both demersal and pelagic fishes due to enhanced bioavailability of these metals along the southwest coast of India (Rejomon *et al.*, 2010). The present study bears testimony to this recent finding.

Table 4.8 Number of surface water samples (N) which exceed the minimal risk concentration (MRC) of heavy metals, for each variable in each of the coastal transects, together with the total percentage of variables that exceed the MRC in central and northern coast of Kerala.

Transect	Cu	Pb	Cr	Ni	Zn	Cd	Hg	N	%
Cochin	04(1,0,3)	0(0,0,0)	0(0,0,0)	15(6,5,4)	04(0,0,4)	0(0,0,0)	18(6,6,6)	41	32.54
Chettuva	02(0,0,2)	0(0,0,0)	0(0,0,0)	17(6,5,6)	05(0,0,5)	0(0,0,0)	08(3,3,2)	32	25.40
Ponnani	05(0,0,5)	0(0,0,0)	0(0,0,0)	9(2,6,1)	4(0,0,4)	0(0,0,0)	04(3,0,1)	22	17.46
Calicut	03(0,1,2)	0(0,0,0)	0(0,0,0)	13(4,6,3)	4(0,0,4)	0(0,0,0)	9(5,2,2)	29	23.01
Kasargod	01(0,0,1)	0(0,0,0)	0(0,0,0)	16(6,6,4)	6(0,0,6)	0(0,0,0)	03(1,2,0)	26	20.63
N	15	0	0	70	23	0	42		
%	16.67	0	0	77.78	25.56	0	46.67		

Values given in bracket are samples which exceeded the MRC in each season (post monsoon, pre monsoon, monsoon).

Table 4.9 Number of bottom water samples (N) which exceed the minimal risk concentration (MRC) of heavy metals, for each variable in each of the coastal transects, together with the total percentage of variables that exceed the MRC in central and northern coast of Kerala.

Transect	Cu	Pb	Cr	Ni	Zn	Cd	Hg	N	%
Cochin	2(0,1,1)	0(0,0,0)	0(0,0,0)	13(2,6,5)	02(0,0,2)	0(0,0,0)	18(6,6,6)	35	27.78
Chettuva	0(0,0,0)	0(0,0,0)	0(0,0,0)	12(5,6,1)	02(0,0,2)	0(0,0,0)	3(1,1,1)	17	13.49
Ponnani	4(0,0,4)	0(0,0,0)	0(0,0,0)	02(0,2,0)	03(0,0,3)	0(0,0,0)	5(2,1,2)	14	11.11
Calicut	0(0,0,0)	0(0,0,0)	0(0,0,0)	14(6,6,2)	0(0,0,0)	0(0,0,0)	9(5,2,2)	23	18.25
Kasargod	1(0,0,1)	0(0,0,0)	0(0,0,0)	12(6,6,0)	06(0,0,6)	0(0,0,0)	3(1,2,0)	22	17.46
N	7	0	0	53	13	0	38		
%	7.78	0	0	58.89	14.44	0	42.22		

Values given in bracket are samples which exceeded the MRC in each season (post monsoon, pre monsoon, monsoon).

4.4 Conclusion

Results clearly indicated that seasonal variability plays an important role in accentuating the distribution of dissolved metals in coastal waters. Metals like Cu, Zn and Cd received by the coastal water, varied seasonally, with

minimum distribution occurring in post monsoon and maximum in monsoon season. Concentration of Pb showed a relatively restricted range of variability and Ni showed increased concentration in pre monsoon reflecting its involvement in biological production. Chromium was not detectable in all transects though low concentration was observed in the water column at Cochin and Calicut and its meager presence in coastal water could be the removal of Cr by precipitation and deposition in sediments. Mercury did not show any seasonal trend; its concentration being relatively identical in surface and bottom waters at all transects. A similar seasonal variation as that of surface water was also observed in bottom waters due to the shallowness and vertical mixing of the water column. There were instances in which bottom water showed higher concentration of dissolved metal compared to surface layer. It reveals the propensity of these metal reserves in sediments by organic matter deposition to be remobilized; resulting due to digenesis at the sediment water interface. Concentrations of the dissolved metals measured in the coastal waters of central and northern coast of Kerala were comparable with other worldwide ranges and the region is not as much polluted as the other coastal waters of India. As per the quality criteria used to assess the heavy metal contamination in the investigated area revealed contamination of heavy metals in the order Cu> Ni >Cd > Pb> Zn in all the transects. Contamination due to Hg in the coastal water was discerned only at Cochin. Among the transects increased anthropogenic activities noticed along the coast at Cochin might certainly turn it as a hotspot location in terms of land based heavy metal pollution. It was followed by Kasargod, Chettuva, Calicut and Ponnani. The levels of Cu, Ni, Zn and Hg exceeded the limits furnished for minimal risk concentration for heavy metals in all transects as such these metals can pose ecotoxicological risk to organism inhabiting in the waters of the central and northern coast of Kerala.

Chapter 5

HEAVY METALS IN MARINE SEDIMENT

5.1	Introduction
5.2	Results
5.3	Discussion
5.4	Conclusion

5.1 Introduction

Environmental pollution by metals is a major concern worldwide because of the continuous growth of urbanization and industrial development (Alemdaroglu *et al.*, 2003; Heyvaert, 2000). The concern of heavy metals in marine environment is due to their toxicity, persistence and bioaccumulation problems (Tam and Wong, 2000). Metals in marine sediments have a natural or anthropogenic origin and the relative importance of these two sources depends on the metal and its location. Coastal ecosystems are often vulnerable to anthropogenic metal inputs of wide range of chemical compounds of modern society. Once in the water column, metals are quickly adsorbed on to particulate matter and eventually removed to bottom sediments (Groot *et al.*, 1982; Santschi *et al.*, 1984; Blake *et al.*, 2004) thus producing conspicuous metal enrichment. The fate and behavior of the metals are influenced by the characteristics of the sediment, the mineralogical composition, redox state, sorption processes and physical transport. Although, sediments are the main sink for various pollutants, including metals discharged into the environment (Williams *et al.*, 1996; Balls *et al.*, 1997; Dassenakis *et al.*, 1997; Tam and Wong, 2000; Bettinetti *et al.*, 2003) they can also play a significant role in the remobilization of contaminants to the overlying water column under favorable conditions. Furthermore, the burrowing activity of macroinvertebrate organisms in sediments can influence the fluxes of solutes and particles from sediment to water. In foraging, they inadvertently ingest sediments, which accounts for the metal body burden in several deposit feeding invertebrates. Therefore, the metals become available to marine organism and can be channeled to humans through food chain. The prevalent tribulations with heavy metals are that they have long biological half life and they bioaccumulate in time periods (Anu *et al.*, 2010). It is thus pertinent that metal contamination on coastal areas should be monitored as they form the highly productive as well as sensitive areas and also the most affected by the impact of anthropogenic contamination (Arellano *et al.*, 1999; Cohen *et al.*, 2001). It is estimated that about 17,104 m^3 / day of treated and untreated effluents from both medium as well as large scale

industries are being discharged, thus impairing the quality of Kerala coastal waters drastically. There has been a dearth in studies in documenting the heavy metal status for the central and northern coast of Kerala despite of these aforementioned precarious conditions. The present chapter, therefore discusses the levels and distribution of copper (Cu), lead (Pb), chromium (Cr), nickel (Ni), zinc (Zn), cadmium (Cd) and mercury (Hg) in the sediments of central and northern coast of Kerala. The extend of metal pollution was assessed using Index geo accumulation (I_{geo}) (Reddy *et al.*, 2004; Selvaraj *et al.*, 2004; Chen *et al.*, 2007); Pollution Load Index (PLI) (Tomlinson *et al.*, 1980; Ray *et al.*, 2006) and Effective Range Low (ERL) and Effective Range Median (ERM) (Long *et al.*, 1995; 1997; Kwon and Lee, 2001; Ramirez *et al.*, 2005). This can also provide baseline information necessary for developing strategies for future pollution control in the coastal environments of Kerala.

5.2 Results

5.2.1 Sedimentological Analysis

Grain size distribution of sediment in shallow water environments is controlled by the hydrodynamic conditions and therefore, can provide information about the nature of the current or wave motion necessary to account for the erosion, transportation, or deposition of the sediments (Sheppard, 1973). Generally, the fine grain size and the uniform distribution are indicative of stable environments, although cohesive clay bottoms, because of their resistance to friction, can resist high velocity currents that would readily erode silts and very fine sand.

The grain size distribution of the sediment samples and its seasonal variation along the study area are given (Table 5.1, Fig. 5A). The sediment texture along the Cochin coastal region consists mainly of fine fraction(silt + clay), in which its mean value accounted for more than 83% in post monsoon and monsoon while its contribution impeded in pre monsoon where its contribution was only 63.63%. The maximum mean value for sand having 36.37% was observed in pre monsoon and minimum in

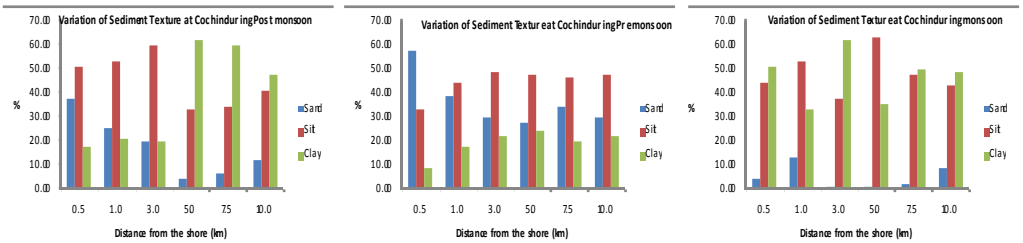
monsoon with a contribution of 5.26%. At Chettuva and Ponnani the texture was associated with fine fraction, in which its mean value accounted for more than 72% and 75% respectively for all seasons. At Chettuva, the maximum mean value for sand having 27.96% was observed in pre monsoon and minimum in post monsoon with a contribution of 15.18% while at Ponnani the maximum mean value for sand having 16.73% was observed in post monsoon and minimum of 11.82% in monsoon. The sediment along the Calicut coastal region was dominated by fine fraction, in which its mean value accounted for more than 75% for all seasons. The maximum mean value for sand having 24.05% was observed in pre monsoon and minimum in monsoon with a contribution of 12.14%.The sediment along the Kasargod coastal region comprise essentially of fine fraction, in which its mean value accounted for more than 68 % for all seasons. The maximum mean value for sand having 31.75% was observed in post monsoon and minimum in monsoon with an input of 13.79%.

Table 5.1 Textural characteristics of the sediments along the central and northern coast of Kerala

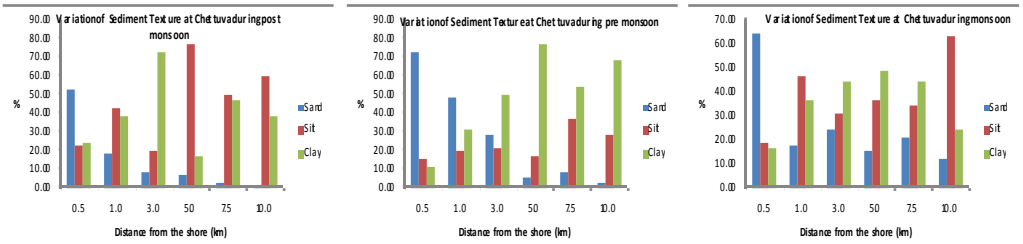
Station Name	Distance from the shore (km)	Sand (%)			Silt (%)			Clay (%)			Organic Matter (%)		
		POM	PM	M	POM	PM	M	POM	PM	M	POM	PM	M
Cochin	0.5	37.35	57.56	4.65	50.36	33.43	44.5	18.09	9.01	50.87	3.98	1.84	6.43
	1	25.21	38.35	13.56	53.28	44.04	53.18	21.51	17.61	33.26	4.24	2.74	5.04
	3	20.17	29.36	1.09	59.84	49.04	37.51	19.99	21.6	61.4	4.50	3.16	7.10
	5	4.88	28.01	1.28	32.63	47.17	63.02	62.49	24.82	35.7	6.04	5.04	5.20
	7.5	6.49	34.68	2.38	33.80	45.88	47.64	59.71	19.44	49.98	4.76	3.76	5.72
	10	11.76	30.29	8.63	40.84	47.16	43.23	47.40	22.55	48.14	4.42	3.48	5.80
	Mean	**17.64**	**36.38**	**5.27**	**45.13**	**44.45**	**48.18**	**38.20**	**19.1717**	**46.56**	**4.66**	**3.34**	**5.88**
Chettuva	0.5	53.17	73.21	64.58	22.59	15.40	18.96	24.24	11.39	16.46	2.21	1.89	2.72
	1	18.62	48.72	17.35	43.21	19.63	46.20	38.17	31.65	36.45	3.28	3.14	3.54
	3	8.04	28.85	24.60	19.32	21.02	30.99	72.64	50.13	44.41	4.92	4.32	3.70
	5	6.36	5.90	15.23	76.65	16.84	36.52	16.99	77.26	48.25	5.03	4.18	4.25
	7.5	3.10	7.80	21.30	49.70	37.60	34.21	47.20	54.60	44.49	4.56	4.12	3.96
	10	1.78	3.27	11.76	59.72	28.77	63.44	38.50	67.96	24.80	4.85	4.57	5.10
	Mean	**15.18**	**27.96**	**25.80**	**45.20**	**23.21**	**38.39**	**39.62**	**48.83**	**35.81**	**4.14**	**3.70**	**3.88**
Ponnani	0.5	55.51	60.14	8.14	19.01	21.36	42.54	25.48	18.50	49.32	1.69	1.38	3.78
	1	24.10	20.18	16.19	22.42	36.39	33.23	53.48	43.53	50.58	2.94	2.75	2.24
	3	4.10	10.33	0.27	48.56	54.37	47.02	47.34	35.30	52.71	4.03	3.96	5.27
	5	3.67	3.76	24.85	78.05	49.64	26.01	18.28	46.60	49.14	3.08	3.02	1.28
	7.5	7.83	1.57	3.16	58.27	45.63	39.04	33.90	52.80	57.80	3.36	3.16	3.10
	10	5.20	1.14	18.34	56.10	60.66	37.34	38.70	46.60	44.32	3.22	2.40	2.90
	Mean	**16.74**	**16.19**	**11.83**	**47.07**	**44.68**	**37.53**	**36.20**	**40.56**	**50.65**	**3.05**	**2.78**	**3.10**
Calicut	0.5	44.55	38.56	11.64	38.78	39.25	55.32	16.67	22.19	33.04	2.34	2.75	3.14
	1	27.82	27.94	27.55	59.36	42.51	54.09	12.82	29.55	18.36	2.18	2.10	2.78
	3	13.63	26.85	0.17	68.57	56.55	66.73	17.80	16.60	33.10	3.63	2.51	3.12
	5	23.23	12.96	21.74	52.67	63.46	30.10	24.10	23.58	49.10	4.15	2.63	1.93
	7.5	11.90	17.80	9.80	66.52	54.67	52.30	21.58	27.53	37.90	3.90	2.89	3.11
	10	10.32	20.18	2.86	58.68	58.16	27.33	31.00	21.66	69.80	4.65	2.55	4.28
	Mean	**21.91**	**24.05**	**12.29**	**57.43**	**52.43**	**47.65**	**20.66**	**23.52**	**40.22**	**3.48**	**2.57**	**3.06**
Kasargod	0.5	74.6	69.56	37.58	15.02	19.28	41.26	10.38	11.16	21.16	1.28	1.89	1.98
	1	62.5	31.28	16.55	29.38	47.54	35.24	8.12	21.18	48.21	2.42	2.05	3.19
	3	11.78	8.65	3.64	69.32	66.01	41.24	18.9	25.34	55.12	4.07	2.20	5.9
	5	14.87	3.27	7.44	45.18	58.43	47.46	39.95	38.3	45.1	3.5	4.00	3.35
	7.5	16.56	11.2	10.3	42.1	52.89	56.78	41.34	35.91	32.92	4.1	2.75	3.78
	10	10.16	20.94	7.25	50.47	47.46	60.25	39.37	31.6	32.5	4.87	2.25	4.61
	Mean	**31.75**	**24.15**	**13.79**	**41.91**	**48.60**	**47.04**	**26.34**	**27.25**	**39.17**	**3.37**	**2.52**	**3.80**

NOTE: POM - postmonsoon, PM - premonsoon, M - monsoon

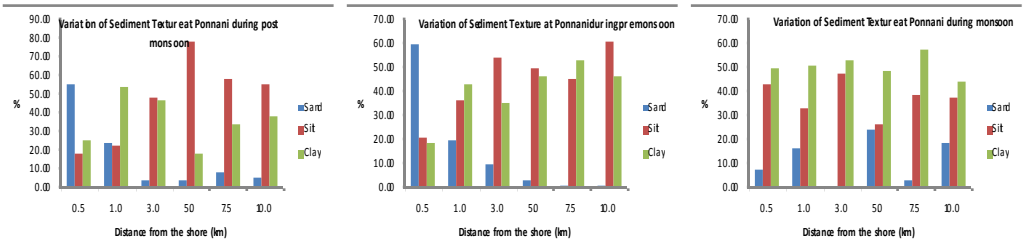
Cochin



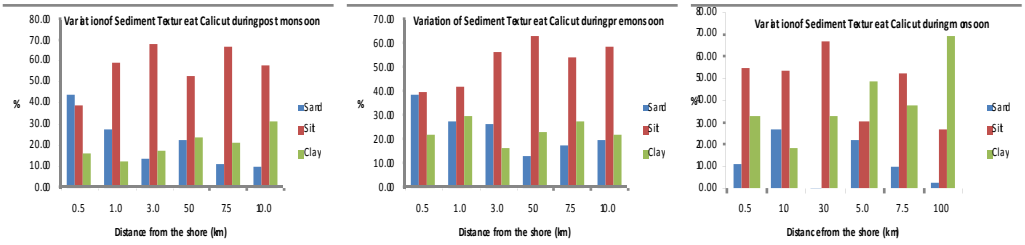
Chettuva



Ponnani



Calicut



Kasargod

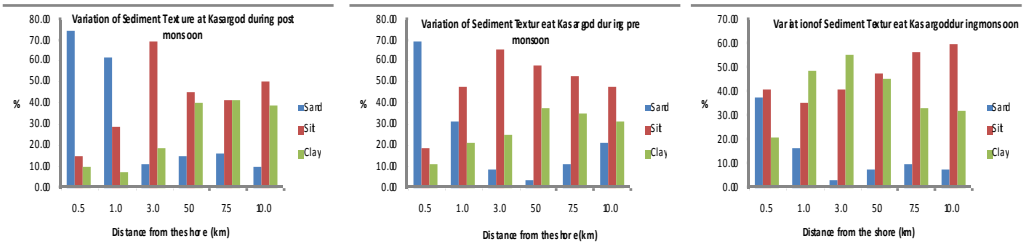


Figure 5A. Seasonal variation of sediment texture among different transects.

5.2.2 Organic Matter

Organic matter (OM) is one of the most important collectors of pollutants in the marine sediments. Organic matter tends to form strong organo-metallic complexes with metals, rendering them immobile. An increase in OM content may result in an increase in levels of metals in marine sediment.

The organic matter content of the sediments of the study region for the three seasons are presented (Table 5.1, Fig. 5B). The concentration of organic matter in the central coast varied from 3.98 - 6.04, 1.84 – 5.04, 5.04 – 7.10 % and 2.21 – 5.03, 1.89 – 4.57, 2.72 – 5.10 % at Cochin and Chettuva respectively for post monsoon, pre monsoon and monsoon season. In the northern coast, organic matter was found to vary from 1.69 – 4.03, 1.38 – 3.96 ,1.28 – 5.27 % at Ponnani, in Calicut it was found to vary from 2.18 – 4.65, 2.10 – 2.89 and 1.93 – 4.28% and at Kasargod it varied from 1.28 – 4.87, 1.89 – 4.00 and 1.98 – 5.90 % for post monsoon, pre monsoon and monsoon season respectively.

The average values of organic matter content discerned a distinct seasonal trend in the northern coast from Ponnani to Kasargod with low values (2.52 – 2.78%) in the pre monsoon and high values (3.05 – 3.48%) in post monsoon. In contrast , the central coast, at Cochin high average values (5.88%) of organic matter content was noticed in monsoon and low values (3.34%) in pre monsoon while at Chettuva low average values (3.70%) was observed in pre monsoon and high values (4.14%) in post monsoon.

The average value of organic matter content in the sediments of the study area varied from a minimum of 2.52% at Kasargod to a maximum of 5.88% at Cochin.

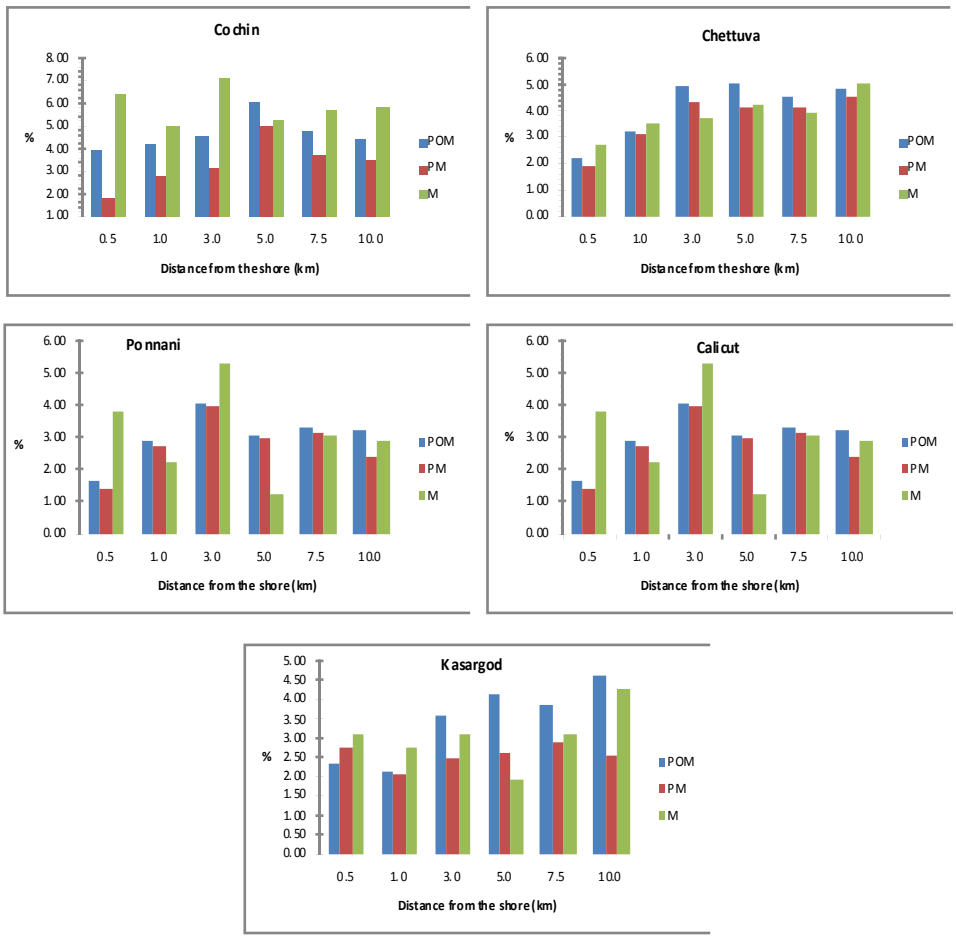


Figure 5B. Seasonal variation of organic matter (%) in surficial sediment among different transects

5.2.3 Heavy Metals in Sediment

5.2.3.1 Copper (Cu)

Cu is widely distributed in nature, especially in sulphide, arsenide, chloride and carbonate deposits. It has been shown that anthropogenic inputs are the major sources of Cu contamination (Nriagu, 1979). Copper contamination of the marine environment could also result from the industrial, municipal and agricultural discharges. It is an essential element for all living organism. It plays a catalytic role for many enzyme systems. The spatial and seasonal distribution of Cu in the surficial sediments of the study area is presented (Table 5.2, Fig. 5C).

The concentration of Cu in sediments in the stations at Cochin ranged between 18.00 – 24.00, 32.60 – 66.46 and 27.70 – 67.80 µg g^{-1} in post monsoon, pre monsoon and monsoon season respectively. The concentration of Cu in sediment was low in post monsoon, while it was comparable for the other two seasons. The distribution of Cu in sediments among stations showed an offshore increase in pre monsoon, while it showed an offshore decrease in its concentration gradient in monsoon. The maximum concentration of 67.80 µg g^{-1} was observed in monsoon while minimum concentration of 18.00 µg g^{-1} was discerned in post monsoon.

At Chettuva, the range of Cu in sediment was found to be between 32.40 – 52.30, 27.50 – 43.04, and 21.00 – 38.40 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. Regarding the seasonal trend the concentration of Cu in sediment showed an increasing trend from post monsoon to pre monsoon and then a drastic decrease in monsoon. The maximum concentration of 52.30 µg g^{-1} was observed in post monsoon while the minimum concentration of 21.00 µg g^{-1} was reported in monsoon.

At Ponnani, no wide fluctuations among seasons as well as between stations was observed. The range was found to be between 27.00 – 35.34, 27.80 – 42.31 and 29.70 – 39.60 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. Not much variation in concentration gradient was observed between stations among seasons. The maximum concentration of 42.31 µg g^{-1} was observed in pre monsoon while the minimum concentration of 27.00 µg g^{-1} was observed in post monsoon.

At Calicut, the concentration of Cu in sediment ranged from 17.00 – 34.00, 35.80 – 48.80, 29.00 – 46.00 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. The maximum concentration of 48.80 µg g^{-1} was observed in pre monsoon while the minimum concentration of 17.00 µg g^{-1} was observed in post monsoon. A linear offshore decrease in the distribution of Cu in sediment in post monsoon was noticed. Increase in concentration gradient upto 5.0 km and then offshore decrease was noticed

in pre monsoon while there wasn't much variation in its distribution between stations in monsoon. The maximum concentration of 48.80 µg g^{-1} was observed in pre monsoon while minimum concentration of 17.00 µg g^{-1} was observed in post monsoon.

At Kasargod, the concentration of Cu in sediment ranged between 15.00 – 31.00, 24.21 – 37.60 and 24.00 – 44.80 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. The maximum concentration of 44.80 µg g^{-1} was observed in monsoon while minimum concentration of 15.00 µg g^{-1} was observed in post monsoon. The concentration range was observed to be low in post monsoon. A distinct seasonal trend with concentration increasing from post monsoon to monsoon was conspicuous. A definite offshore increase in the distribution of Cu in sediments was conspicuous for all seasons.

5.2.3.2 Lead (Pb)

It is one of the oldest metals known to man and, since medieval times, has been used in piping, building materials, soldering, paints, ammunition, and castings. More recently, Pb has been used mainly in storage batteries (35%), in gasoline as tetraethyl lead (5% but is continuously decreasing), cable covering (10%), solders (10%), and chemicals (15%) (Demayo *et al*., 1984). Other uses of Pb are in paints, pigments, ammunition, corrosive liquid containers, glasswares, radiation shielding, and containers (Demayo *et al*., 1984; Moore and Ramamoorthy, 1984). Lead as a pollutant has assumed particular importance due to its relatively high toxicity to humans, especially brain retardation in children. Environmental exposure to low levels of Pb has been associated with a wide range of metabolic disorders and neuropsychological deficits, especially in children (Nriagu, 1988; Silvany Neto *et al*., 1989). Anthropogenic activities are responsible for most of the Pb pollution (Scoullos, 1986). Emissions of Pb into the atmosphere have increased sharply in this century. Combustion of oil and gasoline alone accounts for 50% of all anthropogenic emissions and thus constitutes a major

component of the global cycle of Pb. Schaule and Patterson (1981) found that the major input pathway of Pb in to marine environment is via atmosphere fallout. Most of the Pb in the environment is in the inorganic form. In addition, Pb is also present in the organic form, such as alkyl Pb from auto emissions. In a marine environment, Pb is predominantly associated with the suspended particulates and thus tends to accumulate in sediments (Zabel, 1989). In fresh water – seawater mixing zones Fe tends to precipitate as hydroxides. Being electrically active, these Fe hydroxides scavenge Pb.The spatial and seasonal distribution of Pb in the surficial sediments of the study area is presented (Table 5.2, Fig. 5D).

The concentration of Pb in sediments of the stations at Cochin ranged between 14.00 – 16.00, 8.00 – 23.76 and 32.00 – 38.00 µg g^{-1} in post monsoon, pre monsoon and monsoon season respectively. The concentration of Pb in sediments showed a definite seasonal trend. It was found to increase from post monsoon to monsoon. The enrichment of Pb on moving from shore to offshore was conspicuous for all season. High concentration of Pb throughout the stations was observed in monsoon season while the lowest concentration was reported in post monsoon. At Cochin the maximum concentration of 38.00 µg g^{-1} was observed in monsoon and the minimum concentration of 8.00 µg g^{-1} in pre monsoon.

At Chettuva, the range of Pb in sediments was found to be between 12.00 – 22.40, 9.10 – 17.72 and 14.00 – 27.00 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. The concentration of Pb in sediment generally showed an erratic trend on moving towards offshore in post monsoon and monsoon while a definite concentration gradient was noticed in pre monsoon with an increase in concentration towards offshore. The maximum concentration of 27.00 µg g^{-1} was observed in monsoon while the minimum concentration of 9.10 µg/g was reported in pre monsoon.

At Ponnani, a distinct seasonal pattern was observed in the distribution of Pb in sediment and was found to increase from post monsoon to monsoon. The

range was found to be between 9.20 – 15.84, 10.30 – 26.40 and 14.00 – 27.00 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. The concentration generally showed a linear increase from 0.5 km to 3.0 km from the shore and an erratic distribution from 5.0 km to 10.0 km for all season. The maximum concentration of Pb in sediment of 27.00 µg g^{-1} was observed in monsoon while the minimum concentration of 9.20 µg g^{-1} was observed in post monsoon.

At Calicut, not much wide variations in its distribution in sediment among seasons were noticed. The concentration ranged between 14.00 – 21.40, 14.52 – 24.80 and 14.0 -25.0 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. The distribution of Pb in sediments between stations was comparable for all seasons. The maximum concentration of 25.00 µg g^{-1} was observed in monsoon while the minimum concentration of 14.00 µg g^{-1} was observed in post monsoon and monsoon.

At Kasargod, the concentration of Pb in sediment ranged between 9.00 – 12.00, 7.40 – 19.84 and 10.00 – 21.00 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. The distribution of Pb in the sediments was generally low in post monsoon. The concentration of Pb in sediments between stations was comparable for all seasons. The maximum concentration of 21.00 µg g^{-1} was observed in monsoon while minimum concentration of 7.40 µg g^{-1} was observed in pre monsoon.

5.2.3.3 Chromium (Cr)

It is a white, hard, and lustrous metal. In nature it can exist in many oxidation states from -2 to +6. In oxidized aquatic environments it exists mainly in the Cr (VI) state as oxyanion forms such as CrO_4^{2-}, $HCrO_4^-$ and CrO_7^{2-} species. These species are strongly oxidizing. In the reduced aquatic environments, hydroxyl complexes of Cr (III) are more prevalent. Chromite ($FeOCr_2O_3$ or $FeCr_2O_4$ with a chromic oxide content of 68%) is the only commercially important ore mineral. It is used in the production of ferrous alloys, refractory bricks, and in manufacturing of other

Cr chemicals. The major contributions to airborne Cr are from ferrochrome production and from the handling and production of refractory bricks, coal combustion, and chromium steel production (Moore and Ramamoorthy, 1984). The principal Cr contamination sources of natural waters are effluent discharges from metal – finishing processes, leather tanning, textile dyeing, and laundry chemical industries (Moore and Ramamoorthy, 1984; Nriagu and Nieboer, 1988). Regarding the biological role of Cr, it is biotoxic as well as essential to many mammals. Toxicity of Cr to fish and other marine biota has been well investigated (Wong and Trevors, 1988). Chromium is regarded as a toxic element of human significance (Philips *et al.*, 1982; Mance, 1984). Because of the wide industrial use of Cr metal and its compounds, anthropogenic activities have become the most significant contributor to environmental contamination (Nriagu and Nieboer, 1988). A wide spatial and seasonal variation was observed in the distribution of Cr in sediments of the study area and is presented (Table 5.2, Fig. 5E).

The concentration of Cr in sediment of the stations at Cochin ranged between 111.00 – 142.00, 48.00 – 119.40 and 202.16 – 217.80 µg g^{-1} in post monsoon, pre monsoon and monsoon respectively. Enrichment of Cr in sediments was explicit in monsoon while a low distribution was noticed in pre monsoon. The distribution also did not show much variation between stations for all season. At Cochin the maximum concentration of 217.80 µg g^{-1} was observed in monsoon and the minimum concentration of 48.00 µg g^{-1} in pre monsoon.

At Chettuva, Cr concentration in the sediments was found to be between 112.00 – 135.00, 41.20 – 104.60 and 116.80 – 167.90 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. A concentration gradient with an increase in Cr concentration in sediment was discerned towards offshore for pre monsoon and monsoon, while the variation in the distribution of Cr between stations was comparable in post monsoon. The

maximum concentration of 167.90 µg g^{-1} was observed in monsoon while the minimum concentration of 41.20 µg g^{-1} was reported in pre monsoon.

At Ponnani, the range of Cr in sediments was found to be between 34.00 – 61.00, 89.00 – 112.60 and 56.50 – 153.00 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. The maximum concentration of 153.00 µg g^{-1} was observed in monsoon while the minimum concentration of 34.00 µg g^{-1} was observed in post monsoon. The distribution of Cr in sediment between stations generally showed an offshore decrease for all seasons.

At Calicut, the concentration of Cr in sediment ranged between 110.00 – 204.00, 108.2 – 147.00 and 83.20 – 212.00 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. In post monsoon and monsoon the distribution of Cr in sediments tends to augment towards offshore, on the contrary in pre monsoon it showed an offshore decrease. The maximum concentration of 212.00 µg g^{-1} and the minimum concentration of 83.20 µg g^{-1} of Cr in sediment was observed in monsoon.

At Kasargod, the concentration of Cr in sediment ranged between 36.00 – 82.00, 49.60 – 123.58 and 103.70 – 178.60 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. The maximum concentration of 178.60 µg g^{-1} was observed in monsoon while minimum concentration of 36.00 µg g^{-1} was observed in post monsoon. The concentration range was generally low in post monsoon. A definite seasonal trend was explicit with concentration of Cr in sediments increasing from post monsoon to monsoon. Generally, distribution of Cr in sediments between stations showed an offshore decrease for all seasons.

Table 5.2 Concentrations of heavy metals (Cu, Pb and Cr) in sediments among different seasons along the central and northern coast of Kerala. Concentrations are expressed in µg g^{-1}.

Station Name	Distance from the shore (km)	Cu			Pb			Cr		
		POM	PM	M	POM	PM	M	POM	PM	M
Cochin	0.5	18.00	32.60	67.80	15.20	8.00	38.00	111.00	48.00	204.00
	1	20.00	44.20	58.41	16.00	21.20	35.00	125.00	119.40	202.16
	3	24.00	48.70	48.70	15.00	14.52	33.20	142.00	104.28	217.80
	5	23.00	62.50	36.80	14.00	18.48	37.00	125.00	106.92	215.60
	7.5	21.40	54.80	31.58	15.10	21.40	32.00	127.00	98.07	212.80
	10	22.10	66.46	27.70	14.00	23.76	33.00	131.00	60.72	202.50
Chettuva	0.5	33.00	27.50	24.12	15.00	10.20	14.00	118.00	41.20	116.80
	1	52.30	34.02	38.40	14.00	9.10	25.00	112.00	51.14	128.80
	3	39.00	36.82	31.50	12.00	13.20	27.00	135.00	60.06	128.12
	5	42.96	40.78	27.50	22.40	14.52	22.00	132.00	71.28	141.40
	7.5	32.40	41.20	23.40	14.10	14.80	23.00	131.00	74.24	137.80
	10	34.78	43.04	21.00	17.16	17.72	27.00	130.60	104.64	167.90
Ponnani	NS	27.00	32.50	39.00	9.20	10.30	27.00	34.00	89.00	135.00
	1	32.00	42.31	36.30	14.10	16.10	24.00	51.00	110.25	56.75
	3	26.00	33.33	39.60	11.00	17.82	25.00	61.00	112.56	153.00
	5	35.34	36.52	30.60	14.52	26.40	26.00	34.32	99.36	111.50
	7.5	29.60	37.20	33.40	12.50	23.40	23.00	57.50	108.20	117.50
	10	31.38	27.80	29.70	15.84	21.40	14.00	41.68	95.40	87.50
Calicut	0.5	17.00	35.80	36.00	16.00	19.10	18.00	115.00	108.20	146.24
	1	19.00	44.60	29.00	14.00	24.80	24.00	110.00	147.00	102.00
	3	23.00	42.80	34.70	19.00	23.10	14.00	144.00	135.30	183.00
	5	27.00	48.80	46.00	18.00	14.52	20.00	141.00	123.40	83.20
	7.5	31.00	39.80	35.60	19.00	16.50	18.00	167.00	112.60	167.00
	10	34.00	38.60	38.80	21.40	19.00	25.00	204.00	118.00	212.00
Kasargod	0.5	15.00	24.21	24.00	9.00	7.40	14.00	36.00	49.60	126.24
	1	27.00	32.10	38.40	11.00	11.02	13.00	45.00	93.25	178.60
	3	29.00	34.78	36.00	11.00	19.84	10.00	82.00	123.58	103.70
	5	27.00	36.72	41.60	12.00	15.83	15.00	64.00	110.26	123.40
	7.5	26.00	35.60	39.00	11.00	14.20	14.00	71.00	104.50	110.00
	10	31.00	37.60	44.80	11.00	14.52	21.00	75.00	97.48	112.60

NOTE: POM - postmonsoon, PM - premonsoon, M - monsoon

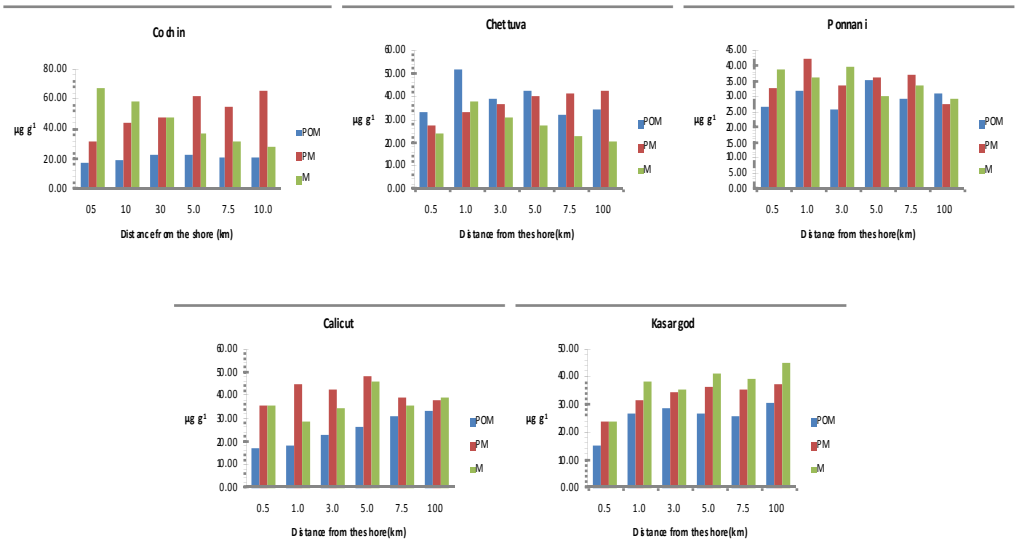


Figure 5C. Seasonal variation of Copper (Cu) in surficial sediments among different transects

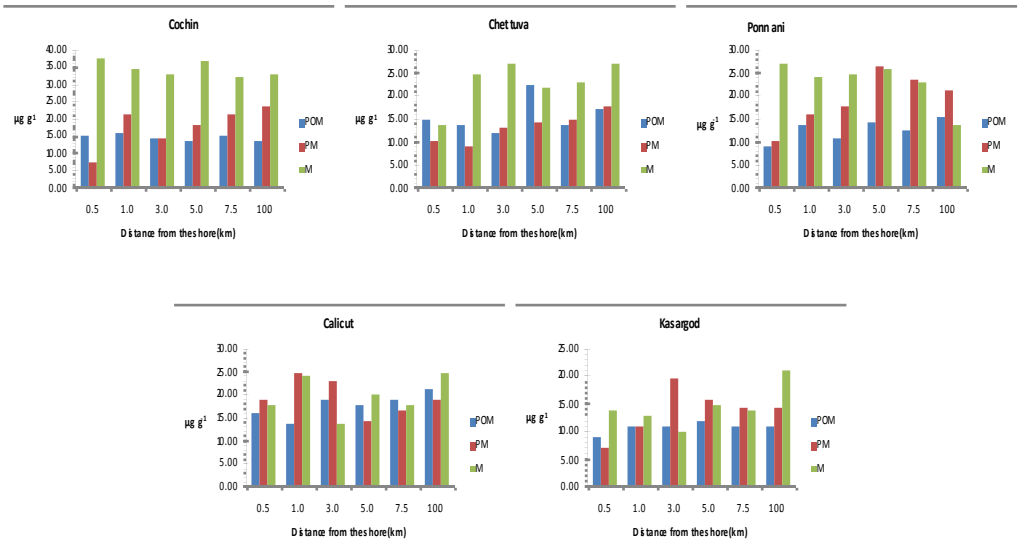


Figure 5D. Seasonal variation of Lead (Pb) in surficial sediments among different transects.

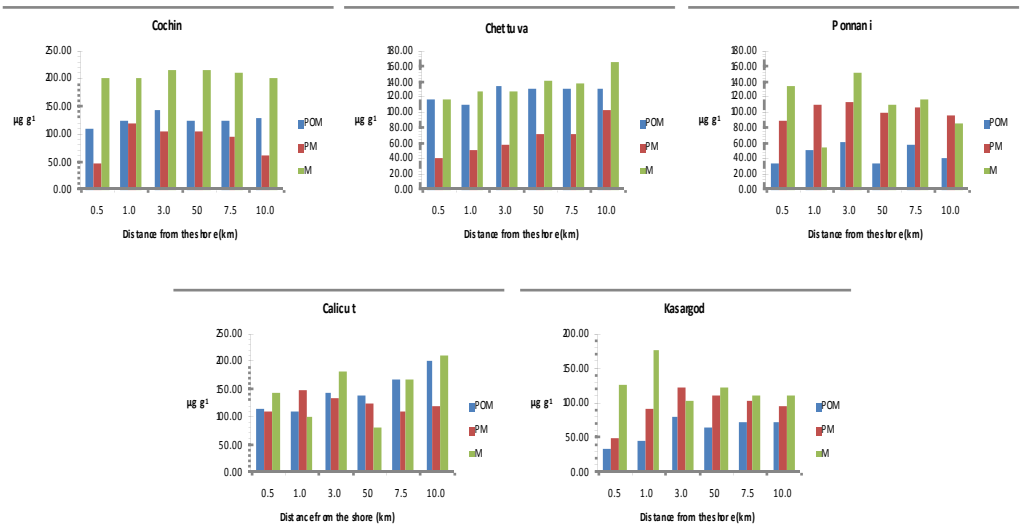


Figure 5E. Seasonal variation of Chromium (Cr) in surficial sediments among different transects.ss

5.2.3.4 Nickel (Ni)

Nickel emissions to the atmosphere are mostly anthropogenic; industrial sources account for more than 80% of the total emission. Nickel is also introduced into the terrestrial environment as solid waste from metallurgical industries or as deposition of atmospheric emissions. Application of phosphate fertilizers to cultivated land is also a source of nickel and this could lead to elevated concentrations since nickel, together with other heavy metals, is found in phosphate minerals in variable amounts. Ni is especially concentrated in the fly ash upon combustion. The spatial and seasonal distribution of Ni in the surficial sediments of the study area is presented (Table 5.3, Fig. 5F).

The concentration of Ni in sediment of the stations at Cochin ranged between 22.00 – 44.00, 19.00 – 51.00 and 88.8 – 134.0 µg g^{-1} in post monsoon, pre monsoon and monsoon season respectively. A distinct seasonal trend was noticed with concentration of Ni in sediments increasing from post monsoon to monsoon. Generally an offshore decrease in the concentration was conspicuous between stations for all seasons. The maximum concentration of Ni in sediment of 134.00 µg g^{-1} was observed in

monsoon while the minimum concentration of 19.00 µg g^{-1} was reported in pre monsoon.

At Chettuva, the range of Ni in sediments of the stations was found to be between 17.20 – 49.00, 14.10 – 58.08 and 43.60 – 67.30 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. In pre monsoon an offshore increase in the concentration was evident while in other seasons an offshore decrease was observed. The maximum concentration of 67.30 µg g^{-1} was observed in monsoon while the minimum concentration of 14.10 µg g^{-1} was reported in pre monsoon.

At Ponnani, the range of Ni in sediment of the stations was found to be between 21.00 – 38.90, 36.00 – 66.00 and 70.60 – 84.00 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. A distinct seasonal trend with a linear increase in the distribution of Ni in sediment from post monsoon to monsoon was conspicuous. The distribution between stations generally showed an increase up to 3.0 km from the shore and after which the distribution remained comparable towards offshore for all seasons. The maximum concentration of Ni in sediment of 84.00 µg g^{-1} was recorded in monsoon and a minimum of 21.00 µg g^{-1} was observed in post monsoon.

At Calicut, the concentration of Ni in sediments ranged between 38.00 – 68.00, 41.20 – 57.20 and 50.30 -97.00 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. The mean value of Ni in sediment was high in monsoon when compared to other seasons. A definite concentration gradient was noticed among stations with an offshore increase in concentration of Ni in sediment in post monsoon and monsoon while the gradient was reversed in pre monsoon by which the concentration tend to decrease towards offshore. The maximum concentration of 97.20 µg g^{-1} was observed in monsoon while a minimum concentration of 38.00 µg g^{-1} was observed in post monsoon.

At Kasargod, the concentration of Ni in sediments ranged between 14.00 – 34.20, 21.04 – 37.52 and 38.40 – 60.40 µg g^{-1} for post monsoon,

pre monsoon and monsoon respectively. A distinct seasonal trend with concentration increasing from post monsoon to monsoon was observed. Generally the distribution of Ni in sediments showed an erratic pattern between stations for all season. The maximum concentration of 60.40 µg g^{-1} was observed in monsoon while minimum concentration of 14.00 µg g^{-1} was observed in post monsoon.

5.2.3.5 Zinc (Zn)

Zinc is an essential trace element for plants, animals and humans as it is associated with many enzymes and with certain other proteins. Zn is relatively more abundant in the earth's crust than some other metals. However, there are not many minerals that contain Zn. Anthropogenic sources of Zn in the environment include printing processes, construction materials, metals (iron, steel and brass coated with Zn), fertilizers, batteries, sewage sludge, animal wastes in the form of manure (dairy, feedlot, swine or chicken), Zn-containing pesticides, atmospheric deposition and coal combustion. Marked variation was observed in the distribution of Zn in the sediments along the central and northern coast of Kerala (Table 5.3, Fig. 5G).

The concentration of Zn in sediments of the stations at Cochin ranged between 54.00 – 76.00, 112.00 – 219.00 and 123.10 – 184.20 µg g^{-1} in post monsoon, pre monsoon and monsoon season respectively. Increased concentration of Zn was noticed in pre monsoon while the lowest concentration was noticed in post monsoon with no wide variations among stations. In post monsoon an offshore increase in the concentration gradient of Zn in sediment was observed and in monsoon the distribution was found to be reversed. The maximum concentration of 219.00 µg g^{-1} was observed in pre monsoon while the minimum concentration of 54.00 µg g^{-1} was reported in post monsoon.

At Chettuva, the range of Zn in sediment of the stations was found to be between 101.20 – 139.62, 51.20 – 115.10 and 54.28 – 111.80 µg g^{-1} for post

monsoon, pre monsoon and monsoon respectively. A definite seasonal trend was conspicuous with the concentration of Zn in sediments showing a decrease from post monsoon to monsoon. The distribution of Zn in sediment between the stations was comparable for all seasons. The maximum concentration of 139.62 µg g^{-1} was observed in post monsoon while the minimum concentration of 51.20 µg g^{-1} was reported in pre monsoon.

At Ponnani, the range of Zn in sediment of the stations was found to be between 65.00 – 121.32, 59.0 – 138.30 and 74.40 – 92.30 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. In post monsoon and monsoon, variation of Zn in sediment among stations was comparable but in pre monsoon the concentration gradient showed a linear increase up to 5.0 km and declined towards offshore. The maximum concentration of 138.30 µg g^{-1} of Zn in sediment and the minimum of 59.00 µg g^{-1} were observed in pre monsoon.

At Calicut, the concentration of Zn in sediments of the stations ranged between 36.00 – 61.00, 117.80 – 137.12 and 48.00 - 94.20 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. The concentration of Zn in sediments was high in pre monsoon when compared to other seasons. A definite concentration gradient, with an offshore increase in concentration of Zn in sediment among stations in post monsoon and monsoon was explicit. In pre monsoon, the variation in the distribution of Zn in sediments between stations was comparable. The maximum concentration of 137.12 µg g^{-1} was observed in pre monsoon and monsoon while the minimum concentration of 36.00 µg g^{-1} was observed in post monsoon.

At Kasargod, the concentration of Zn in sediment of the stations ranged between 25.00 – 74.00, 48.12 – 122.46 and 32.00 – 44.80 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. The mean value and concentration range was observed to be low in monsoon while it was high in pre monsoon. A distinct increase in concentration trend from shore

to offshore was conspicuous in pre monsoon and was comparable for other seasons. The maximum concentration of 122.46 µg g^{-1} was observed in pre monsoon while the minimum concentration of 25.00 µg g^{-1} was observed in post monsoon.

5.2.3.6 Cadmium (Cd)

It is a relatively rare earth element that is almost uniformly distributed in the earth's crust with an average concentration of 0.15 – 0.20 mg Kg^{-1}. Cadmium is probably the most biotoxic element and is regarded as a priority pollutant. It is widely used in various industrial products and processes including electroplating, pigments, plastic stabilization, batteries and metallic alloys. Because of its wide variety of uses anthropogenic inputs into the marine environment is considered as the principal source of Cd contamination. It is therefore expected that human activities in the estuarine and coastal areas may result in relatively high concentration of Cd. In general, Cd enters the marine environment via atmospheric deposition and through effluent discharges from point sources in near shore areas (Nriagu, 1980). Cadmium in marine environment generally subsists as positively charged divalent ions and thus can be adsorbed onto the solid surface with negative electrical charges. Many electrically charged surfaces are reported in both sediment and sea water. The most important of these solids are organic matter, hydroxides of Fe and Mn, clays and particles of biogenic carbonate minerals. Cadmium generally showed wide variation in its distribution in sediments along the central and northern coast of Kerala (Table 5.3, Fig. 5H)

The concentration of Cd in sediment in the stations at Cochin ranged between 0.32 – 1.68, 0.41 – 3.60 and 1.90 – 2.90 µg g^{-1} in post monsoon, pre monsoon and monsoon season respectively. The concentration gradient of Cd in sediment between stations in post monsoon and monsoon showed an offshore increase while it decreased in pre monsoon. A definite seasonal trend in the distribution of Cd in sediment was noticed at Cochin with the concentration increasing from post monsoon to

monsoon. The maximum concentration of 3.60 µg g^{-1} was observed in pre monsoon while the minimum concentration of 0.32 µg g^{-1} was observed in post monsoon.

At Chettuva, the range of Cd in sediment was 0.17 – 0.55, 0.12 – 0.48 and 0.09 – 0.23 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. A definite seasonal trend was noticed with the concentration of Cd in sediments showing a decrease from post monsoon to monsoon. The concentration gradient between stations increased on moving towards offshore in post and pre monsoon while the concentration gradient reversed in monsoon with high concentration in the near shore and a decrease towards offshore. The maximum concentration of 0.55 µg g^{-1} was observed in post monsoon while the minimum concentration of 0.09 µg g^{-1} was reported in monsoon.

At Ponnani, the range of Cd in sediment was between 0.19 – 0.62, 0.18 – 0.62 and 0.11 – 0.56 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. No distinct seasonal trend was observed in the distribution of Cd in sediment. Among stations, the distribution of Cd in sediment was high on moving towards offshore in post monsoon and pre monsoon. In monsoon the concentration gradient showed a linear increase upto 5.0 km then declined towards offshore. The maximum concentration of Cd of 0.62 µg g^{-1} was observed in post monsoon and pre monsoon while the minimum concentration of 0.11 µg g^{-1} was observed in monsoon.

At Calicut, the concentration of Cd in sediment ranged between 0.16 – 0.20, 0.45 – 0.81 and 0.21-0.81 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. The concentration was low in sediment in post monsoon and was comparable for other two seasons. A steady decrease in concentration gradient was observed towards offshore in pre monsoon, while in monsoon high and low pulses in concentration was observed in moving from shore to offshore. In post monsoon the distribution of Cd in sediment between stations was comparable. The maximum concentration

of 0.81 µg g^{-1} was observed in pre monsoon and monsoon while the minimum concentration of 0.16 µg g^{-1} was observed in post monsoon.

At Kasargod, the concentration of Cd in sediment ranged between 0.08 – 0.21, 0.14 – 0.42 and 0.08 – 0.45 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. A distinct seasonal trend with concentration of Cd in sediment increasing from post monsoon to monsoon was conspicuous. Cadmium concentration in sediment increased on moving towards offshore for all season. The maximum concentration of 0.45 µg g^{-1} was observed in monsoon while the minimum concentration of 0.08 µg g^{-1} was observed in post monsoon.

5.2.3.7 Mercury (Hg)

Mercury as one of the most toxic elements and its toxicity to humans has been well established (Janicki *et al.*, 1987). The concern about Hg pollution in the marine environments started with the celebrated case of Minamata in Japan where in the 1950s several people died or became terminally sick after consuming fish and shellfish containing relatively high concentrations of methylmercury (Kurland *et al.*, 1960). It has been established that seafoods contribute appreciably to the total Hg intake by humans. Because of its toxicity to aquatic organisms and potential hazards to human health, many countries have set a maximum limit on Hg concentrations in seafoods. The toxicity of Hg to marine biota is well established (Atchison *et al.*, 1987; McLusky *et al.*, 1986; Thain, 1984). Mercury is probably the most ubiquitous of all the heavy metals. This is because Hg is the only metal that can exist as both a liquid and as a volatile form at ambient temperatures. Due to easy transformation of physical forms, Hg cycles readily and continuously in nature. Both anthropogenic and natural sources contribute to environmental contamination by Hg. However, anthropogenic inputs are more significant than those from natural sources. Man has used mercuric oxide (HgO) and cinnabar (HgS) as a pigment or a cosmetic since prehistoric times (Saha, 1972). Presently, Hg is extensively used in chloralkali plants, insecticides,

fungicides, electrical products and processes, paints, instruments, dental preparation, catalysts in plastic manufacture, mercurial slimacides used in paper and pulp industry and in antifungal applications. Mercury was found to in the sediments in detectable amounts and showed marked variation in its distribution along the central and northern coast of Kerala (Table 5.3, Fig. 5I).

The concentration of Hg in sediment of the stations at Cochin ranged between 0.18 – 0.65, 0.23 – 0.49 and 0.23 – 0.47 µg g^{-1} in post monsoon, pre monsoon and monsoon respectively. A distinct seasonal trend was conspicuous with concentration of Hg in sediment declining from post monsoon to monsoon. Generally an offshore increase in the concentration of Hg in sediment was explicit in post monsoon, while in pre monsoon and monsoon an offshore decrease was noticed. The maximum concentration of 0.65 µg g^{-1} and the minimum concentration of 0.18 µg g^{-1} were reported in post monsoon.

At Chettuva, the range of Hg in sediment varied between 0.08 – 0.14, 0.06 – 0.23 and 0.01 – 0.11 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. The distribution of Hg in sediment generally showed an erratic pattern between stations for all season.The maximum concentration of 0.23 µg g^{-1} was observed in pre monsoon while the minimum concentration of 0.01 µg g^{-1} was reported in monsoon.

At Ponnani, a distinct seasonal pattern with a linear increase in the distribution of Hg in sediment from post monsoon to monsoon was evident. The maximum concentration of Hg of 0.31 µg g^{-1} was recorded in monsoon and a minimum of 0.05 µg g^{-1} was observed in post monsoon. The range was found to be between 0.05 – 0.19, 0.09 – 0.24 and 0.13 – 0.31 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. The distribution generally showed an erratic pattern towards offshore in post monsoon and pre monsoon while in monsoon the distribution of Hg in sediment showed an offshore decrease.

At Calicut, the concentration ranged between 0.09 – 0.24, 0.19 – 0.28, and 0.08 – 0.28 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. The concentration in sediments generally showed an offshore increase in post monsoon while in pre monsoon and monsoon the distribution generally showed an irregular pattern. The maximum concentration of 0.28 µg g^{-1} was observed in pre monsoon while the minimum concentration of 0.08 µg g^{-1} was discerned in monsoon.

At Kasargod, the concentration of Hg in sediment ranged between 0.05 – 0.19, 0.08 – 0.21 and 0.05 – 0.19 µg g^{-1} for post monsoon, pre monsoon and monsoon respectively. In general, the distribution of Hg in sediment showed an increase from shore to offshore in post monsoon and pre monsoon. In monsoon the distribution of Hg showed an increase up to 5.0 km and then started decreasing towards offshore.

The maximum concentration of 0.21 µg g^{-1} was observed in pre monsoon while the minimum concentration of 0.05 µg g^{-1} was observed in post monsoon and monsoon.

Table 5.3 Concentrations of heavy metals (Ni, Zn, Cd and Hg) in sediments among different seasons along the central and northern coast of Kerala. Concentrations are expressed in µg g^{-1}.

Station Name	Distance from the shore (km)	Ni			Zn			Cd			Hg		
		POM	PM	M	POM	PM	M	POM	PM	M	POM	PM	M
Cochin	0.5	22.00	19.00	127.20	54.00	112.00	157.80	0.32	0.41	2.66	0.18	0.23	0.42
	1	31.00	51.00	134.00	76.00	185.66	154.00	0.65	1.35	2.90	0.49	0.49	0.47
	3	44.00	46.20	124.80	74.00	172.26	184.20	0.90	0.66	2.30	0.23	0.45	0.35
	5	36.00	46.86	102.70	75.00	170.94	147.60	1.10	3.60	1.90	0.56	0.35	0.28
	7.5	32.00	31.80	107.80	67.00	198.60	138.60	1.32	2.70	2.10	0.54	0.37	0.32
	10	39.00	26.40	88.80	74.00	219.00	123.10	1.68	2.30	2.10	0.65	0.32	0.23
Chettuva	0.5	17.20	19.65	43.6	103.00	51.20	54.28	0.17	0.12	0.09	0.09	0.06	0.01
	1	28.20	14.10	67.3	101.20	87.80	111.8	0.32	0.48	0.23	0.08	0.23	0.08
	3	49.00	23.50	61.1	123.00	101.44	95.8	0.55	0.32	0.17	0.11	0.09	0.06
	5	32.14	31.02	61.2	139.62	111.02	93.6	0.44	0.32	0.09	0.08	0.11	0.11
	7.5	28.90	37.20	54.9	112.80	92.80	90.2	0.31	0.31	0.12	0.14	0.17	0.08
	10	27.06	58.08	52.5	108.70	115.10	82.7	0.51	0.32	0.11	0.04	0.19	0.08
Ponnani	NS	21.00	36.00	84.00	65.00	59.00	82.00	0.19	0.18	0.32	0.05	0.09	0.28
	1	30.20	52.10	70.60	121.32	110.20	74.90	0.59	0.32	0.18	0.19	0.12	0.13
	3	38.00	62.04	83.10	106.00	132.60	84.40	0.62	0.37	0.37	0.12	0.11	0.31
	5	38.28	66.00	78.20	105.96	138.30	92.30	0.53	0.62	0.56	0.13	0.24	0.18
	7.5	38.40	57.80	81.20	104.90	115.80	86.40	0.42	0.57	0.37	0.13	0.21	0.17
	10	38.94	54.78	77.40	102.42	111.90	74.40	0.53	0.62	0.11	0.17	0.21	0.15
Calicut	0.5	47.00	44.10	69.00	41.00	124.60	54.00	0.16	0.81	0.35	0.09	0.28	0.18
	1	55.00	57.20	51.00	43.00	137.12	48.00	0.18	0.72	0.69	0.13	0.23	0.24
	3	38.00	46.20	93.10	36.00	126.72	85.90	0.19	0.66	0.65	0.11	0.19	0.08
	5	47.00	46.02	50.30	61.00	129.36	55.70	0.16	0.56	0.21	0.16	0.21	0.28
	7.5	54.00	41.20	72.30	61.00	122.40	76.20	0.20	0.51	0.45	0.21	0.22	0.21
	10	68.00	43.20	97.00	61.00	117.80	94.20	0.19	0.45	0.81	0.24	0.20	0.15
Kasargod	0.5	14.00	21.04	42.00	25.00	48.12	32.00	0.08	0.14	0.12	0.05	0.08	0.05
	1	30.12	30.20	51.50	74.00	89.32	38.40	0.11	0.19	0.08	0.07	0.09	0.08
	3	34.14	30.92	38.40	45.00	96.06	36.00	0.09	0.36	0.15	0.20	0.11	0.15
	5	28.06	34.88	57.90	58.00	103.98	41.60	0.20	0.36	0.45	0.13	0.15	0.19
	7.5	34.20	32.80	45.60	67.00	110.20	39.40	0.21	0.36	0.29	0.17	0.17	0.17
	10	31.20	37.52	60.40	64.00	122.46	44.80	0.18	0.42	0.40	0.19	0.21	0.13

NOTE: POM - post monsoon, PM - pre monsoon, M - monsoon

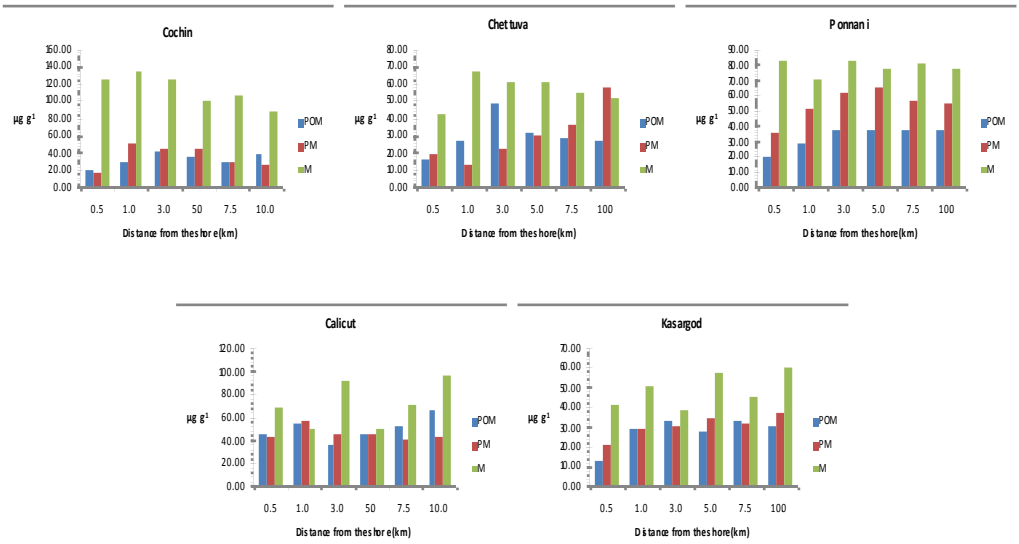


Figure 5F. Seasonal variation of Nickel (Ni) in surficial sediments among different transects.

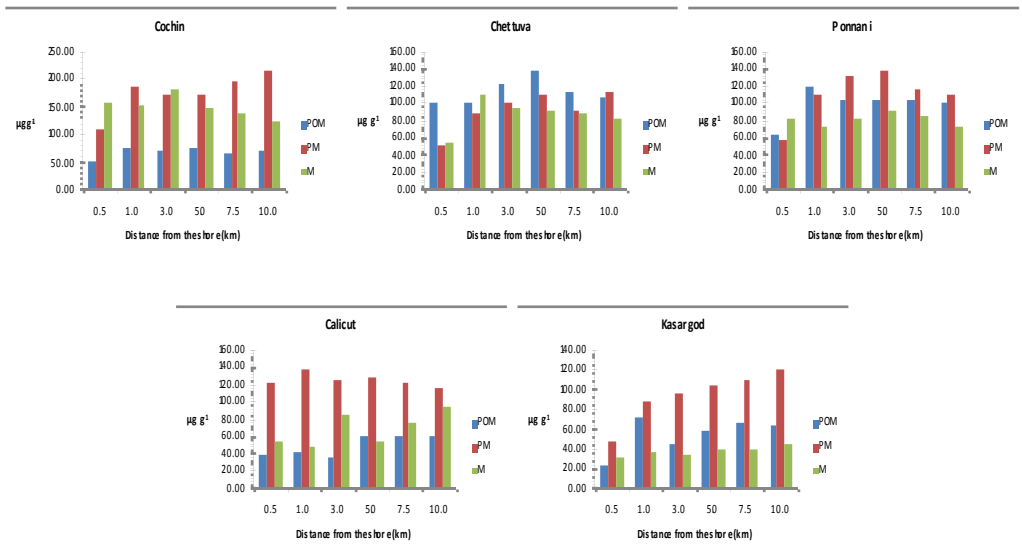


Figure 5G. Seasonal variation of Zinc (Zn) in surficial sediments among different transects.

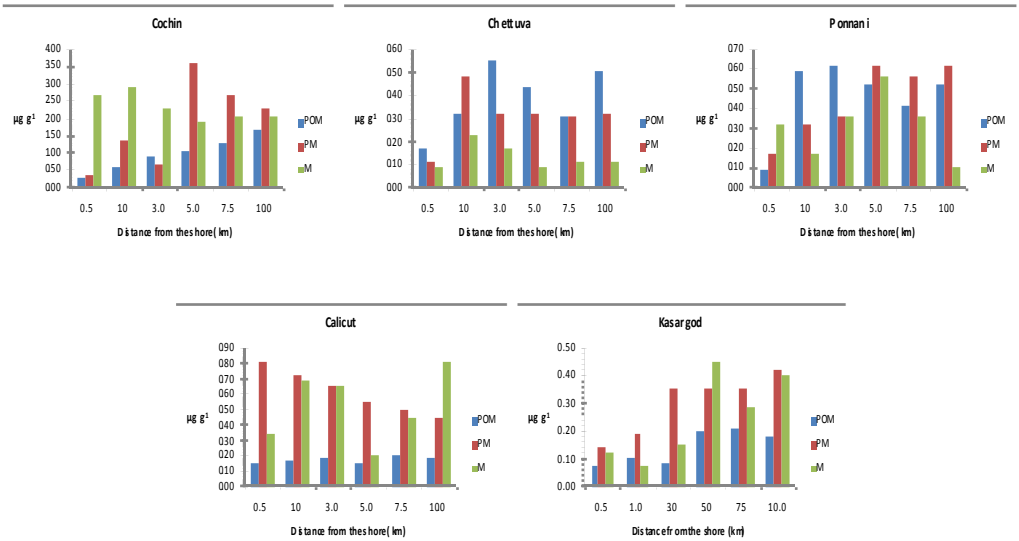


Figure 5H. Seasonal variation of Cadmium (Cd) in surficial sediments among different transects.

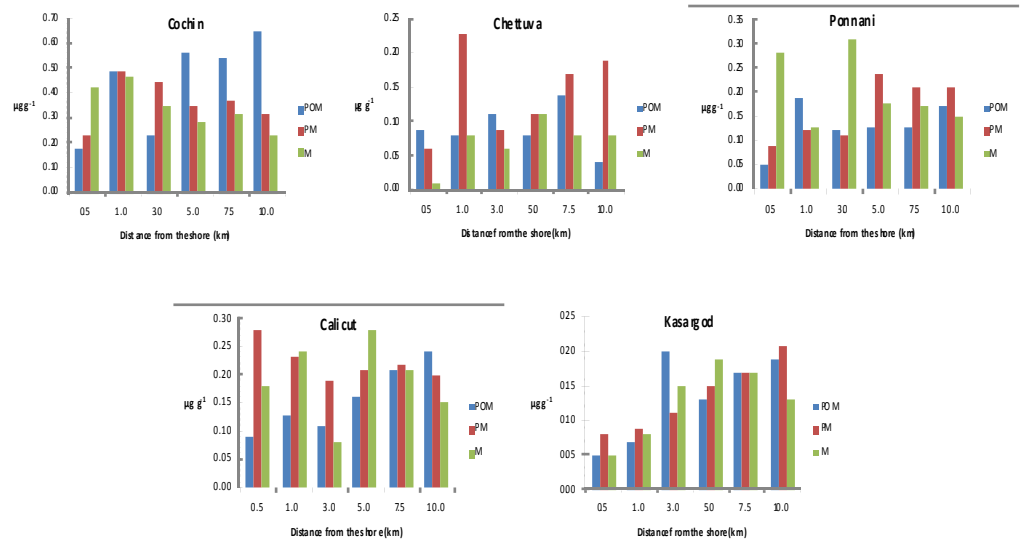


Figure 5I. Seasonal variation of Mercury (Hg) in surficial sediments among different transects.

The mean concentration of heavy metals (in $\mu g\ g^{-1}$) in sediment at Cochin in post monsoon and monsoon represented the order Cr > Zn > Ni > Cu >Pb > Cd > Hg while in pre monsoon it represented Zn >Cr> Cu > Ni >Pb > Cd > Hg.The mean concentration of heavy metals in sediments at Chettuva in post monsoon and monsoon followed the decreasing order Cr > Zn > Ni > Cu >Pb > Cd > Hg while in pre monsoon it represented Zn > Cr> Cu > Ni >Pb > Cd > Hg. At Ponnani in post monsoon and pre monsoon the distribution followed the decreasing order Zn > Cr > Ni > Cu >Pb > Cd > Hg while in monsoon it was Cr > Zn > Ni > Cu > Pb > Cd > Hg. At Calicut the mean concentration of total heavy metals in sediments in post monsoon and monsoon represented the order Cr > Ni > Zn > Cu >Pb > Cd > Hg while in pre monsoon it was found to be in the order Zn > Cr > Ni > Cu >Pb > Cd > Hg. The distribution of heavy metals in sediments at Kasargod in post monsoon represented the order Cr > Zn > Ni > Cu >Pb > Cd > Hg while in pre monsoon it represented Cr > Zn > Cu > Ni >Pb > Cd > Hg and in monsoon it was found to be Cr > Ni > Zn > Cu >Pb > Cd > Hg.

In the study area Pb, Cd, Hg showed the lowest concentration for all seasons while there was much variation in the concentration of metals like Cr, Ni, Zn and Cu among seasons (Fig. 5K). The concentration of Pb, Ni was low at all transects in post monsoon and was high in monsoon. Zinc generally showed an erratic pattern in its distribution, the concentration was relatively lower in monsoon compared to other seasons, except at Cochin and Calicut where low values are noticed in post monsoon. High concentration was reported in pre monsoon at all transects for Zn. The concentration of Cd and Hg did not show any marked fluctuations between seasons except at Cochin where the distribution in sediment was found to have wide variation.

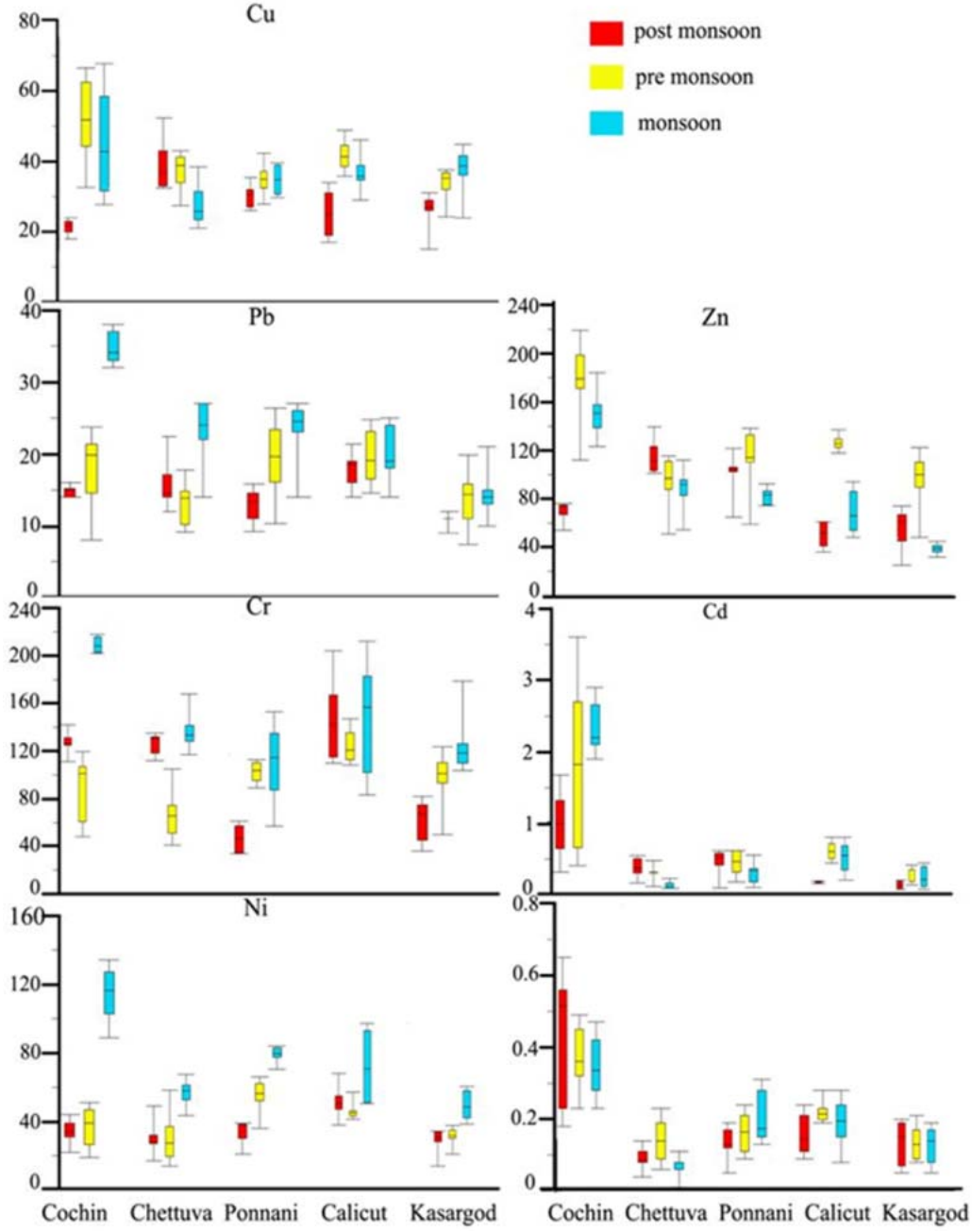


Figure 5K. Heavy metal concentration (µg g^{-1} dry wt.) in surficial sediment along the central and northern coast of Kerala shown through box whisker plot.

5.2.4 Pollution Load Index (PLI)

The Pollution load index (PLI) was proposed by Tomlinson *et al.*, (1980) for detecting pollution which permits a comparison of pollution levels between sites and at different times. The PLI was obtained as a concentration factor of each heavy metal with respect to the background value in the sediment. In this study, the world average concentrations of the metals studied reported for shale (Turekian and Wedephol, 1961) were used as the background for those heavy metals studied. PLI values of zero, one, or larger than one suggest absence of baseline pollutants, presence of them, or progressive deterioration of sediment quality, respectively. PLI was evaluated using the equation PLI= (product of *n* number of CF values) $^{1/n}$, where CF is the contamination factor and *n* is the number of metals. CF was obtained as a concentration of each metal with respect to the background value of the metal constituent in the sediment. The transects were partitioned into polluted (PLI > 1) and unpolluted (PLI < 1) due to heavy metals on the basis of PLI formulated at each sampled transect. Pollution load index (PLI) calculated for each transects are represented in Fig. 5J.

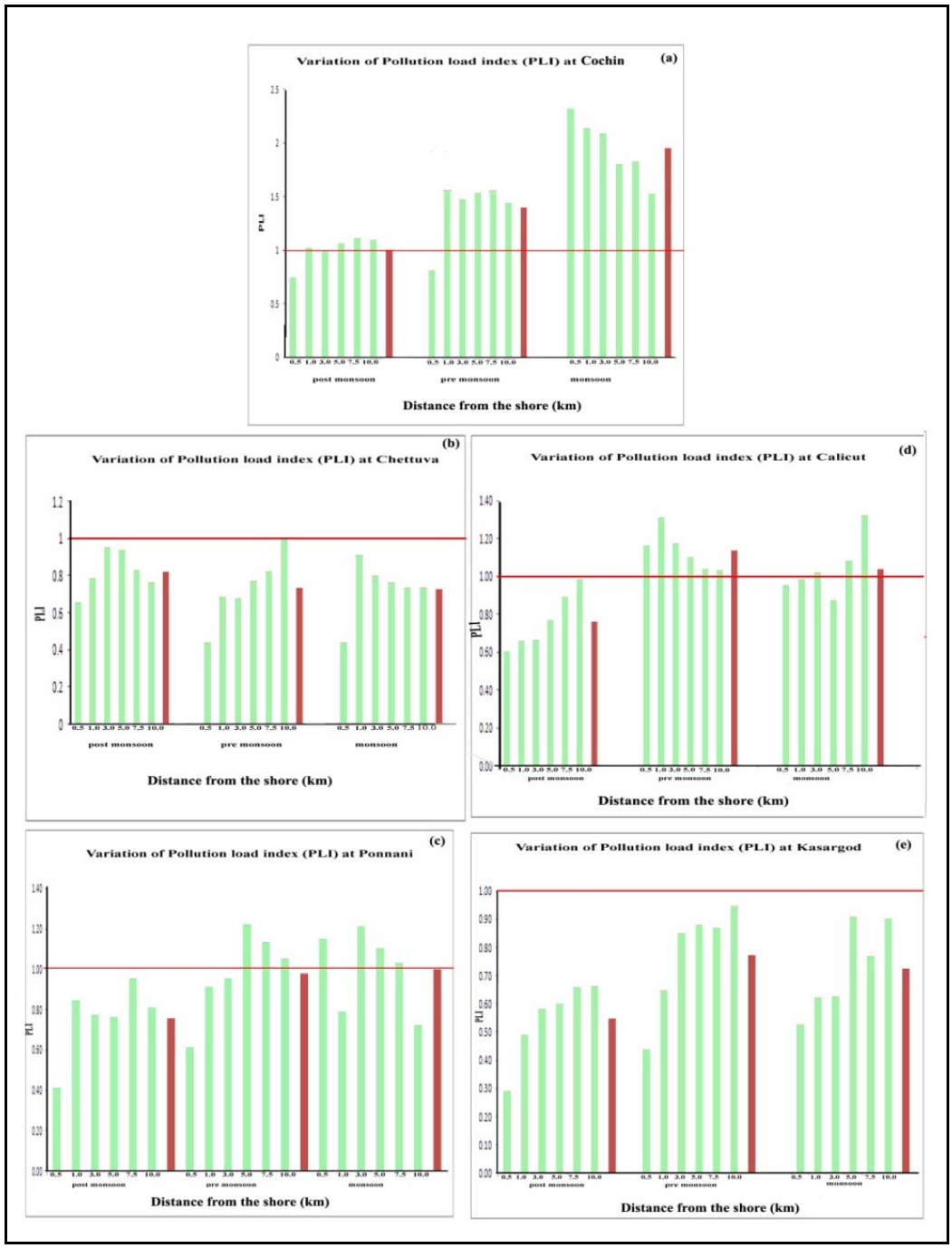


Figure 5J. Variation of Pollution Load Index (PLI) among different seasons for each transects along the central and northern coast of Kerala.

Fig. 5Ja shows the seasonal variation of PLI at Cochin transect. The overall average PLI value of 1.0, 1.40 and 1.95 (brown bar in Fig. 5Ja) for post monsoon, pre monsoon and monsoon respectively is a concern due to heavy metals in this coastal region. In post monsoon PLI at the stations were closer to one while in other seasons it was well above one. High PLI observed in monsoon is an indication of heavy metal load reaching to this coastal milieu from inland region.

At Chettuva the overall average PLI values were 0.82, 0.73 and 0.73 (brown bar in Fig. 5Jb) for post monsoon, pre monsoon and monsoon respectively. The PLI values were less than one at all stations indicating low pollution concern due to heavy metals.

At Ponnani, the overall average PLI values were 0.76, 0.98 and 1.0 (brown bar in Fig. 5Jc) for post monsoon, pre monsoon and monsoon respectively. The PLI values especially at offshore stations showed values >1 in pre monsoon and monsoon. This suggests that this zone is being affected by metal pollutants. A plausible explanation for the overall average value of one in monsoon can be due to the rivers and several sewerage systems pouring their water mass enriched with inland inorganic metallic wastes in to this coastal area.

At Calicut the overall average PLI values were 0.76, 1.14 and 1.04 (brown bar in Fig. 5Jd) for post monsoon, pre monsoon and monsoon respectively. The average PLI value was high in pre monsoon. PLI generally declined towards offshore in pre monsoon, showing the onshore–offshore gradient which characterizes sediment metal concentrations, and subsequent dilution with distance from the coast are the most important factor in determining the distributions of metals in this period. In post monsoon PLI showed less than one signifying less metal contamination. The overall average value of PLI > 1 in monsoon could be due to the rivers and several sewerage systems and land run off pouring their water mass enriched with inland inorganic metallic wastes in to this coastal area.

At Kasargod, the overall average PLI values were 0.55, 0.77 and 0.72 (brown bar in Fig. 5Je) for post monsoon, pre monsoon and monsoon respectively. Low PLI value generally signifies lower metals contamination in sediments. This can probably due to low anthropogenic activities in the area.

5.2.5 Geoaccumulation Index

The geoaccumulation index (I_{geo}) introduced by Muller (1979), has been used to quantitatively measure metal pollution in aquatic sediments. Based on pollution intensity classification (I_{geo} class) that consists of seven grades or classes 0 to 6 (Table 5.4), the highest grade reflecting a 100 fold enrichment above baseline values. The I_{geo} can be calculated using the equation (Muller, 1979):

$$I_{geo} = \log_2 \frac{[Me]_{studiedarea}}{1.5\,[Me]_{baseline}}$$

Where, $[Me]_{studied\ area,}$ represents the concentration of metals in the sediment sample and $[Me]_{baseline}$ represents the corresponding metal concentration in average shales taken from Turekian and Wedepohl (1961) and Li and Schoonmaker (2005), with a "1.5" factor included because of possible variations in the background data due to lithogenic effects (Salomons and Forstner, 1984).

Table 5.4 Geoaccumulation index in relation to pollution extent.

I_{geo}	I_{geo} class	Pollution Intensity
> 5	6	Very strongly polluted
4-5	5	Strongly to Very strongly polluted
3-4	4	Strongly polluted
2-3	3	Moderately to strongly polluted
1-2	2	Moderately polluted
0-1	1	Unpolluted to moderately polluted
< 0	0	Unpolluted

Results from this study (Table 5.5) indicated that at Cochin in post monsoon 73.81% of the elements belonged to I_{geo} class 0 (unpolluted), 16.67% of the elements belonged to I_{geo} class 1(unpolluted to moderately polluted), with only 9.52% positioned in I_{geo} class 2 (moderately polluted). The elements that were placed in moderately polluting section were Cd and Hg, in addition to Cu, Cr which found its place both in the unpolluted and moderately polluted segment.

In pre monsoon, 64.28 % of the elements belonged to I_{geo} class 0 (unpolluted), 26.19 % of the elements belonged to I_{geo} class 1(unpolluted to moderately polluted), with only 2.38% positioned in I_{geo} class 2 (moderately polluted) and 7.14% in I_{geo} class 3 (moderately to strongly polluted). The element that was placed in moderately to strongly polluting segment is Cd. The elements which found place in the unpolluted and moderately polluted segment were Zn, Cd and Hg.

In monsoon 21.43 % of the elements belonged to I_{geo} class 0 (unpolluted), 64.28% of the elements belonged to I_{geo} class 1(unpolluted to moderately polluted), with no elements positioned in I_{geo} class 2 (moderately polluted) and 14.28 % in I_{geo} class 3 (moderately to strongly polluted). The elements which found place in the unpolluted and moderately polluted segment were Pb, Cr, Ni, Zn and Hg. The element that was placed in moderately to strongly polluting segment is Cd.

Table 5.5 Classes of analyzed heavy metals in sediments according to their geoaccumulation index (I_{geo}) at Cochin

Distance from the shore (Km)	Season	I_{geo} class						
		0 (0) >	0 - 1 (1)	1 - 2 (2)	2 - 3 (3)	3 - 4 (4)	4 - 5 (5)	> 5 (6)
0.5	POM	Cu, Pb, Cr, Ni, Zn, Cd, Hg						
1		Cu, Pb, Cr, Ni, Zn, Cd, Hg						
3		Cu, Pb, Cr, Ni, Zn, Hg	Cd					
5		Cu, Pb, Cr, Ni, Zn, Cd, Hg						
7.5		Cu, Pb, Cr, Ni, Zn, Cd, Hg						
10		Cu, Pb, Cr, Ni, Zn, Hg	Cd					
No. of metals in the class (Total metals)		**40 (42)**	**2 (42)**					
% of metals in the class		**95.24**	**4.76**					
0.5	PM	Cu, Pb, Cr, Ni, Zn, Cd, Hg						
1		Cu, Pb, Cr, Ni, Zn, Hg	Cd					
3		Cu, Pb, Cr, Ni, Zn, Cd, Hg						
5		Cu, Pb, Cr, Ni, Zn, Cd, Hg						
7.5		Cu, Pb, Cr, Ni, Zn, Cd, Hg						
10		Cu, Pb, Cr, Ni, Zn, Cd, Hg						
No. of metals in the class (Total metals)		**41 (42)**	**1 (42)**					
% of metals in the class		**97.62**	**2.38**					
0.5	M	Cu, Pb, Cr, Ni, Zn, Cd, Hg						
1		Cu, Pb, Cr, Ni, Zn, Cd, Hg						
3		Cu, Pb, Cr, Ni, Zn, Cd, Hg						
5		Cu, Pb, Ni, Zn, Cd, Hg	Cr					
7.5		Cu, Pb, Ni, Zn, Cd, Hg	Cr					
10		Cu, Pb, Ni, Zn, Cd, Hg	Cr					
No. of metals in the class (Total metals)		**39 (42)**	**3 (42)**					
% of metals in the class		**92.86**	**7.14**					
Overall % of Metals in the class		**95.24**	**4.76**					
NOTE: POM - post monsoon, PM - pre monsoon, M - monsoon								

The I_{geo} of metals in sediment and its classes for Chettuva is given in **Table 5.6**. The percentage of elements which belonged to I_{geo} class 0 (unpolluted) was 95.24%, 97.62% and 92.86% for post monsoon, pre monsoon and monsoon respectively. In post monsoon and pre monsoon Cd was the single element which belonged to I_{geo} class 1(unpolluted to moderately polluted) contributing 4.76 % and 2.38% respectively. In monsoon Cr was the sole element contributing 7.14% to the I_{geo} class 1(unpolluted to moderately polluted).

Table 5.6 Classes of analysed heavy metals in sediments according to their geoaccumulation index (I_{geo}) at Chettuva.

Distance from the shore (Km)	Season	< 0 (0)	0 - 1 (1)	1 - 2 (2)	2 - 3 (3)	3 - 4 (4)	4 - 5 (5)	> 5 (6)
0.5	POM	Cu, Pb, Cr, Ni, Zn, Cd,Hg						
1		Cu, Pb, Cr, Ni, Zn, Cd,Hg						
3		Cu, Pb, Cr, Ni, Zn,Hg	Cd					
5		Cu, Pb, Cr, Ni, Zn, Cd,Hg						
7.5		Cu, Pb, Cr, Ni, Zn, Cd,Hg						
10		Cu, Pb, Cr, Ni, Zn,Hg	Cd					
No. of metals in the class (Total metals)		**40 (42)**	**2 (42)**					
% of metals in the class		**95.24**	**4.76**					
0.5	PM	Cu, Pb, Cr, Ni, Zn, Cd,Hg						
1		Cu, Pb, Cr, Ni, Zn,Hg	Cd					
3		Cu, Pb, Cr, Ni, Zn, Cd,Hg						
5		Cu, Pb, Cr, Ni, Zn, Cd,Hg						
7.5		Cu, Pb, Cr, Ni, Zn, Cd,Hg						
10		Cu, Pb, Cr, Ni, Zn, Cd,Hg						
No. of metals in the class (Total metals)		**41 (42)**	**1 (42)**					
% of metals in the class		**97.62**	**2.38**					
0.5	M	Cu, Pb, Cr, Ni, Zn, Cd,Hg						
1		Cu, Pb, Cr, Ni, Zn, Cd,Hg						
3		Cu, Pb, Cr, Ni, Zn, Cd,Hg						
5		Cu, Pb, Ni, Zn,Cd,Hg	Cr					
7.5		Cu, Pb, Ni, Zn,Cd,Hg	Cr					
10		Cu, Pb, Ni, Zn,Cd,Hg	Cr					
No. of metals in the class (Total metals)		**39 (42)**	**3 (42)**					
% of metals in the class		**92.86**	**7.14**					
Overall % of Metals in the class		**95.24**	**4.76**					
NOTE: POM - post monsoon, PM - pre monsoon, M - monsoon								

The I_{geo} of metals in sediment and its classes for Ponnani is given in Table 5.7. The percentage of elements which belonged to I_{geo} class 0 (unpolluted) was 90.48%, 92.86% and 92.86% for post monsoon, pre monsoon and monsoon respectively. In post monsoon and pre monsoon Cd was the only element which belonged to I_{geo} class 1(unpolluted to moderately polluted) contributing 9.52 % and 7.14% respectively. In monsoon Cd, Cr and Hg were the elements contributing 7.14% to the I_{geo} class 1(unpolluted to moderately polluted).

Table 5.7 Classes of analyzed heavy metals in sediments according to their geoaccumulation index (I geo) at Ponnani.

Distance from the shore (Km)	Season	I_{geo} class						
		< 0 (0)	0 - 1 (1)	1 - 2 (2)	2 - 3 (3)	3 - 4 (4)	4 - 5 (5)	> 5 (6)
0.5	POM	Cu, Pb, Cr, Ni, Zn,Cd, Hg						
1		Cu, Pb, Cr, Ni, Zn,Hg	Cd					
3		Cu, Pb, Cr, Ni, Zn,Hg	Cd					
5		Cu, Pb, Cr, Ni, Zn,Hg	Cd					
7.5		Cu, Pb, Cr, Ni, Zn,Cd, Hg						
10		Cu, Pb, Cr, Ni, Zn,Hg	Cd					
No. of metals in the class (Total metals)		**38 (42)**	**4 (42)**					
% of metals in the class		**90.48**	**9.52**					
0.5	PM	Cu, Pb, Cr, Ni, Zn,Cd, Hg						
1		Cu, Pb, Cr, Ni, Zn,Cd, Hg						
3		Cu, Pb, Cr, Ni, Zn,Cd, Hg						
5		Cu, Pb, Cr, Ni, Zn,Hg	Cd					
7.5		Cu, Pb, Cr, Ni, Zn,Hg	Cd					
10		Cu, Pb, Cr, Ni, Zn,Hg	Cd					
No. of metals in the class (Total metals)		**39 (42)**	**3 (42)**					
% of metals in the class		**92.86**	**7.14**					
0.5	M	Cu, Pb, Cr, Ni, Zn,Cd, Hg						
1		Cu, Pb, Cr, Ni, Zn,Cd, Hg						
3		Cu, Pb, Ni, Zn,Cd	Cr,Hg					
5		Cu, Pb, Ni, Zn,Hg	Cd					
7.5		Cu, Pb, Ni, Zn,Cd,Hg						
10		Cu, Pb, Ni, Zn,Cd,Hg						
No. of metals in the class (Total metals)		**39 (42)**	**3 (42)**					
% of metals in the class		**92.86**	**7.14**					
Overall % of Metals in the class		**92.06**	**7.94**					
NOTE: POM - post monsoon, PM - pre monsoon, M - monsoon								

The I_{geo} of metals in sediment and its classes for Calicut is presented in Table 5.8. The results showed that 90.48%, 85.71% and 85.71% of the elements belonged to I_{geo} class 0 (unpolluted) for post monsoon, pre monsoon and monsoon respectively. In post monsoon 9.52% of elements belonged to I_{geo} class 1(unpolluted to moderately polluted). Cr was the sole element which belonged to this segment. In pre monsoon and monsoon Cd and Cr were the elements contributing 14.29% to the I_{geo} class 1 (unpolluted to moderately polluted).

Table 5.8 Classes of analyzed heavy metals in sediments according to their geoaccumulation index (I_{geo}) at Calicut

Distance from the shore (Km)	Season	I_{geo} class						
		0 (0) <	0 - 1 (1)	1 - 2 (2)	2 - 3 (3)	3 - 4 (4)	4 - 5 (5)	> 5 (6)
0.5	POM	Cu, Pb, Cr, Ni, Zn,Cd,Hg						
1		Cu, Pb, Cr, Ni, Zn, Cd,Hg						
3		Cu, Pb, Ni, Zn,Cd,Hg	Cr					
5		Cu, Pb, Ni, Zn,Cd,Hg	Cr					
7.5		Cu, Pb, Ni, Zn,Cd,Hg	Cr					
10		Cu, Pb, Ni, Zn,Cd,Hg	Cr					
No. of metals in the class (Total metals)		**38 (42)**	**4 (42)**					
% of metals in the class		**90.48**	**9.52**					
0.5	PM	Cu, Pb, Cr, Ni, Zn,Hg	Cd					
1		Cu, Pb, Ni, Zn,Hg	Cr,Cd					
3		Cu, Pb, Cr, Ni, Zn,Hg	Cd					
5		Cu, Pb, Cr, Ni, Zn,Hg	Cd					
7.5		Cu, Pb, Cr, Ni, Zn,Hg	Cd					
10		Cu, Pb, Cr, Ni, Zn,Cd,Hg						
No. of metals in the class (Total metals)		**36 (42)**	**6 (42)**					
% of metals in the class		**85.71**	**14.29**					
0.5	M	Cu, Pb, Ni, Zn,Cd,Hg	Cr					
1		Cu, Pb, Cr, Ni, Zn,Hg	Cd					
3		Cu, Pb, Cr, Ni, Zn,Hg	Cd					
5		Cu, Pb, Cr, Ni, Zn,Cd,Hg						
7.5		Cu, Pb, Ni, Zn,Cd,Hg	Cr					
10		Cu, Pb, Ni, Zn,Hg	Cr,Cd					
No. of metals in the class (Total metals)		**36 (42)**	**6 (42)**					
% of metals in the class		**85.71**	**14.29**					
Overall % of Metals in the class		**87.30**	**12.70**					
NOTE: POM - post monsoon, PM - pre monsoon, M - monsoon								

The I_{geo} of metals in sediment and its classes for Kasargod is presented in Table 5.9. The results showed 100%, 100% and 97.61% of the elements belonged to I_{geo} class 0(unpolluted) for post monsoon, pre monsoon and monsoon respectively. None of the analyzed elements were positioned in the polluted classes except Cr in monsoon contributing merely 2.39% to I_{geo} class 1(unpolluted to moderately polluted).

Table 5.9 Classes of analysed heavy metals in sediments according to their geoaccumulation index (I_{geo}) at Kasargod.

Distance from the shore (Km)	Season	I_{geo} class						
		< 0 (0)	0 - 1 (1)	1 - 2 (2)	2 - 3 (3)	3 - 4 (4)	4 - 5 (5)	> 5 (6)
0.5	POM	Cu, Pb, Cr, Ni, Zn, Cd, Hg						
1		Cu, Pb, Cr, Ni, Zn, Cd, Hg						
3		Cu, Pb, Ni, Zn, Cd, Hg	Cr					
5		Cu, Pb, Ni, Zn, Cd, Hg	Cr					
7.5		Cu, Pb, Ni, Zn, Cd, Hg	Cr					
10		Cu, Pb, Ni, Zn, Cd, Hg	Cr					
No. of metals in the class (Total metals)		**38 (42)**	**4 (42)**					
% of metals in the class		**90.48**	**9.52**					
0.5	PM	Cu, Pb, Cr, Ni, Zn, Hg	Cd					
1		Cu, Pb, Ni, Zn, Hg	Cr, Cd					
3		Cu, Pb, Cr, Ni, Zn, Hg	Cd					
5		Cu, Pb, Cr, Ni, Zn, Hg	Cd					
7.5		Cu, Pb, Cr, Ni, Zn, Hg	Cd					
10		Cu, Pb, Cr, Ni, Zn, Cd, Hg						
No. of metals in the class (Total metals)		**36 (42)**	**6 (42)**					
% of metals in the class		**85.71**	**14.29**					
0.5	M	Cu, Pb, Ni, Zn, Cd, Hg	Cr					
1		Cu, Pb, Cr, Ni, Zn, Hg	Cd					
3		Cu, Pb, Cr, Ni, Zn, Hg	Cd					
5		Cu, Pb, Cr, Ni, Zn, Cd, Hg						
7.5		Cu, Pb, Ni, Zn, Cd, Hg	Cr					
10		Cu, Pb, Ni, Zn, Hg	Cr, Cd					
No. of metals in the class (Total metals)		**36 (42)**	**6 (42)**					
% of metals in the class		**85.71**	**14.29**					
Overall % of Metals in the class		**87.30**	**12.70**					
NOTE: POM - post monsoon, PM - pre monsoon, M - monsoon								

5.2.6 Sediment Quality Guidelines

Comparison of total metal concentrations in the sediment with NOAA's (National Oceanic and Atmospheric Administration) sediment quality guidelines (Long *et al.*, 1995) can be used to evaluate the possible biological consequences of the levels of metals in the central and northern coast of Kerala. Long *et al.*, (1995) matched biological and chemical data compiled from numerous modeling, laboratory, and field studies performed in marine and estuarine sediments. Using these data, effects range – low (ERL: lower 10^{th} percentile of the effects data) and range median (ERM: the median or 50^{th} percentile of the effects data) guideline values were determined for the examined metals in the study area and are presented in Table 5.10. These two guideline values (ERL and ERM) delineate three concentration ranges (< ERL, ERL – ERM, > ERM) for a particular metal. Hence, concentrations below the ERL value will represent a minimal – effects range, ERL - ERM a range intended to estimate conditions in which biological effects would be rarely observed. Concentrations equal to and above the ERL, but below the ERM, will represent a probable - effects range within which effects would frequently occur (Long *et al.*, 1995).

At Cochin, in post monsoon, the proportion of the metals Cu, Pb and Zn were in the < ERL range (100%). Chromium, Ni and Hg were distributed in the ERL – ERM range (100%), whereas Cd was distributed between the < ERL and ERL – ERM ranges (66.66% and 33.33% respectively). In pre monsoon Cu and Zn were distributed between the < ERL and ERL – ERM ranges (16.67 % and 83.33% respectively), whereas Cr and Cd were distributed between the < ERL and ERL – ERM ranges (33.33% and 66.66 % respectively). The proportion of Pb was in the < ERL range (100%); while Hg and Ni were distributed between the ERL – ERM ranges (100%). In monsoon Cu was distributed between the < ERL and ERL – ERM ranges (33.33% and 66.66 % respectively). The proportion of Pb was in the < ERL range (100%); Cr,Cd and Hg were distributed in the ERL – ERM ranges (100%), Zn was equally distributed between the < ERL and ERL – ERM ranges (50 %), while Ni distribution was in > ERM range (100%).

At Chettuva, in post monsoon, Cu was equally distributed between < ERL and ERL – ERM ranges (50 % each), the proportion of the metals Pb, Zn, Cd and Hg were in the < ERL range (100%). Cr and Ni were distributed in the ERL – ERM ranges (100%). In pre monsoon Cu was distributed between the < ERL and ERL – ERM ranges (16.67 % and 83.33% respectively). Metals like Pb, Zn and Cd were in the < ERL range (100%). Chromium was distributed between the < ERL and ERL – ERM ranges (83.33% and 16.67% respectively), while Ni was distributed between ERL – ERM and > ERM ranges (16.67% and 83.33% respectively). Mercury was found to be equally distributed between the < ERL and ERL – ERM ranges (50 % each). In monsoon Cu was distributed between the < ERL and ERL – ERM ranges (83.33 % and 16.67% respectively). Metals like Pb, Zn , Cd and Hg were in the < ERL range (100%). Chromium was distributed in the ERL – ERM range (100%), while Ni was distributed between ERL – ERM and > ERM ranges (16.67% and 83.33% respectively).

At Ponnani, in post monsoon, Cu was distributed between the < ERL and ERL – ERM ranges (83.33 % and 16.67% respectively), while the metals like Pb, Cr, Zn and Cd were positioned in the < ERL range (100%). Ni was distributed in the ERL – ERM range (100%), while Hg was distributed between the < ERL and ERL – ERM ranges (66.66% and 33.33% respectively). In pre monsoon Cu and Hg was equally distributed between the < ERL and ERL – ERM ranges (50 % each), the proportion of the metals Pb, Zn and Cd were in the < ERL range (100%). Cr was distributed in the ERL – ERM range (100%), while Ni was distributed between the < ERL and ERL – ERM ranges (16.67% and 83.33% respectively). In monsoon Cu was equally distributed between the < ERL and ERL – ERM ranges (50 % each). The proportion of metals Pb, Zn and Cd were distributed in the < ERL range (100%), while Cr and Hg were distributed in the < ERL and ERL – ERM ranges (16.67% and 83.33% respectively). Nickel was positioned in the > ERM range (100%).

At Calicut, in post monsoon, Cu was distributed between the < ERL and ERL – ERM ranges (83.33% and 16.67% respectively), the proportion of the

metals Pb, Zn, and Cd were in the < ERL range (100%). Cr was distributed in the ERL – ERM ranges (100%). Ni and Hg was equally distributed between ERL – ERM and > ERM range (50% each). In pre monsoon Cu was positioned in the ERL – ERM range (100%). Metals like Pb, Zn and Cd were positioned in the < ERL range (100%). Chromium and Hg was distributed in the ERL – ERM range (100%), while Ni was distributed between ERL – ERM and > ERM ranges (83.33% and 16.67% respectively). In monsoon, Cu was distributed between the < ERL and ERL – ERM ranges (16.67% and 83.33 % respectively) while Pb, Zn and Cd were in the < ERL range (100%). Chromium was distributed in the ERL – ERM range (100%), while Ni was distributed between ERL – ERM and > ERM ranges (16.67% and 83.33% respectively). Mercury was positioned in the < ERL and ERL – ERM ranges (16.67% and 83.33 % respectively).

At Kasargod, in post monsoon, Cu was distributed in the < ERL range (100%), the proportion of the metals Pb, Cr, Zn and Cd were in the < ERL range (100%). Nickel was distributed between < ERL and ERL – ERM ranges (16.67 % and 83.33% respectively), while Hg was equally distributed between < ERL and ERL – ERM ranges (50% each). In pre monsoon Cu was distributed in the < ERL and ERL – ERM ranges (33.33% and 66.66% respectively) while Pb, Zn and Cd were in the < ERL range (100%). Chromium was distributed in the< ERL and ERL – ERM range s(16.67 % and 83.33% respectively) and Ni was distributed between ERL – ERM (100%). Mercury was equally distributed between < ERL and ERL – ERM ranges (50% each). In monsoon, Cu was distributed between the < ERL and ERL – ERM ranges (16.67% and 83.33 % respectively) while Pb, Zn and Cd were in the < ERL range (100%). Chromium was distributed in the ERL – ERM range (100%), while Ni was equally distributed between ERL – ERM and > ERM ranges (50% each). Mercury was also equally positioned in the < ERL and ERL – ERM ranges (50% each).

The individual metal concentrations (both spatial and temporal) distributed along the central and northern coast of Kerala sediments when compared with the NOAA's sediment quality guidelines showed Cu being distributed in the < ERL and ERL – ERM ranges (48.89% and 51.11% respectively). Lead was distributed

in the < ERL range (100 %). Chromium was distributed in the < ERL and ERL – ERM range (38.89 % and 61.11% respectively), while Ni was distributed between three concentration ranges < ERL, ERL – ERM and > ERM ranges (1.11%, 60.00% and 38.89% respectively). Zinc and Cd were distributed in the < ERL and ERL – ERM range (91.11% and 8.89%, 86.67% and 13.37% respectively). Mercury was also distributed between < ERL and ERL – ERM ranges (40% and 60% respectively).

Table 5.10 Effects range-low (ERL) and range- median (ERM) guideline values for heavy metals (µg g^{-1} dry weight basis) and percent incidence of sediment concentration values in concentration ranges defined by the two guideline values for the study area.

Transect	Season	Incidence for each concentration range			Total percentage incidence (%)		
	(n = 6)	< ERL	ERL - ERM	> ERM	< ERL	ERL - ERM	> ERM
Cu: 34 - 270 $\mu g\ g^{-1}$							
Cochin	POM	6			100		
	PM	1	5		16.67	83.33	
	M	2	4		33.33	66.66	
	Overall incidence (n= 18)	9	9		50	50	
Chettuva	POM	3	3		50	50	
	PM	1	5		16.67	83.33	
	M	5	1		83.33	16.67	
	Overall incidence (n= 18)	9	9		50	50	
Ponnani	POM	5	1		83.33	16.67	
	PM	3	3		50	50	
	M	3	3		50	50	
	Overall incidence (n= 18)	11	7		61.11	38.89	
Calicut	POM	5	1		83.33	16.67	
	PM		6			100	
	M	1	5		16.67	83.33	
	Overall incidence (n= 18)	6	12		33.33	66.67	
Kasargod	POM	6			100		
	PM	2	4		33.33	66.66	
	M	1	5		16.67	83.33	
	Overall incidence (n= 18)	9	9		50	50	

Pb: 47 - 218 μg g^{-1}							
Cochin	POM	6			100		
	PM	6			100		
	M	6			100		
	Overall incidence (n = 18)	18			100		
Chettuva	POM	6			100		
	PM	6			100		
	M	6			100		
	Overall incidence (n = 18)	18			100		
Ponnani	POM	6			100		
	PM	6			100		
	M	6			100		
	Overall incidence (n = 18)	18			100		
Calicut	POM	6			100		
	PM	6			100		
	M	6			100		
	Overall incidence (n = 18)	18			100		
Kasargod	POM	6			100		
	PM	6			100		
	M	6			100		
	Overall incidence (n = 18)	18			100		
Cr: 81 - 370 μg g^{-1}							
Cochin	POM		6			100	
	PM	2	4		33.33	66.66	
	M		6			100	
	Overall incidence (n = 18)	2	16		11.11	88.89	
Chettuva	POM		6			100	
	PM	5	1		83.33	16.67	
	M		6			100	
	Overall incidence (n = 18)	5	13		27.78	72.22	
Ponnani	POM	6			100		
	PM		6			100	
	M	1	5		16.67	83.33	
	Overall incidence (n = 18)	7	11		38.89	61.11	
Calicut	POM		6			100	
	PM		6			100	
	M		6			100	
	Overall incidence (n = 18)		18			100	
Kasargod	POM	6			100		
	PM	1	5		16.67	83.33	
	M		6			100	
	Overall incidence (n = 18)	7	11		38.89	61.11	

Ni: 21 - 52 μg g^{-1}							
Cochin	POM		6			100	
	PM		6			100	
	M			6			100
	Overall incidence (n = 18)		12	6		75	25
Chettuva	POM		6			100	
	PM		5	1		83.33	16.67
	M		1	5		16.67	83.33
	Overall incidence (n = 18)		12	6		75	25
Ponnani	POM		6	0		100	
	PM		1	5		16.67	83.33
	M			6			100
	Overall incidence (n = 18)		7	11		38.89	61.11
Calicut	POM		3	3		50	50
	PM		5	1		83.33	16.67
	M		1	5		16.67	83.33
	Overall incidence (n = 18)		9	9		50	50
Kasargod	POM	1	5		16.67	83.33	
	PM		6			100	
	M		3	3		50	50
	Overall incidence (n = 18)	1	14	3	5.55	77.78	16.67
Zn : 150 - 410 μg g^{-1}							
Cochin	POM	6			100		
	PM	1	5		16.67	83.33	
	M	3	3		50	50	
	Overall incidence (n = 18)	10	8		55.56	44.44	
Chettuva	POM	6			100		
	PM	6			100		
	M	6			100		
	Overall incidence (n = 18)	18			100		
Ponnani	POM	6			100		
	PM	6			100		
	M	6			100		
	Overall incidence (n = 18)	18			100		
Calicut	POM	6			100		
	PM	6			100		
	M	6			100		
	Overall incidence (n = 18)	18			100		
Kasargod	POM	6			100		
	PM	6			100		
	M	6			100		
	Overall incidence (n = 18)	18			100		

Cd: 1.2 - 9.6 $\mu g\ g^{-1}$							
Cochin	POM	4	2		66.66	33.33	
	PM	2	4		33.33	66.66	
	M	0	6		0	100	
	Overall incidence (n = 18)	6	12		33.33	66.67	
Chettuva	POM	6			100		
	PM	6			100		
	M	6			100		
	Overall incidence (n = 18)	18			100		
Ponnani	POM	6			100		
	PM	6			100		
	M	6			100		
	Overall incidence (n = 18)	18			100		
Calicut	POM	6			100		
	PM	6			100		
	M	6			100		
	Overall incidence (n = 18)	18			100		
Kasargod	POM	6			100		
	PM	6			100		
	M	6			100		
	Overall incidence (n = 18)	18			100		

Hg: 0.15 - 0.71 $\mu g\ g^{-1}$							
Cochin	POM		6			100	
	PM		6			100	
	M		6			100	
	Overall incidence (n = 18)		18			100	
Chettuva	POM	6			100		
	PM	3	3		50	50	
	M	6			100		
	Overall incidence (n = 18)	15	3		83.33	16.67	
Ponnani	POM	4	2		66.66	33.33	
	PM	3	3		50	50	
	M	1	5		16.67	83.33	

	Overall incidence (n = 18)	8	10		44.44	55.56	
Calicut	POM	3	3		50	50	
	PM		6			100	
	M	1	5		16.67	83.33	
	Overall incidence (n = 18)	4	14		22.22	77.78	
Kasargod	POM	3	3		50	50	
	PM	3	3		50	50	
	M	3	3		50	50	
	Overall incidence (n = 18)	9	9		50	50	

NOTE: POM - post monsoon, PM - pre monsoon, M - monsoon, Values given along with metals are ERL-ERM standard values

5.3 Discussion

The normal trend of sediment distribution shows a decreasing sand proportion with increasing silt and clay components with increase in the depth toward seaward direction at all transects. This may be due to the sorting of sediments by waves and currents prevailing near the coast. Significant variations in the grain size of the sediments of the near shore coastal region can be explained in terms of both seasonal fluctuations and erosion of river channel sediments. Fining of sediment could also be related to a progressive decrease in the influence of the riverine flow and a decrease in its transport competency and capacity. Fine grained sediments supplied by a river would be carried in suspension, reaching filter areas on the shelf. Coarser sediments are transported as bed load, being deposited nearer the river mouth. The sediment along the investigated area consists mainly of fine fraction (silt & clay) (mean > 80%), together with less than 20% coarse sediments (the mean value for all samples). The contribution of clay towards the fine fraction is about 35.47%. From the above observations, it is conspicuous that the coastal region of the present study area is not under high hydrodynamic conditions. The dominancy of fine fraction, with

contribution from clay forming a principal part signifies the sediment is susceptible for sorption of metal content (Rubio *et al*., 2000; Cho *et al.*, 1999; Martincic *et al*., 1986; Salomons and Forstner, 1984). It is known that the fine grained fraction of sediments, consisting of clay minerals is associated with the highest metal content; this is related in turn to the surface area of the particles.

On an average, the percentage of organic matter reported at each transects for all season in this study is above the world average of 2.5 % for near shore sediments (Trask, 1939). According to Paropkari *et al.*, (1992) the high productivity in Arabian Sea is the basis for the organic enrichment in bottom sediments. Considering the distribution of organic matter towards offshore from the coast an on shore-offshore gradient was however noticed at all transects for all season. The organic matter content in offshore (3.0 – 10.0 km) sediments is high compared to that in nearby coast for all seasons except at Calicut and Ponnani in monsoon which showed an inverse trend. A number of factors are responsible for the accumulation of organic matter in marine sediments. The important among them are supply of organic material to the environment of deposition through surface waters, rate of decomposition of organic substances, and texture of sediments and above all phytoplankton and zooplankton are the most abundant source of organic material in the sediments (Grathwohl, 1990). In this study the low values of organic content in the near shore can be explained due to the rapid deposition of coarser inorganic constituents in relation to the organic material. The sandy texture of the sediments in the nearshore region and high dissolved oxygen content in the near bottom waters in the region are favourable for the waters to permeate through the sands and oxidize the organic matter deposited from the overlying waters. It has been observed that fine grained sediments are richer in organic matter than coarse grained (Pettijohn, 1957; Stewart, 1958). Towards offshore at all transects fining of the sediment was conspicuous hence high organic content while at Calicut and Ponnani in monsoon the offshore sediment was found to have greater proportion of sand in

sediment. The concentration of organic matter content was noted high in the central coast (Cochin and Chettuva) compared to the northern coast (Ponnani, Calicut and Kasargod). The enrichment of organic matter towards central coasts shelf could be due to Cochin , being a fast growing commercial city, anthropogenic activities are generating 104 x 10^3 m^3 of industrial and 260 m^3 of domestic wastes per day, which are being released directly into the coastal water without treatment (Balachandran *et al.*, 2006; Martin *et al.*, 2006) thus the modern sediments are heavily laden with organic detritus of the Periyar river resulting in its deposition and ultimately preserving the organic matter. In Chettuva it may be due to the influence of continuous inflow of organic rich domestic waste impinging in to the coastal water from the establishments of hinterland pilgrimage centre where millions of pilgrims visit each year. Similar observation due to the inflow of organic rich domestic wastes has also been made in Visakhapatnam coastal region (Satyanarayana *et al.*, 1993). The high organic matter content noticed in post monsoon in the northern coast could be due to the higher rate of deposition of phytoplankton. The maximum production of phytoplankton biomass along the northern coast was found to take place during monsoon due to upwelling and its subsequent deposition in post monsoon can be expected. Madhupratap (1987) has reported the export of unconsumed phytoplankton due to intense organic production with the retreat of monsoon, from the estuary to the sea during post monsoon, facilitating organic enrichment in southwest coastal sediments. Badarudeen *et al.*, (1998) has reported the upwelled nutrient rich waters resulting in high productivity in the overlying waters and fine texture of the sediment preserving the depositional organic matter. The low organic matter content observed in pre monsoon season can be due to the less riverine flow, decreased nutrients and thus low phytoplankton biomass, active predation by higher organism ensuing in lower organic matter content.

Sediments are recognized as sinks for many contaminants discharged into surface waters owing to the adsorption processes of particulate matter, which then settles on the sediment. From the regional distribution of metals

concentrations in sediments on a seasonal scale, a relationship between the various sedimentary and hydrodynamic influences on sediments can be observed. On the basis of highest concentration of metal reported in sediments along the study area it followed the order Zn > Cr > Ni > Cu > Pb > Cd > Hg. Heavy metals like Pb, Cd, Hg showed the lowest concentration for all seasons while there was much spatial and temporal variation in the concentration of Cr, Ni, Zn and Cu among seasons as such a definite order in the distribution of metals in sediments both spatially and temporally could not be figured. The wide variation in metal distribution in sediments among seasons supports the view that anthropogenic activity contributes significantly to the contamination of marine sediments due to industry and urban activities. The maximum concentration of all studied metals was found high at Cochin in different season. Concentration of these heavy metals in the sediments is much higher than those of world average concentrations of shale (Turekian and Wedephol, 1961). This is reflected in relatively high contamination factor (PLI >1) in sediments which can be attributed to their incorporation by anthropogenic inputs. The industrial assortment at Cochin includes fertilizer, pesticide, chemical and allied industries, radioactive mineral processing, petroleum refining, metal plating and fish-processing units.

Metals like Cr, Ni showed enrichment at all transects during monsoon signifying the monsoonal flushing of terrestrial inputs into coastal water enhancing its concentration in sediments. Contamination due to Cr (exceeded above average shale for Cr) was discerned at Calicut all throughout the seasons. It is presumed that effluent released from the tile industries which include production of ceramics, crockery, stoneware pipes and insulation materials in which Cr is main constituent is the cause for the enrichment of Cr in sediments at Calicut. The sediments collected during post monsoon reflected low metal enrichment throughout the study sites. The influence of northerly currents that are capable of dispersing their deposition along the southwest coast of India has been documented (Shetye *et al.,* 1991) thus averting the additions of metal inputs in sediment.

The metal distribution showed an erratic pattern in the concentration gradient towards offshore and inshore. This gradient takes place across sediment of similar texture and composition, and can attributed to the regional influence as a result of coastal input which are diverse at each transect. The distribution may probably also be affected by the prevailing currents leading to distinct regional accumulation of sediment. The currents are northerly during November – February and southerly during April – September. On moving towards offshore, heavy metal concentration was higher compared to near shore due to the fine texture of sediments and offshore drift in sediments dispersion.

5.3.1 Pollution Indices

The extent of contamination of aquatic sediments has been quantified by comparing with an uncontaminated natural background (world shale average) for a specific constituent (Turekian and Wedephol, 1961; Forstner and Muller, 1973). In an attempt to summarize the extent of pollution by metals in sediments of this study, contamination factors (CF), pollution load index (PLI) and geo – accumulation index (I_{geo}) have been evaluated for all the metals studied both in the lowest and highest range of concentrations. The range of values of CF, PLI and I_{geo} of each heavy metal is tabulated so as to project the data of a location on a pollutant scale. An evaluation based on PLI formulates the fact that the average values of PLI for Chettuva, Ponnani and Kasargod were less than one for all seasons indicating low pollution concern due to metals. In Cochin and Calicut the PLI formulated were greater than one in pre monsoon and monsoon indicating the significant role of anthropogenic inputs such as industrial effluents, domestic sewage, mining activities and land runoff towards metal incorporation in sediments. Similar high values of PLI of 1.45 – 1.78 have been reported for Vishakhapatnam harbor (Panigrahy *et al.*, 1997), 3.82 for Vishakapatnam inner harbor (Satyanarayana *et al.*, 1994), indicating metal pollution. Interestingly the PLI was less than one in post monsoon at Cochin and Calicut, could be due to the dispersion/ dilution or redistribution of contaminated marine sediments by coastal currents. This imply seasonal

variation, difference in the energy of environmental factors, changing wind patterns, biogenic association are all playing a fundamental part in regulating (impoverish) the deposit of elemental concentration in the study region.

On the basis of seasonal range of PLI values, metal contamination in the transects, followed the order Cochin > Calicut > Ponnani> Chettuva > Kasargod. Low metal concentration in Chettuva and Kasargod is probably due to low anthropogenic activities in the area. An assessment of PLI among seasons revealed PLI < 1 at all transects in post monsoon, suggestive of region having less input from external metal contaminants. This findings corroborate with the studies of Balachandran *et al.*, (2005) and Kaladharan *et al.*, (2011), according to them, the impoverishment of metals in sediments of southwest coastal region (present study area) is probably because of the prevalent northerly currents which are capable of dispersing their deposition and biogenic association. The present observation corroborates with the above findings.

The overall results of geo-accumulation index of heavy metals in the study area, showed that Pb,Cr, Ni, Zn, Hg fall into class I (unpolluted to moderately polluted) and Cd falls into class 2 & 3 (moderately polluted & moderately to strongly polluted) at Cochin. The enrichment of Cd in the sediment matrix is mainly due to quantum of metal input from the contiguous industrial establishments situated along the coast. The industrial assortment includes fertilizer, pesticide, chemical and allied industries, radioactive mineral processing, petroleum refining, metal plating and fish processing units etc. The major sources of Cd are also contributed by sewage sludge from wastewater treatment and agricultural runoff from the hinterland. The high concentration observed for Cd (strongly polluted) in monsoon is due to the washing of the polluted coast. The monsoonal discharge through the Cochin backwaters, supported by the annual minimum sea level along this coast in this period (Srinivas, 2000), favor increased flushing of the backwater derived materials into the coastal zone. For all the other transects Cd and Cr were the metals which fell into class 1 (unpolluted to moderately polluted) except Kasargod ; where the overall average I_{geo} values of all metals fall into class 0 which can be

categorized as unpolluted. The geo-accumulation index (I_{geo}) was also in agreement with contamination factors recorded for the elements. Based on I_{geo} it can be inferred that Cochin has the highest anthropogenic activities while Kasargod the lowest in terms of metal contamination in sediments. At other transects anthropogenic activities has resulted in moderate contamination of Cd and Cr in sediments. The major sources of pollutant input can attributed due to urban wastes, agricultural runoff and fishing boat trafficking. Overall average of I_{geo} values of all the metals in sediments from the central and northern coast of Kerala fall into class 0 and 1 which is categorized as unpolluted to moderately polluted environment except at Cochin where it is moderately - strongly polluted with cadmium (Cd) metal.

In order to estimate possible environmental consequences of the analyzed metals at the studied site, concentration of the metals were compared with the sediment quality guidelines of effect range low (ERL) and effect range median (ERM) proposed by Long *et al.*, (1995;1997). A comparison between transects revealed the concentration of metals in sediment matrix are in the range enough to cause the incidence of occasional toxicity to aquatic organism due to Cu, Cr, Ni, Zn, Cd , Hg and Cu, Cr and Ni at Cochin and Chettuva respectively along the central coast of Kerala. In the northern coast of Kerala, toxicity presenting an occasional threat to organisms due to concentrations of Cr and Hg was noted at Ponnani, and due to Cu, Cr, Ni and Hg at Calicut and Kasargod. As per the foregoing comparison for the incidence of toxicity along the central and northern coast of Kerala, greater than 50% of sediments have the metal concentration in the matrix which is expected to be occasionally associated with the toxic effects on aquatic organisms due to Cu, Cr, Ni and Hg, if these metals become bioavailable from the sediment due to any chemical processes. However, concentrations of Ni metal in an average of 38.89% of sediments exceeded the ERM value. Thus there is a propensity of Ni metal to enhance the incidence of adverse negative effects on living resources frequently. In monsoon the concentration of Ni in sediment matrix is such that it is enough to jeopardize the biota at all transects, and in Ponnani it was also

discerned in pre monsoon. Although most of the metal concentrations were still below the concentration enough to cause frequent incidence of toxicity to aquatic living resources, follow up monitoring is essential in the case of Ni and should be continued at all transects. Nickel is generally associated with industrial processes such as smelting, waste incineration; fossil fuel combustion, impurity in phopshatic fertilizers and also is present in highest concentration in crude oil and residual fuel oils (Potter and Simmons, 1998). In this study, the increase in concentration in monsoon could be the flushing of fuel oil residues, agricultural runoff from land into the coastal environment.

In general, the use of geochemical tools and sediment quality guidelines to account for the magnitude of heavy metal contamination in the study area revealed high contamination in monsoon and impoverishment in post monsoon. This observation is agreeable with that of Balachandran *et al.*, (2005), that the coastal currents and stable biogenic association is normalizing the metal deposition in south west coast of India.

5.3.2 Comparison with Other Studies

The total metal concentrations in this study were comparable to other studies reported in the literature (Table 5.11). However, concentrations of Ni found in this study were higher than other coastal regions of India and other regions of the world but much lower than the polluted Mahim coast of India (175 µg g^{-1}: Zingde, 1985) and the Red sea (185.95 µg g^{-1}: El Nemr *et al.*, 2006). Zinc concentrations were also higher than most of the coastal regions in India and across the world, but much lower than those reported for Bombay coast, India (308 µg g^{-1}),Semerang coast, Indonesia (259 µg g^{-1}), southwest coast of Spain (259 µg g^{-1}), Trabzon coast (286.30 µg g^{-1}) and continental shelf of North sea(4000 µg g^{-1}). High value of Ni (134 µg g^{-1}) and Zn (219 µg g^{-1}) was recorded at Cochin in monsoon, could have emanated from industrial effluent input. In general, with the exception of high value of Zn and Ni in sediments at Cochin, heavy metal concentrations in the coastal sediments of the study area were still comparable to the non polluted coastal environments of the world.

Table 5.11 Heavy metal concentrations in the sediments of study area and in other parts of the world.

Location	Cu	Pb	Cr	Ni	Zn	Cd	Hg	References
Central and Northern Coast of Kerala,SW India	15.0 - 67.0	7.40 - 38.0	34.00 - 217.80	14.00 - 134.00	25.00 - 219.00	0.08 - 3.60	0.01 -0.65	This Study
Cochin Coast,India	6.00 - 32.70	13.1 -39.60	35- 195	5.1 -72.10	7.00 -132.00	1.470 -3.270	-	Balachandran *et al*., 2005
Beypore coast, India	13.00 -39.00	19.00 - 32.00	131.00 - 289.00	40.00 - 89.00	34.00 - 60.00	-	-	Nair and Ramachandran, 2002
SW Coast of India	22 .00 - 69.00	-	155.00 - 324.00	43.00 - 73.00	85.00 - 121.00	-	-	Manjunatha *et al*.,1998
Nagapattinam Coast,SE India	18.5	57.00	3204.00	75.00	71.00	-	-	Sujatha *et al*., 2008
Bombay Coast,India	87.00 - 106.00	9.00 - 36.00	102.00 - 120.00	42.00 - 59.00	95.00 - 147.00	0.50 -3.30	-	Dilli,1986
Mahim coast, India	105.00 - 198.00	25.00- 42.00	-	89.00 -175.00	110.00 - 308.00	-	-	Zingde,1985
Bay of Bengal	26.00	-	-	64.00	-	-	-	Subramanian and Mohanachandran,1990
Semerang coast, Indonesia	33.00 - 72.00	18.00 - 44.00	-	1.00 -29.00	84.00 - 259.00	-	-	Takarina *et al*., 2004
Offshore west coast, Malaysia	0.25 - 13.80	3.59 - 25.36	-		4.00 - 79.05	0.10 -1.42	-	Yap *et al*., 2003
Dumai coast, Indonesia	1.61 -13.84	14.63 - 84.90	-	7.26 - 19.97	31.49 -87.11	0.46 - 1.89	-	Amin *et al*., 2009
Northern Bohai and Yellow Seas, China	0.53 - 35.0	9.50 - 49.00	4.20 - 94.00		9.80 - 170	0.050 - 0.83	0.020 - 0.18	Luo *et al*., 2010
Coast of Trabzon, Black Sea	13.68 -315.99	12.34 -83.78	-	10.60 - 29.20	56.50 - 286.30	-	-	Ozseker and Eruz, 2011
West Port, Malaysia	7.40 - 27.60	22.30 - 80.0	11.5 -61.50	7.20 - 22.20	23.00 - 98.30	0.24 -3.53	0.11 -0.40	Tavakoly Sany *et al*., 2011
NW Coast of Spain	7.93 - 42.44	23.23 - 89.09	11.72 - 52.08	10.72 - 33.77	30.68 - 158.38	3.03 -3.43	-	Rubia *et al*., 2000
The Gulf of Suez, Red Sea	27.14 -718.75	42.61 -151.32	37.21- 129.07	47.33 - 185.95	64.36 - 151.32	6.51 -24.77	-	El Nemr *et al*., 2006
Egyptian Coast, Mediterranean Sea	10.41 -189.96	39.92 -119.75	16.08 - 413.41	40.84 - 117.97	24.14 - 131.03	2.73 -10.61	-	El Nemr *et al*.,2007
Continental shelf of North Sea	25.00 - 240.00	75.00 - 630.00	-	-	400.00 - 4000.00	3.00 - 30.00	-	Everaarts and Fischer, 1992
Eastern Arabian Sea	11.60 -46.60	-	31.33 -66.00	-	68.60 - 132.30	-		Shetye *et al*., 2009
Sothern Caspian Coast	5.52 - 85.20	0.50 - 34.56	-	2.02 - 9.80	5.60 - 45.80	0.05 -0.82	-	Parizanganeh *et al*., 2007

5.3.3 Correlations between the Sediment Components of the Transects

Principal component analysis was used to reduce the dimensionality of the data and to identify the 'latent' factors that may be influencing metal concentrations in the sediments (Meglen, 1992). PCA analysis extracted three components each with eigen values >1, which explained 85.90%, 81.12%, 78.67% and 83.10% of the total variance for Cochin, Chettuva, Ponnani and Kasargod, respectively. In the case of Calicut, four components accounted for 84.18% of the total variance (Table 5.12). Correlation coefficients among the metals and textural characteristics for each transects are given in Table 5.13.

In Cochin, a firmly related group (PC1) which explained 43.18% variance was formed by Pb, Cr, Ni, Clay, and Org-M which had strong negative correlation with sand. This firmly explains industrial source in which organic matter and fine texture are involved in the sorption while sand tend to impoverish their distribution. The second group (PC2) explained 26.05% variance was formed by Cu, Zn and Cd. Cu and Zn are involved in biological production and Cd is significantly correlated with organic matter. Cadmium is removed from surface waters by phytoplankton, and zooplankton grazing subsequently returns Cd to the sediment as fecal pellets (Boyle *et al.*, 1976; Simpson, 1981). This signifies diagenetic reactions (organic matter degradation) mediated by sedimentary microorganisms which in turn, regulates the behavior of these reactive metals. The third group (PC3) explained 16.68% variance which was contributed by Hg having negative correlation with silt (Mercury Factor). Mercury may thus be from an alternative natural source to all the other metals or from a diffuse anthropogenic source.

At Chettuva, the first factor (PC1) which explained 33.49% variance and gives information about the variation in Cu, Zn, Cd and Org-M. This reflects the complex nature of organic matter as well as the important role played by the diagenetic reactions driven by its degradation, which in turn regulates the behavior of these reactive metals (Diaz *et al.*, 2008). The

second group (PC2) explained 30.53% variance which was formed by Pb, Cr, and Ni. This can be due to anthropogenic input. The third group (PC3) explained 17.10% variance which was contributed by Hg and clay. Mercury may be from an alternative natural source to all the other metals or from a diffuse anthropogenic source. It is being strongly binded with fine sediments such as clay. Since agriculture is the main economy of this region, Hg source can be traced to its increased use of pesticides and fungicides.

At Ponnani, the first factor (PC1) which explained 37.89 % variance was formed by Pb, Cr, Ni, Hg and Clay. The metals mainly traced to anthropogenic inputs and are being strongly melded with clay. The second group (PC2) explained 20.56% variance which was formed by Zn and Cd. This metals being involved in biological production, signifies diagenetic reactions driven by its degradation, which regulates the behavior of these reactive metals. The third group (PC3) explained 20.22% variance which was contributed by sand and silt in which silt was negatively corelated with sand. Both sand and silt didn't show correlation to any of the metals and thus did not play a role in their distribution.

At Calicut four components explained 84.18% variance when compared to three components of other transects. The first factor (PC1) which explained 30.17% variance was comprised of Cr, Ni, Org-M showing inverse relationship with sand. The strong association of Cr and Ni signifies effluent discharges from metal finishing processes, ceramic industries and it strong association with organic matter in the form of organic complexes, while increase in sand distribution tends to impoverish this complex. The second group (PC2) explained 23.15% variance which was formed by Cu, Zn and Cd. This signifies diagenetic reactions driven by its degradation of organic material, which regulates the behavior of these reactive metals. The third group (PC3) explained 17.09% variance which was contributed only by clay. Thus clay may thus be from an alternative source to the coastal environment (source traced to contiguous brick factory establishment) and the fourth group (PC4) was formed by Pb and Hg. Lead should have been

contributed from the gasoline due to heavy boat trafficking and harbor activities; while Hg due to increased use of pesticides and fungicides.

At Kasargod, a firmly related group (PC1) was formed by Cu, Pb, Cr, and Ni which explained 31.52% variance, indicates common source which indicate anthropogenic inputs, while the second group (PC2) which explained 29.10% variance was formed by Hg, Clay and Org-M having a negative relation with sand. Mercury may thus be from an alternative natural source to all the other metals or from a diffuse anthropogenic source which are binded to organic matter and clay particles while increase in sand distribution tend to dilute them. Since agriculture is the main economy of this region, Hg source can be traced to its increased use of pesticides and fungicides. The third group was formed by Zn and Cd which explained 22.47% variance. These metals being involved in biological production, it also signifies diagenetic reactions driven by its degradation of organic material, which regulates the behavior of these reactive metals.

Results of PCA analysis reflected anthropogenic activities, biogenic association and its diagentic reaction driven by its degradation regulating the behavior of reactive metals especially Cu, Zn and Cd in all transects. Positive values of mercury and its association with fine sediments were discerned at all transects except at Ponnani, reveals, alternative natural source of this metal or from a diffuse anthropogenic source. Since agriculture is the major economy of the study region, Hg source can be traced to its increased use in pesticides and fungicides. The significant increase in metals towards offshore reflects the retention of organic content in the fine grained sediment, as there is a significant correlation between them.

Table 5.12 Varimax factor analysis using PCA and identified principal components of the sedimentary variables of the study area.

Cochin			
	PC1	**PC2**	**PC3**
Cu	-0.0167	**0.967**	3.44E-02
Pb	**0.766**	0.501	0.303
Cr	**0.951**	5.52E-02	0.212
Ni	**0.828**	0.386	0.202
Zn	-0.0545	**0.939**	9.72E-02
Cd	0.406	**0.790**	-0.0734
Hg	8.64E-02	-0.0156	**-0.765**
Sand	**-0.943**	6.36E-02	0.184
Silt	0.113	4.24E-02	**0.837**
Clay	**0.803**	-0.108	-0.55
Org-M	**0.923**	4.56E-02	-0.14
Eigen	4.75	2.87	1.84
% Variance	43.18	26.05	16.68
% Cumulative Variance	43.18	69.22	85.90

Chettuva			
	PC1	**PC2**	**PC3**
Cu	**0.691**	-0.335	0.226
Pb	1.81E-02	**0.888**	-0.258
Cr	0.185	**0.810**	-0.337
Ni	-0.114	**0.891**	0.243
Zn	**0.886**	0.182	0.115
Cd	**0.813**	-0.388	0.142
Hg	0.314	-0.256	**0.601**
Sand	**-0.791**	-0.511	-0.228
Silt	0.567	0.435	**-0.629**
Clay	0.390	0.187	**0.857**
Org-M	**0.718**	0.522	0.118
Eigen	3.67	3.36	1.88
% Variance	33.49	30.53	17.10
% Cumulative Variance	33.49	64.02	81.12

Ponnani			
	PC1	**PC2**	**PC3**
Cu	0.578	-0.281	0.378
Pb	**0.894**	0.198	6.81E-02
Cr	**0.847**	-0.154	0.128
Ni	**0.901**	-0.149	0.111
Zn	1.97E-02	**0.764**	0.376
Cd	1.35E-02	**0.936**	0.161
Hg	**0.791**	0.273	0.275
Sand	-0.406	-0.529	**-0.672**
Silt	-0.134	0.339	**0.852**
Clay	**0.780**	0.396	-0.133
Org-M	0.297	0.11	0.781
Eigen	4.17	2.26	2.22
% Variance	37.89	20.56	20.22
% Cumulative Variance	37.89	58.45	78.67

Calicut				
	PC1	**PC2**	**PC3**	**PC4**
Cu	0.113	**0.853**	7.37E-02	0.325
Pb	0.152	0.125	0.409	**0.722**
Cr	**0.930**	-0.0165	9.22E-02	-0.0247
Ni	**0.746**	0.123	0.49	-0.306
Zn	-0.0887	**0.912**	-0.0596	0.117
Cd	5.43E-02	**0.787**	0.296	4.66E-02
Hg	-0.223	0.369	1.11E-02	**0.789**
Sand	**-0.888**	-0.19	0.118	0.125
Silt	0.235	-0.0661	-0.91	-0.243
Clay	0.541	0.220	**0.716**	0.114
Org-M	**0.815**	-0.337	-0.117	0.258
Eigen	3.32	2.55	1.88	1.51
% Variance	30.17	23.15	17.09	13.77
% Cumulative Variance	30.17	53.32	70.42	84.18

Kasargod			
	PC1	**PC2**	**PC3**
Cu	**0.740**	0.432	0.358
Pb	**0.769**	-0.0121	0.514
Cr	**0.885**	0.165	-0.0011
Ni	**0.870**	0.335	-4.91E-02
Zn	-0.107	-0.0569	**0.886**
Cd	0.450	0.16	**0.756**
Hg	-0.0239	**0.776**	0.502
Sand	-0.49	**-0.759**	-0.345
Silt	0.394	0.466	0.577
Clay	0.401	**0.776**	-3.82E-02
Org-M	0.133	**0.921**	-0.125
Eigen	3.47	3.20	2.47
% Variance	31.52	29.10	22.47
% Cumulative Variance	31.52	60.62	83.10

Table 5.13 Summary of the correlation coefficients among the heavy metals, sediment texture and organic matter in the study area.

Cochin											
	Cu	**Pb**	**Cr**	**Ni**	**Zn**	**Cd**	**Hg**	**Sand**	**Silt**	**Clay**	**Org. Matter**
Cu	1										
Pb	0.461	1									
Cr	0.024	**.834(**)**	1								
Ni	0.376	**.910(**)**	**.908(**)**	1							
Zn	**.879(**)**	**.475(*)**	0.035	0.333	1						
Cd	**.721(**)**	**.636(**)**	0.382	**.543(*)**	**.619(**)**	1					
Hg	-0.033	-0.176	-0.031	-0.055	-0.109	0.051	1				
Sand	0.074	**-.614(**)**	**-.822(**)**	**-.660(**)**	0.107	-0.358	-0.275	1			
Silt	0.093	0.312	0.268	0.211	0.092	0.071	-0.351	-0.049	1		
Clay	-0.138	0.401	**.618(**)**	**.488(*)**	-0.172	0.268	0.393	**-.879(**)**	-0.428	1	
Org Matter	0.053	**.637(**)**	**.804(**)**	**.692(**)**	-0.045	**.476(*)**	0.078	**-.890(**)**	-0.03	**.827(**)**	1

Chettuva											
	Cu	**Pb**	**Cr**	**Ni**	**Zn**	**Cd**	**Hg**	**Sand**	**Silt**	**Clay**	**Org. Matter**
Cu	1										
Pb	-0.268	1									
Cr	-0.249	**.711(**)**	1								
Ni	-0.198	**.746(**)**	**.604(**)**	1							
Zn	**.624(**)**	0.198	0.31	0.095	1						
Cd	**.627(**)**	-0.401	-0.169	-0.357	**.641(**)**	1					
Hg	0.315	-0.31	-0.359	-0.132	0.265	0.386	1				
Sand	-0.412	-0.389	-0.452	-0.374	**-.762(**)**	-0.434	-0.237	1			
Silt	0.089	**.577(*)**	**.609(**)**	0.166	0.439	0.151	-0.167	**-.567(*)**	1		
Clay	0.397	-0.088	-0.044	0.281	**.476(*)**	0.364	0.434	**-.633(**)**	-0.278	1	
Org. Matter	0.16	0.379	**.475(*)**	0.344	**.646(**)**	0.444	0.163	**-.888(**)**	**.578(*)**	**.494(*)**	1

Ponnani											
	Cu	**Pb**	**Cr**	**Ni**	**Zn**	**Cd**	**Hg**	**Sand**	**Silt**	**Clay**	**Org. Matter**
Cu	1										
Pb	**.537(*)**	1									
Cr	**.535(*)**	**.674(**)**	1								
Ni	0.453	**.822(**)**	**.789(**)**	1							
Zn	0.126	0.186	0.036	-0.084	1						
Cd	-0.125	0.225	-0.056	-0.156	**.751(**)**	1					
Hg	0.46	**.768(**)**	**.633(**)**	**.623(**)**	0.224	0.363	1				
Sand	-0.246	**-.517(*)**	-0.269	-0.433	**-.578(*)**	**-.552(*)**	**-.593(**)**	1			
Silt	0.065	0.097	-0.068	0.017	.501(*)	0.454	0.21	**-.751(**)**	1		
Clay	0.23	**.658(**)**	**.499(*)**	**.617(**)**	0.222	0.269	**.629(**)**	**-.526(*)**	-0.156	1	
Org. Matter	0.313	0.19	0.347	0.273	0.344	0.201	**.519(*)**	**-.692(**)**	**.513(*)**	0.326	1

Calicut											
	Cu	**Pb**	**Cr**	**Ni**	**Zn**	**Cd**	**Hg**	**Sand**	**Silt**	**Clay**	**Org. Matter**
Cu	1										
Pb	0.299	1									
Cr	0.028	0.226	1								
Ni	0.106	0.116	**.757(**)**	1							
Zn	**.742(**)**	0.178	-0.013	-0.067	1						
Cd	**.535(*)**	0.414	0.103	0.296	**.715(**)**	1					
Hg	**.591(**)**	0.418	-0.291	-0.283	0.363	0.241	1				
Sand	-0.307	0.042	**-.699(**)**	**-.648(**)**	0.016	-0.055	0.162	1			
Silt	-0.198	-0.436	0.131	-0.167	-0.107	-0.264	-0.287	-0.347	1		
Clay	0.442	0.353	**.470(*)**	**.697(**)**	0.079	0.277	0.124	**-.539(*)**	**-.603(**)**	1	
Org. Matter	-0.183	0.174	**.769(**)**	0.386	-0.252	-0.166	-0.142	**-.564(*)**	0.204	0.291	1

Kasargod											
	Cu	**Pb**	**Cr**	**Ni**	**Zn**	**Cd**	**Hg**	**Sand**	**Silt**	**Clay**	**Org. Matter**
Cu	1										
Pb	**.680(**)**	1									
Cr	**.698(**)**	**.587(*)**	1								
Ni	**.809(**)**	**.614(**)**	**.746(**)**	1							
Zn	0.247	0.295	0.012	-0.192	1						
Cd	**.702(**)**	**.735(**)**	0.318	0.46	**.530(*)**	1					
Hg	**.510(*)**	0.181	0.099	0.298	0.329	**.542(*)**	1				
Sand	**-.751(**)**	**-.564(*)**	**-.615(**)**	**-.597(**)**	-0.226	**-.538(*)**	**-.702(**)**	1			
Silt	**.617(**)**	**.668(**)**	0.438	0.432	0.35	**.532(*)**	**.618(**)**	**-.826(**)**	1		
Clay	**.600(**)**	0.231	**.564(*)**	**.541(*)**	0.004	0.333	**.519(*)**	**-.796(**)**	0.316	1	
Org. Matter	**.472(*)**	0.109	0.189	0.43	-0.183	0.102	**.575(*)**	**-.705(**)**	0.443	**.710(**)**	1

5.5 Conclusion

Sediment texture was mainly contributed by fine fraction, with contribution from clay forming a principal part signifies the sediment is susceptible for sorption of metal content. The average percentage of organic matter reported at each transects for all seasons was above the world average of 2.5 % for near shore sediments due to enhanced productivity in the overlying water. In the central coast (Cochin and Chettuva) a definite seasonal trend was not noticed and the sediment was highly enriched with organic matter compared to northern coast, presumed to be due to the heavy input of domestic wastes. The wide variation in metal distribution in sediments among seasons supports the view that anthropogenic activity contributes significantly to the contamination of marine sediments due to industry and urban activities. On the basis of highest concentration of metal reported along the study area it followed the order Zn > Cr > Ni > Cu > Pb > Cd > Hg. The maximum concentration of all studied metals was found high at Cochin in different season presumed to be due to the input of contaminants from the broader heavily industrialized catchment area. There was much spatial variation in the concentration of Cr, Ni, Zn and Cu among seasons as such a definite order in the distribution of metals in sediments both spatially and

temporally could not be figured. Metals like Cr, Ni showed enrichment at all transects during monsoon signifying the monsoonal flushing of terrestrial inputs into coastal water enhancing its concentration in sediments. Contamination due to Cr was discerned at Calicut all throughout the seasons presumed to be the effluent released from the contiguous ceramic industries in which Cr is a main constituent. The sediments collected during post monsoon reflected low metal enrichment throughout the study sites could be facilitated due to coastal currents and biogenic association. On moving towards offshore in all transects, heavy metal concentration was higher compared to near shore is an indication of offshore drift in sediments and association with fine grained sediments.

On the basis of PLI which shows the magnitude and extent of the heavy metals deposition in sediment, regional contamination followed the order Cochin > Calicut > Ponnani> Chettuva > Kasargod. Thus, Cochin has the highest anthropogenic activities while Kasargod the lowest in terms of metal contamination in sediments. The geo-accumulation index, a pollution indicator which accounts for anthropogenic inputs of heavy metals, categorized the study area as unpolluted to moderately polluted environment except at Cochin where it is moderately to strongly polluted with Cd. Based on comparisons to the effect-range classification, there is a propensity of Ni metal to enhance the incidence of adverse negative effects on living resources frequently especially in monsoon at all transects. The total metal concentrations in this study were comparable to other studies reported in the literature; however concentrations of Ni and Zn found in this study especially at Cochin were higher than other coastal regions of India and other regions of the world but much lower than those reported for polluted coasts. High value of Ni (134 µg/g) and Zn (219 µg/g) was recorded at Cochin in monsoon, could have emanated from industrial effluent input.

Results of PCA analysis reflected anthropogenic activities, biogenic association and its diagentic reaction driven by its degradation regulating the behavior of reactive metals especially Cu, Zn and Cd in all transects. An

assessment of PLI among seasons revealed PLI < 1 at all transects in post monsoon, suggestive of region having low input of metal contaminants. In general, though the region is being influenced by metal contamination through anthropogenic forces, with high input in monsoon, local hydrodynamic conditions especially coastal currents and biogenic association are playing a vital role to negate this enrichment of metals in the sediments.

Chapter 6

HEAVY METALS IN THE BENTHIC POLYCHAETE *GLYCERA LONGIPINNIS*

6.1 Introduction

6.2 Results

6.3 Discussion

6.4 Conclusion

6.1 Introduction

The determination of heavy metals in benthic organisms has received added impetus owing to increased awareness of environmental pollution in aquatic realms. Generally, as a primary assessment tool, quantitative analysis of benthic communities is given precedence over the interpretation of contaminant effects, which are treated only as secondary, especially at sites where there is intense contamination. In the marine environment, sediments act as a sink for heavy metals which can be taken up by contaminant-tolerant benthic invertebrates like polychaetes (Waring *et al.*, 2006). Marine benthic invertebrates have been successfully employed in numerous biomonitoring studies because of their sessile nature, long and stable life span, moderately fast response to stress, and vulnerability to the effect of sediment contamination through their food and feeding (Gesteira and Dauvin, 2005). Polychaetes are a species-rich component of marine benthic communities and are considered as a good anthropogenic pollutant indicator along the southwest coast of India (Sukumaran and Sarala Devi, 2009). Heavy metal pollution by untreated industrial discharge and domestic waste through rivers into the southwest coast of India is well documented (Balachandran *et al.*, 2005; Martin *et al.*, 2006). Information on the bioavailability of heavy metals in sediments and their accumulation in benthic-level organisms distributed along the Indian coasts is scanty. This is particularly true of polychaetes, which form one of the most important components of the benthic community as well as an important food source for demersal fish. A recent study conducted along the inshore waters of Kerala recorded a high abundance of the polychaete *Glycera longipinnis* among the benthic community at all depths and in all seasons (Joice Thomas *et al.*, 2006). It is a medium sized free living polychaete worm, burrow in muddy sediment, feeding as a predator on invertebrates and detritus in the sediment. It is unlikely to be sensitive to small amounts of sediment mobilization, has a relatively long life span of five years and the size range can vary from 1 -20 cm (Rouse and Pleijel, 2001). This chapter discusses the temporal and spatial variability in the accumulation of heavy metals, viz. Cu, Pb, Cr, Ni, Zn, Cd and

Hg in the polychaete *G. longipinnis*, and its usefulness as biological indicator of heavy metal pollution along the central and northern coast of Kerala.

6.2 Results

6. 2. 1 Seasonal Variation of Heavy Metals in Sediment and Polychaete

Seasonal variations in the heavy metal concentration in sediment and in *G. longipinnis* pooled from the sampling transects are summarized in Table 6.1 and Fig. 6A. The distribution of metals in sediment from the sampled transects showed wide seasonal variation. Concentrations in sediments varied as follows: Cu, 19.08 – 62.70 µg g^{-1}; Pb, 13.79 – 40.97 µg g^{-1}; Cr, 80.79 – 282.80 µg g^{-1}; Ni, 28.10– 121.12 µg g^{-1}; Zn, 42.24–148.21 µg g^{-1}; Cd, 0.18–2.80 µg g^{-1}; and Hg, 0.08–0.56 µg g^{-1}. Organic carbon in sediments varied from 1.37 to 5.35% (Table 6.2, Fig. 6B). Seasonal variations in heavy metal concentrations in sediment were as follows: Cu, pre-monsoon> post monsoon>monsoon; Pb and Zn, monsoon > pre monsoon > post monsoon; Ni, monsoon> pre monsoon> post monsoon; Cr and Hg, monsoon > post monsoon> pre monsoon; and Cd, pre monsoon> monsoon > post monsoon. Accumulation of heavy metals in *G. longipinnis* was in the range: Cu, 2.21 – 27.08 µg g^{-1}; Pb, 0.06 – 4.92 µg g^{-1}; Cr, 1.73 – 29.20 µg g^{-1}; Ni, 1.60 – 4.61 µg g^{-1}; Zn, 42.84 – 82.30 µg g^{-1}; Cd, 0.04 – 1.38 µg g^{-1}; and Hg, below detectable limits to 0.86 µg g^{-1}. Seasonally, it was noted that the accumulation levels in *G. longipinnis* for Cd, Ni, Cu, Zn were higher during pre monsoon than in monsoon in all transects. During post monsoon, however, the accumulation levels were found to be intermediate in all transects. In the case of Cr, the accumulation level was high in the monsoon season, followed by post and pre monsoon seasons at all transects. The concentration of Pb, however, showed a consistent pattern, and remained high at Cochin and Calicut during pre monsoon and monsoon periods. The accumulation level of Hg showed high values during the monsoon followed by pre monsoon and post monsoon periods. The concentrations of Cd and Hg were high in the majority of polychaetes compared to that in sediment.

Table 6.1 Concentrations of heavy metals in sediment (S) and polychaete *G. longipinnis* (P) among different seasons in the sampled transects. Concentration is expressed in µg g^{-1} dry weight.

Transect	Season	Sample	Cu	Pb	Cr	Ni	Zn	Cd	Hg
Cochin	POM	S	27.20	24.42	125.18	52.67	75.80	1.14	0.56
		P	14.24	3.40	8.76	3.02	29.60	0.90	0.66
	PM	S	62.70	36.14	107.80	47.50	131.28	2.80	0.35
		P	24.64	4.92	3.10	4.61	82.30	1.38	0.66
	M	S	47.89	41.12	215.67	121.30	148.10	1.90	0.48
		P	5.40	1.20	23.20	2.80	18.80	1.20	0.86
Chettuva	POM	S	19.34	14.32	102.86	31.50	59.76	0.24	0.08
		P	8.07	1.93	2.24	2.69	19.28	0.49	0.10
	PM	S	35.60	21.40	81.36	32.18	91.40	0.66	0.11
		P	27.08	1.14	1.73	1.93	52.60	0.69	0.20
	M	S	27.50	27.89	142.12	61.08	94.38	0.18	0.13
		P	3.20	0.18	6.60	1.60	16.87	0.06	0.12
Ponnani	POM	S	35.77	12.76	57.71	38.14	75.50	0.49	0.13
		P	10.86	1.59	4.38	1.52	26.80	0.27	0.11
	PM	S	59.96	22.11	135.96	64.02	110.00	0.42	0.17
		P	24.62	1.83	0.91	0.97	58.60	0.86	0.22
	M	S	45.10	25.40	209.62	120.52	88.20	0.41	0.25
		P	5.20	0.28	10.87	1.28	20.13	0.12	0.16
Calicut	POM	S	23.64	20.34	141.56	47.20	61.60	0.57	0.26
		P	12.80	2.12	11.30	2.68	25.80	0.74	0.30
	PM	S	49.40	28.64	123.40	46.16	109.80	1.12	0.21
		P	18.26	1.75	4.82	2.78	29.05	0.90	0.38
	M	S	39.00	34.30	282.86	90.12	66.40	0.74	0.28
		P	4.00	1.40	29.21	2.16	21.62	0.92	0.52
Kasargod	POM	S	21.40	18.34	84.20	28.62	48.80	0.20	0.19
		P	12.40	0.80	2.18	3.36	18.40	0.26	BDL
	PM	S	41.10	24.40	90.00	35.20	84.30	0.56	0.25
		P	8.21	2.14	2.71	1.78	15.00	0.78	0.10
	M	S	31.42	21.00	163.00	77.00	42.00	0.47	0.19
		P	2.21	0.06	10.64	1.95	14.72	0.04	0.10

Note: POM- post monsoon, PM - pre monsoon, M- Monsoon, S- sediment, P- Polychaete *G. longipinnis*.

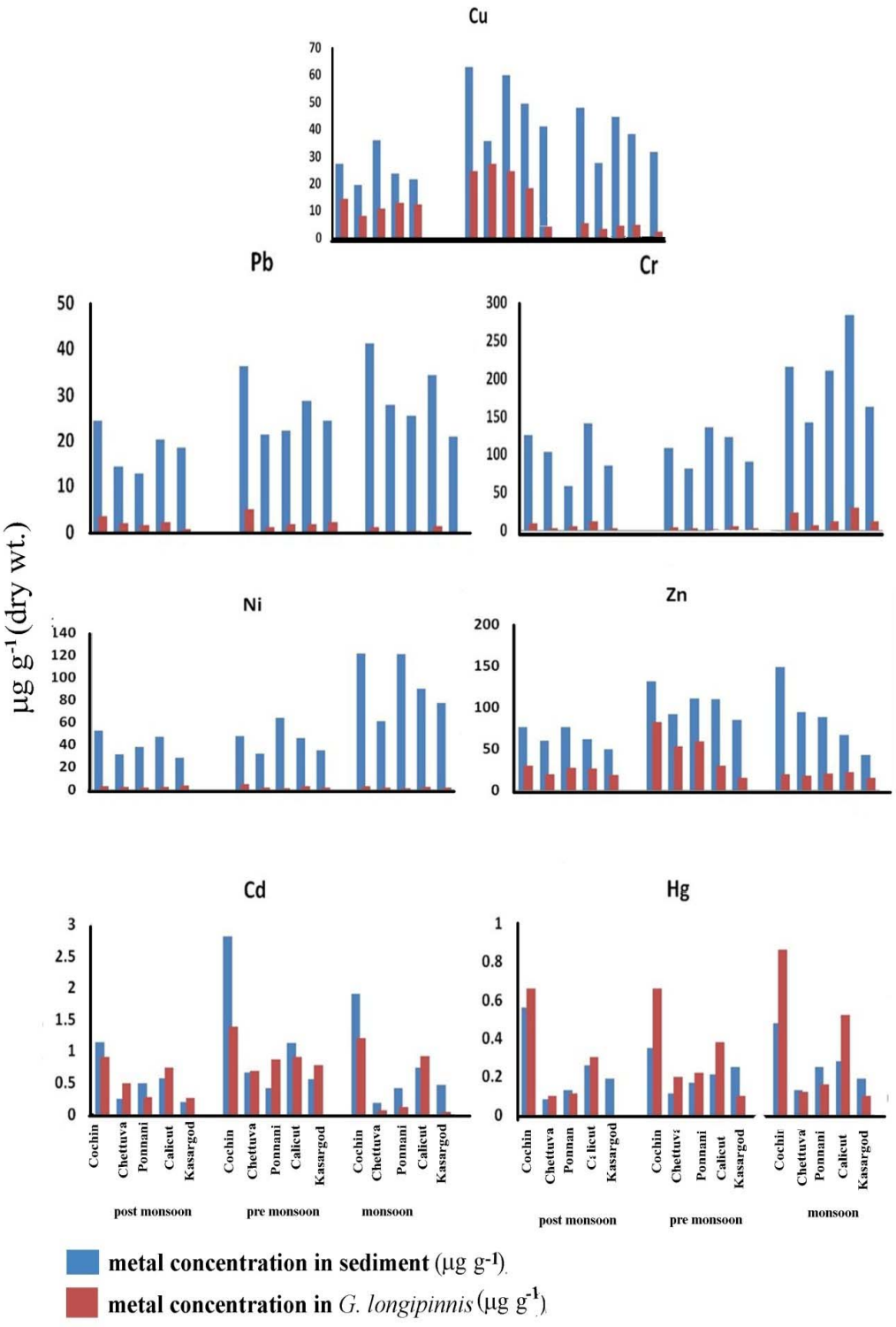


Figure 6A: Variations in the concentrations of heary metals in sediment and *G. longipinnis* among different seasons in the sampled transects.

Table 6.2 Concentration of Organic carbon (%) in sediment among different seasons in the sampled transects.

Transect	Seasons		
	POM	PM	M
Cochin	3.54	3.92	5.35
Chettuva	3.58	3.76	3.34
Ponnani	2.72	3.01	2.14
Calicut	2.54	2.42	1.91
Kasargod	2.32	2.76	1.37

Note: POM- post monsoon, PM- pre monsoon, M- monsoon

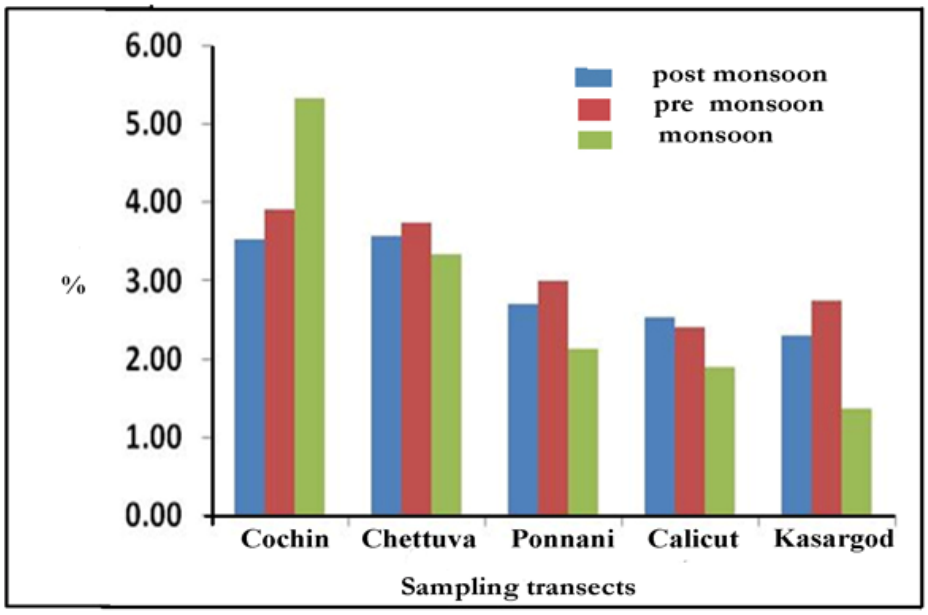


Figure 6B: Seasonal variations of organic carbon in sediments of sampling stations along the central and northern coast of Kerala.

6.2.2 Relationship of Heavy Metal Concentration in Sediment and Polychaete between Polluted and Non-polluted transects

An assessment based on the pollution load index (PLI) was employed to find the extent of pollution by metals in sediments (Tomlison *et al.*, 1980). PLI was evaluated using the equation PLI= (product of *n* number of CF values) 1/*n*, where CF is the contamination factor and *n* is the number of metals. CF was obtained as a concentration of each metal with respect to the background value of the metal constituent in the sediment. The world average concentration of the

metals reported for shale was used as the uncontaminated natural background value for a specific metal in the present study (Forstner and Muller, 1973). The transects were partitioned into polluted (PLI > 1) and unpolluted (PLI < 1) due to heavy metals on the basis of PLI formulated at each sampled transect. An evaluation based on PLI among the transects revealed values >1 at Cochin during all the seasons and in Calicut, Ponnani during the post monsoon and monsoon seasons compared with transects Chettuva and Kasargod where the values remained <1 in all seasons (Fig. 6C). Transects as per PLI values, therefore, were categorised as polluted and unpolluted zones respectively.

Results of analysis using Pearson's correlation revealed significant correlation between the Cr and Cd content in polychaetes and that found in sediment in the polluted zone (Table 6.3). In the unpolluted zone (Table 6.4), significant correlations were observed between bioaccumulated Cr and Cr in sediment.

The bioconcentration factors (BCF) of the heavy metals in the polychaete samples were obtained using equation given by Falusi and Olanipekun (2007).

BCF = C_{biota} / $C_{sed.}$ Where, C_{biota} is the concentration of metal in the organism (µg g^{-1} dry wt) and C_{sed} is the concentration of the same metal in the sediment (µg g^{-1} dry wt). The bioconcentration factor (BCF) was calculated for the metals studied at each transect to determine bioaccumulation in *G. longipinnis* (Table 6.5). Bioaccumulation of metals by organisms occurs if the BCF > 1 (Falusi and Olanipekun, 2007). In this study, the BCF generally showed high values for Cd at transects Chettuva, Ponnani, Calicut and Hg at Cochin, Chettuva and Calicut. The BCF for all the other metals under study was <1.

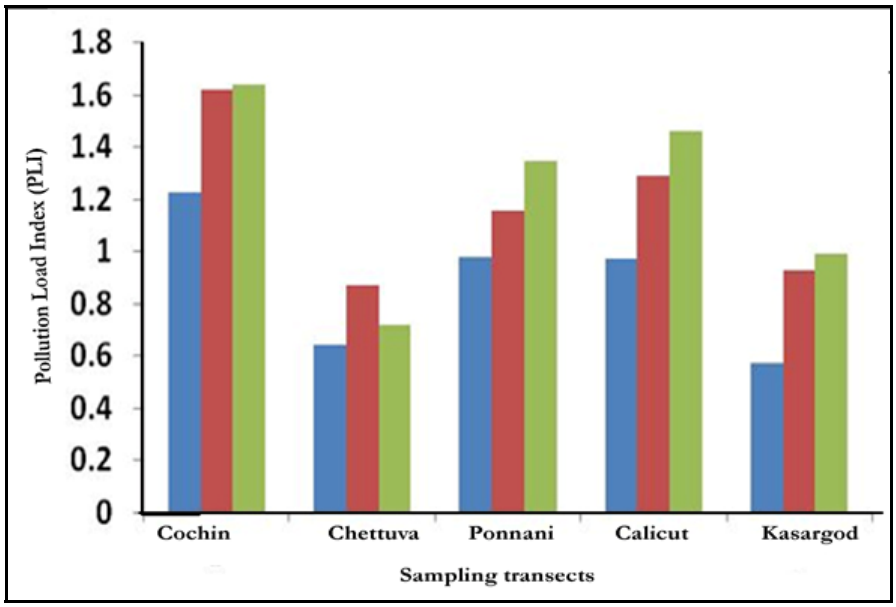


Figure 6C. Seasonal variations in pollution load Index (PLI) for sampling transects along the central and northern coast of Kerala.

Table 6.3. Results of Pearson correlation coefficient among heavy metals in Sediment and *G. longipinnis* in polluted zone.

	P#Cu	P#Pb	P#Cr	P#Ni	P#Zn	P#Cd	P#Hg
S#Cu	0.517	0.319	-0.325	0.655	0.704	0.792	0.038
S#Pb	-0.309	-0.2	0.476	0.135	0.158	0.711	0.578
S#Cr	-0.903(*)	-0.707	**0.985(**)**	-0.718	-0.564	-0.222	0.123
S#Ni	-0.855	-0.673	0.862	-0.49	-0.523	0.127	0.604
S#Zn	0.242	0.088	-0.218	0.508	0.344	0.775	0.52
S#Cd	0.566	0.644	-0.426	0.898(*)	0.82	**0.970(**)**	0.507
S#Hg	-0.185	0.217	0.051	0.12	-0.107	0.134	0.786
S#OC	-0.009	0.198	-0.052	0.412	0.157	0.637	**0.926(*)**

Notes: * Correlation is significant at $P < 0.05$ level (2-tailed); ** Correlation is significant at $P < 0.01$ level (2-tailed); S# Concentration of heavy metal in Sediment; P# Concentration of heavy metal in *G. longipinnis*.

Table 6.4. Results of Pearson correlation coefficient among heavy metals in Sediment and *G. longipinni* in unpolluted zone.

	P#Cu	P#Pb	P#Cr	P#Ni	P#Zn	P#Cd	P#Hg
S#Cu	0.155	0.012	-0.12	-0.749	0.206	0.295	-0.068
S#Pb	-0.222	-0.388	0.236	-0.756(*)	-0.083	-0.208	0.019
S#Cr	-0.643	-0.433	**0.925(**)**	-0.301	-0.412	-0.531	0.16
S#Ni	-0.617	-0.64	0.806(*)	-0.499	-0.357	-0.641	-0.044
S#Zn	0.321	0.105	-0.342	-0.661	0.419	0.316	0.192
S#Cd	0.536	0.373	0.175	-0.338	0.566	0.668	0.575
S#Hg	-0.171	0.287	0.471	0.084	-0.331	0.292	0.293
S#OC	0.447	0.208	-0.591	-0.214	0.529	0.275	0.117

Notes: * Correlation is significant at P $<$ 0.05 level (2-tailed); ** Correlation is significant at P $<$ 0.01 level (2-tailed); S# Concentration of heavy metal in Sediment; P# Concentration of heavy metal in *G. longipinnis*.

Table 6.5 Bioconcentration factors for heavy metals (n = 3, mean ±SD) at the sampled transects.

Transects	Cu	Pb	Cr	Ni	Zn	Cd	Hg
Cochin	0.34±0.21	0.10±0.06	0.07±0.04	0.06±0.04	0.43±0.33	0.65±0.17	**1.62±0.38**
Chettuva	0.44±0.33	0.07±0.07	0.03±0.02	0.06±0.03	0.36±0.20	**1.14±0.86**	**1.33±0.46**
Ponnani	0.28±0.15	0.07±0.05	0.04±0.03	0.02±0.01	0.37±0.15	**1.0±0.96**	0.93±0.33
Calicut	0.35±0.23	0.07±0.04	0.07±0.03	0.05±0.02	0.34±0.08	**1.11±0.27**	**1.61±0.40**
Kasargod	0.29±0.27	0.04±0.05	0.04±0.02	0.07±0.05	0.35±0.03	0.93±0.73	0

6.3 Discussion

The results of this study clearly show that the order of heavy metal accumulation in sediment and *G. longipinnis* was not consistent throughout the seasons. These observations are more or less comparable with earlier findings carried out in polychaetes along the east coast of India (Saha *et al.*, 2006). Analogous observations were recorded in benthic bivalves and other bottom-dwelling organisms owing to increased feeding rate,warming of seawater, particulate material run-off into the environment and reproductive development (Sivadasan and Nambisan,1988; Cain and Luoma, 1990). In our study, the seasonal variations can be attributed to the different inputs of metals for accumulation and the feeding habits of the polychaete. The results revealed high concentrations for most of the heavy metals (Cu, Pb, Zn, Cd, and Hg) in sediments as well as *G. longipinnis* in the pre monsoon season during which a corresponding increase in organic carbon concentrations was also noted. Obviously this could facilitate scavenging of heavy metals, which can be accumulated in the polychaete through dietary intake. The sediments collected during post monsoon reflected low metal enrichment throughout the study sites. The influence of northerly currents that are capable of dispersing their deposition along the southwest coast of India has been described previously (Shetye *et al.*, 1991). Heavy metals were found to accumulate at noticeable levels in *G. longipinnis* along the central and northern coast of Kerala. Table 6.6 gives a comparison of heavy metal content of polychaete species from this coast with those of other coastal areas. The Cr content recorded in the polychaete species during this study was considerably higher than that reported from other coastal regions of the world. The increased Cr content was reported from transects Cochin and Calicut where there is a heavy influence of industrial drainage. All the other heavy metal content was, in general, of a similar magnitude to values reported for other polychaete species.

The concentration of heavy metals in *G. longipinnis* varied considerably among the different transects. This may be due to feeding on subtly different available food sources with consequently different inputs of metals for

accumulation, which are diverse at each transect. The effectiveness of metal uptake from the same sources varying in relation to ecological needs, metabolism, environmental contamination and various abiotic factors has been reported (Roesijadi and Robinson, 1994). In this study, accumulation was high in regions of Cochin, Ponnani and Calicut where there is a heavy influence of industrial and domestic wastes. Considering the spatial variation in heavy metal concentration in *G. longipinnis* in this study, it was found that higher accumulation occurred at Cochin compared with the other transects. Assessing the species host sediment, however, checked this aberration. At transect Cochin, the enrichment of heavy metals in the sediment matrix is mainly due to quantum metal input from the contiguous industrial establishments situated along the coast. The industrial assortment includes fertilizer, pesticide, chemical and allied industries, radioactive mineral processing, petroleum refining, metal plating and fish-processing units.

Results of Pearson's correlation showed the relevance of metal availability from sediments to the organisms. In polluted regions (Cochin, Ponnani and Calicut) significant correlation occurred between Cd and Cr in sediment and that accumulated in *G. longipinnis*. The concentration of both metals in sediments was relatively high; because *G. longipinnis* are exposed to contaminants there is every possibility of accumulation via several different paths. Bioaccumulated Hg in *G. longipinnis* was positively correlated with organic carbon indicating the source of Hg through organic matter. According to Fauchland and Jumars (1979), *Glycera* sp. feeding types include carnivorous/detritivore/omnivore. Although the polluted site showed increased concentrations of other toxic metals, its effect was not noticeable in *G. longipinnis*. Adsorption of many toxic substances onto the sediments and organic material has been recognised, rendering them less available to benthic organisms (Dean, 2008). This may be the reason for these species thriving in sediments with greatly elevated levels of toxicants. In an unpolluted site, the increased concentration of Cr in the sediment facilitated a significant correlation with bioaccumulated Cr.

Table 6.6 Average metal concentrations (µg g^{-1} dry wt) found in polychaete sp. from various regions of the world.

Location	Cd	Cr	Cu	Ni	Pb	Zn	Hg	References
Central and Northern coast of Kerala	0.043-1.38	1.73-29.2	2.21 – 27.08	1.6-4.61	0.06-4.92	14.72-82.3	BDL– 0.86	This study
Oualidia lagoon	0.09	2.0	6.8	1.7	1.0	115	-	Idardare, 2008
UK estuaries	0.03-10	0.1-10	10-1430	0.6-15	0-1190	91-510	-	Bryan *et al*., 1980
Urdaibai estuary	0.1-1.7	0.1-1.5	6.3-39	1.3-7	0-10	25-300	-	Diez *et al*., 2000
Australian coast	0.07-17	-	3.4-26	-	0.09-3.2	47-225	0.08-0.88	Waring *et al*., 2006
Barents Sea	0.34	-	6.8	11.0	0.8	47.0	-	Zauke *et al*., 2003
Hugli estuary, NÉ India	-	11.10-54.05	8.15-30.66	-	-	18.28-102.25	BDL-0.44	Saha *et al*., 2006

NOTE: BDL:- below detectable limit

A BCF value >1.0 for Hg in *G. longipinnis* at the polluted transects Cochin, and for Cd and Hg at Calicut, indicates heavy bioaccumulation of these metals in the tissue due to the influence of industrial discharge. A BCF value >1.0 for Cd in *G. longipinnis* at the polluted transects Ponnani also indicate bioaccumulation due to Cd. This could be due to the discharge of untreated effluents form the small scale metal processing units operating in the neighborhood and by agriculture run off. Cadmium is added to agricultural lands that use phosphate fertilizers (Garrett, 2007) thus can find its source into the coastal sediments. This accumulation of metals in the tissue signifies their excellent accumulation capacity which might cause acute toxicity to other organisms and human beings via the marine food chain. A review of toxicological studies using polychaetes cited Cu and Hg as the most toxic metals tested, whereas the least toxic metals followed the order Cr, Cd, Zn and Pb (Dean, 2008). Under captive conditions, Bryan (1984) demonstrated that the polychaete *Capitella capitata* when exposed to polluted sediments took up Cd with little or no demonstrable effects. In contrast to this, at the unpolluted transect Chettuva, where there is no industrial influence, the bioavailability of Hg and Cd can be attributed to the increased use of pesticides and fungicides, fertilizers containing these metals. Moreover, at this transect the percentage of organic carbon is higher, signifying increased productivity, which in turn can remove metals from solution and deposit them in sediment. A significant correlation of Hg with organic-rich sediments and its availability to polychaetes through feeding may be expected. The low bioaccumulation of metals Cr, Zn and Ni in *G. longipinnis* in contaminated sites Cochin and Calicut might be related to the capacity of polychaetes to control metal incorporation from contaminated sediments. The absence of additional metal bioaccumulation in the presence of very high metal concentration in sediments has also been reported (Idardare *et al.*, 2008).

6.4 Conclusion

Heavy metal accumulation in the polychaete *G. longipinnis* signified that it is being influenced by an increasing number of diverse sources such as

urbanisation, industrial activities and agricultural run-off. Results of Pearson's correlation showed the relevance of Cd and Cr availability from sediments to the organisms. Cr content (1.73 - 29.20 µg g^{-1}) recorded for *G. longipinnis* during this study is considerably higher than that reported from other coastal regions of the world. The bioconcentration factor revealed the ability of this organism to accumulate Hg and Cd more than in sediments in both polluted and unpolluted transects. Organic carbon was found to play a pivotal role in the availability of mercury in sediments. Thus, the results of this study strongly suggest that the polychaete *G. longipinnis* is a useful indicator for contamination of heavy metals such as Cd, Hg and Cr (in a long run) due to anthropogenic sources along the southwest coast of India.

Chapter 7

HEAVY METAL LEVELS IN FLATFISH (MALABAR TONGUE SOLE; *CYNOGLOSSUS MACROSTOMUS*)

7.1 Introduction

7.2 Results

7.3 Discussion

7.4 Conclusion

7.1 Introduction

Contamination of aquatic realm by heavy metals is of major importance in terms of the biological availability of metals. Among the chemical contaminants heavy metals are considered as serious pollutant because of its toxicity, persistence and bioaccumulation problems (Tam and Wong, 2000). The two key factors that are of major importance to mankind are the amount of heavy metal present in the sea food they consume and the toxic effects of these metals in the ecosphere. Aquatic organisms take up metals by different routes either directly from the surrounding medium or through ingestion by food and inorganic particulates (Phillips, 1977). The tendency of metal to get accumulated is one of the key factors in determining tissue metal concentrations in polluted environment (Krishnamurti and Nair, 1999). The fishes form an important target for biomagnifications of metals as they are at the top of the aquatic food web (Mansour and Sidky, 2002). The levels of contaminants in fish are also of great concern because of the potential effects on the fish themselves and its subsequent transfer to human through food chain (Hammond, 1971; Forstner and Wittman, 1981; Fowler *et al*., 1993; Khan and Weis, 1993; Jargensen and Pedersen, 1994; Adeyeye *et al*., 1996). Flatfishes are an economically and ecologically important component of continental shelf and have a bottom dwelling habitat. Flat fishes especially the soles constitute a fishery of considerable importance along the southwest coast of India. Landings of flatfishes along the Kerala coast nearly accounts for 3.10 % of the total fish catches and it nearly constitutes 40.66 % of the total demersal resources (CMFRI, 2008). Accumulation of metals of several high orders in benthic dwellers is well documented (Campbell *et al*., 1988). This has resulted in employing benthic fish as bio-indicators of marine pollution by metals (Evans *et al*., 1993). The bioaccumulation of metals at elevated levels in fish is therefore an index of the pollution status of the relevant water body. Since flatfishes are benthic, sluggish and usually inhabit the nearshore coastal sediments, preying on benthic invertebrates; can prove a useful tool for studying the biological availability of metals. Due to the different roles of tissues in the bioaccumulation processes, the tissue flesh (muscle), liver and gills are those most frequently used for assessment.

Flesh is preferred because it is a target tissue for metal storage and is the main edible part of the fish. Liver is an important organ for heavy metal storage and decontamination in fish where the synthesis of metallothionein induced by heavy metals take place and gill which is in continuous contact with the overlying aqueous medium and the contaminants contained therein. Therefore, its study constitutes a tool for environmental assessment and for determining public health risk (Reinfelder *et al.*, 1998). Increasingly, the public, policymakers, and managers require information about contaminants in biota to assess the health, environment and well-being of organisms and the consumers that eat them. Therefore, monitoring and control of the food originating from these areas is very important, especially with regard to the presence of these metals. Due to coastal upwelling, the coastal waters of the southwest coast of India are among the most productive regions in the world, supporting abundant invertebrate and fish populations, many of which are harvested as food. Random reports on the metal concentrations in some species of fishes from the selected portions adjacent to the Indian Seas are available (Kureishy *et al.*, 1981, 1983; Singbal *et al.*, 1982; Maheswari *et al.*, 1997; Asha and Vijayalakshmy, 1999; Maheswari *et al.*, 2006; Rejomon *et al.*, 2010). Heavy metal concentrations tested in stationary fish was used as an environmental indicator in water areas affected by human activities and as a monitoring technique for assessing the efficiency of control measures (Jargensen and Pedersen, 1994).

The present chapter describe and discuss the concentration levels of copper (Cu), lead (Pb), chromium (Cr), nickel (Ni), zinc (Zn), cadmium (Cd), and mercury (Hg) in the benthic fish *Cynoglossus macrostomus*,it's risk assessment to humans and the usefulness as a biological indicator along the central and northern coast of Kerala.

7.2 Results

7.2.1 Length-weight relationship

The length and weight of flatfish showed wide variation in all the studied stations during the study period. At Cochin it varied from 12.40 ± 0.30 cm to 21.90 ± 0.80 cm and weight from 21.90 ± 0.80 g to 41.80 ± 2.90 g. At Chettuva

it varied from 18.80 ± 0.30 cm to 31.70 ± 1.40 cm and weight from 32.55 ± 1.30 g to 202.00 ± 4.10 g. At Ponnani the length of flatfish varied from 16.80 ± 0.40 cm to 23.9 ± 0.80 cm and weight varied from 30.70 ± 1.20 g to 102.20 ± 3.10 g. At Calicut the length varied from 31.30 ± 0.50 cm to 31.90 ± 0.30 cm, and weight varied from 202.20 ± 4.50 g to 202.60 ± 4.90 g and at Kasargod the length and weight varied from 16.50 ±1.70 cm to 23.50 ±1.90 cm and 29.80 ±0.80 g to 102.00 ±2.90 g respectively.

7.2.2 Heavy metals in the organs of Flatfish (Malabar tongue sole; *Cynoglossus macrostomus*)

The range and average values (given in bracket) of heavy metals in the organs of flatfish from the studied transects are described below (Table 7.1).

7.2.2.1 Copper

Copper is essential for normal growth and metabolism of all living organisms (Eisler, 1998). Copper is a biogenic element necessary for supporting the metabolic processes of the living organism. However, its excess levels beyond permissible limit can induce inhibition in the liver, kidneys and cornea.The variation of Cu in different organs among transects are presented (Fig. 7A).

At Cochin, the range and average values (given in bracket) of Cu concentration for liver, gill and muscle of flat fish were 34.28 - 69.06 (46.59 ± 15.50), 4.72 - 9.02 (6.68 ± 2.17) and 0.78 - 4.34 (2.57±1.49) µg g^{-1} wet weight respectively in post monsoon. In pre monsoon, levels of Cu generally showed an increase and varied in the range 45.28 - 106.78 (64.26 ± 20.36), 16.80 - 30.24 (22.01± 4.61), 6.90 - 19.23(11.15 ±4.45) µg g^{-1} wet weight for liver, gill and muscle respectively. In monsoon the range of Cu concentration for liver and gill of flatfish were 33.80 - 49.40 (41.15 ± 6.43) and 4.90 – 8.40 (6.85± 1.57) µg g^{-1} wet weight respectively and were comparable with the values obtained in post monsoon, while in muscle it varied in the range 4.98 - 6.40 (5.72± 0.59) µg g^{-1} wet weight which was intermediate between the values obtained for other seasons.

At Chettuva, the range and average values of Cu concentration for liver, gill and muscle of flat fish were 25.43- 31.17 (28.30 ± 4.06), 2.89 – 3.90(3.39 ± 0.71) and 1.14 – 1.49 (1.31 ± 0.25) µg g^{-1} wet weight respectively in post monsoon. In pre monsoon the range showed an increase and was found to vary in the range 39.60- 42.46 (41.03± 2.02), 6.45- 11.20 (8.83 ± 3.36), 3.17- 4.34(3.76 ± 0.83) µg g^{-1} wet weight for liver, gill and muscle respectively. In monsoon the range of Cu concentration in the tissues was comparable with that obtained in post monsoon and were found to vary in the range 14.88 – 30.21 (22.55 ± 10.84), 2.78 – 3.90 (3.34± 0.79) and1.90 – 2.10(2.00± 0.14) µg g^{-1} wet weight for liver, gill and muscle respectively.

At Ponnani, the range and average values of Cu concentration for liver, gill and muscle of flat fish were 26.90 - 40.90 (33.77 ± 7.00), 3.40 – 5.16 (4.25 ± 0.72) and 1.05 – 2.07 (1.41 ± 0.57) µg g^{-1} wet weight respectively in post monsoon. In pre monsoon the concentration in the tissues showed an increase and were in the range 40.60- 59.50 (49.97± 9.45), 7.89- 12.56 (10.23 ± 2.34) and 2.80- 3.89 (3.33 ± 0.55) µg g^{-1} wet weight respectively. In monsoon, the average values of Cu concentration for liver 8.30 – 13.12 (10.70 ± 2.41) was the lowest of the seasons, while in gill and muscle of flatfish it were in the range 3.45 – 5.66 (4.33 ± 1.17) and 2.40 – 3.40 (2.87± 0.20) µg g^{-1} wet weight respectively.

At Calicut, the range and average values of Cu concentration for liver, gill and muscle of flatfish were 22.22- 60.89 (36.14 ± 21.49), 4.32 – 5.98 (5.43 ± 0.96), 2.50 – 3.12 (2.80± 0.31) µg g^{-1} wet weight respectively in post monsoon. In pre monsoon the concentration of Cu in tissues showed the higher values compared to other two season and were 27.68 – 101.09 (65.45± 36.79), 6.72 - 32.56 (17.29 ± 11.13) and 2.80- 16.50 (7.55 ± 6.15) µg g^{-1} wet weight for liver, gill and muscle respectively. In monsoon season the range and average values of Cu concentration for liver and gill were comparable with the values obtained in pre monsoon and were in the range 20.60 – 31.50 (25.91± 5.46) and 3.67 – 5.12 (4.59± 0.73) µg g^{-1} wet weight respectively while in muscle of flatfish it was 4.50 – 5.80 (4.97± 0.72) µg g^{-1} wet weight.

Table 7.1 Concentration of heavy metals (µg g^{-1} wet wt.) in the tissues of flatfish (*Cynoglossus macrostomus*) pooled along the central and northern coast of Kerala during the year 2008.

			Heavy metal concentration (µg g^{-1} wet weight)							
Transect	Season	Organ	Cu	Pb	Cr	Ni	Zn	Cd	Hg	MPI
COCHIN		Liver	46.59	1.25	3.60	2.24	121.50	0.43	0.16	3.25
	POM	Gill	6.68	2.16	1.03	1.06	40.64	0.22	0.11	1.47
		Muscle	2.57	0.23	0.89	0.27	17.91	0.17	0.04	0.65
		Liver	64.26	1.71	2.30	6.09	101.32	0.61	0.06	3.45
	PM	Gill	22.01	3.70	1.53	3.45	69.61	0.11	0.05	2.05
		Muscle	11.15	0.35	0.69	1.93	39.89	0.08	0.03	1.06
		Liver	41.15	1.98	2.18	5.79	100.60	0.12	0.18	2.99
	MON	Gill	6.85	1.26	1.41	2.10	46.74	0.08	0.03	1.06
		Muscle	5.72	0.21	0.77	1.97	30.43	0.08	0.10	0.99
CHETTUVA	POM	Liver	28.30	0.64	1.73	1.86	99.39	0.04	0.03	1.31
		Gill	3.39	0.33	0.58	0.75	40.25	0.02	0.02	0.52
		Muscle	1.31	0.06	0.40	0.26	20.39	0.10	0.02	0.32
	PM	Liver	41.03	0.80	0.90	4.78	86.32	0.04	0.01	1.28
		Gill	8.83	0.13	0.34	2.15	54.62	0.02	0.01	0.50
		Muscle	3.76	BDL	0.21	0.61	34.67	BDL	BDL	0.21
	MON	Liver	22.55	0.05	0.70	2.60	58.03	0.03	0.03	0.73
		Gill	3.34	0.05	0.43	1.81	27.59	0.04	0.05	0.51
		Muscle	2.00	BDL	0.37	0.21	8.67	0.03	0.03	0.19
PONNANI		Liver	33.77	1.15	1.61	1.66	87.13	0.05	0.03	0.98
	POM	Gill	4.25	0.75	1.09	1.17	34.25	0.09	0.03	0.61
		Muscle	1.41	0.19	0.60	0.51	15.64	0.01	0.01	0.11
		Liver	49.97	1.11	0.78	2.94	112.34	0.03	0.02	1.35
	PM	Gill	10.23	0.90	0.32	2.15	45.30	0.03	0.02	0.74
		Muscle	3.33	0.18	0.24	0.53	29.85	0.01	0.01	0.35
		Liver	10.70	0.93	0.55	5.20	81.81	0.05	0.02	1.77
	MON	Gill	4.33	1.09	0.33	3.24	59.34	0.02	0.01	0.05
		Muscle	2.87	0.24	0.39	2.37	19.74	0.03	0.03	0.01
CALICUT		Liver	36.14	1.13	2.36	2.71	101.93	0.08	0.06	1.29
	POM	Gill	5.43	0.85	1.89	1.80	24.15	0.10	0.03	0.65
		Muscle	2.80	0.23	0.94	0.81	18.81	0.05	0.02	0.37
		Liver	65.45	2.43	3.16	5.68	117.50	0.06	0.03	2.54
	PM	Gill	17.29	1.72	1.57	2.08	47.38	0.02	0.02	1.03
		Muscle	7.55	0.23	1.10	0.76	38.84	0.02	0.01	0.52

		Liver	25.91	2.60	2.95	3.08	102.99	0.06	0.03	1.99
	MON	Gill	4.59	1.14	1.56	1.73	48.54	0.04	0.01	0.86
		Muscle	4.97	0.40	1.21	1.03	28.81	0.01	0.02	0.57
KASARGOD		Liver	29.94	0.57	0.93	1.66	97.05	0.05	0.01	1.61
	POM	Gill	3.64	0.38	0.61	0.89	28.60	0.04	0.02	0.33
		Muscle	1.37	0.13	0.25	0.31	14.79	BDL	0.01	0.18
		Liver	53.29	0.12	0.65	3.80	79.58	0.02	0.02	0.93
	PM	Gill	12.36	0.16	0.28	1.96	39.73	0.02	0.01	0.51
		Muscle	4.07	0.01	0.17	0.93	30.46	0.01	0.01	0.19
		Liver	9.72	0.06	0.66	1.99	76.25	0.03	0.03	0.63
	MON	Gill	3.51	0.04	0.31	1.56	33.74	0.02	BDL	0.34
		Muscle	2.78	0.01	0.14	0.51	25.73	0.01	BDL	0.17
NOTE: POM - post monsoon, PM - pre monsoon, M - monsoon, BDL - below detectable limit										

At Kasargod, the range and average values of Cu concentration for liver, gill and muscle of flat fish were 29.66- 30.22 (29.94 ± 0.40), 2.38 – 4.90 (3.64 ± 1.78), 1.28 – 1.46 (1.37 ± 0.13) µg g^{-1} wet weight respectively in post monsoon. In pre monsoon, as that observed in other transects, the concentration in the tissues showed an increase and the range , average values for liver, gill and muscle were 50.28 – 56.29 (53.29± 4.25), 10.45 – 14.26 (12.36 ± 2.69), 3.80- 4.34(4.07 ± 0.38) µg g^{-1} wet weight respectively. In monsoon the range and average values of Cu concentration for liver 7.88 – 11.56 (9.72± 2.60) was lower compared to other seasons and in gill and muscle of flatfish it were 3.12 – 3.89 (3.51± 0.54) and 2.45 – 3.10 (2.78 ± 0.46) µg g^{-1} wet weight respectively.

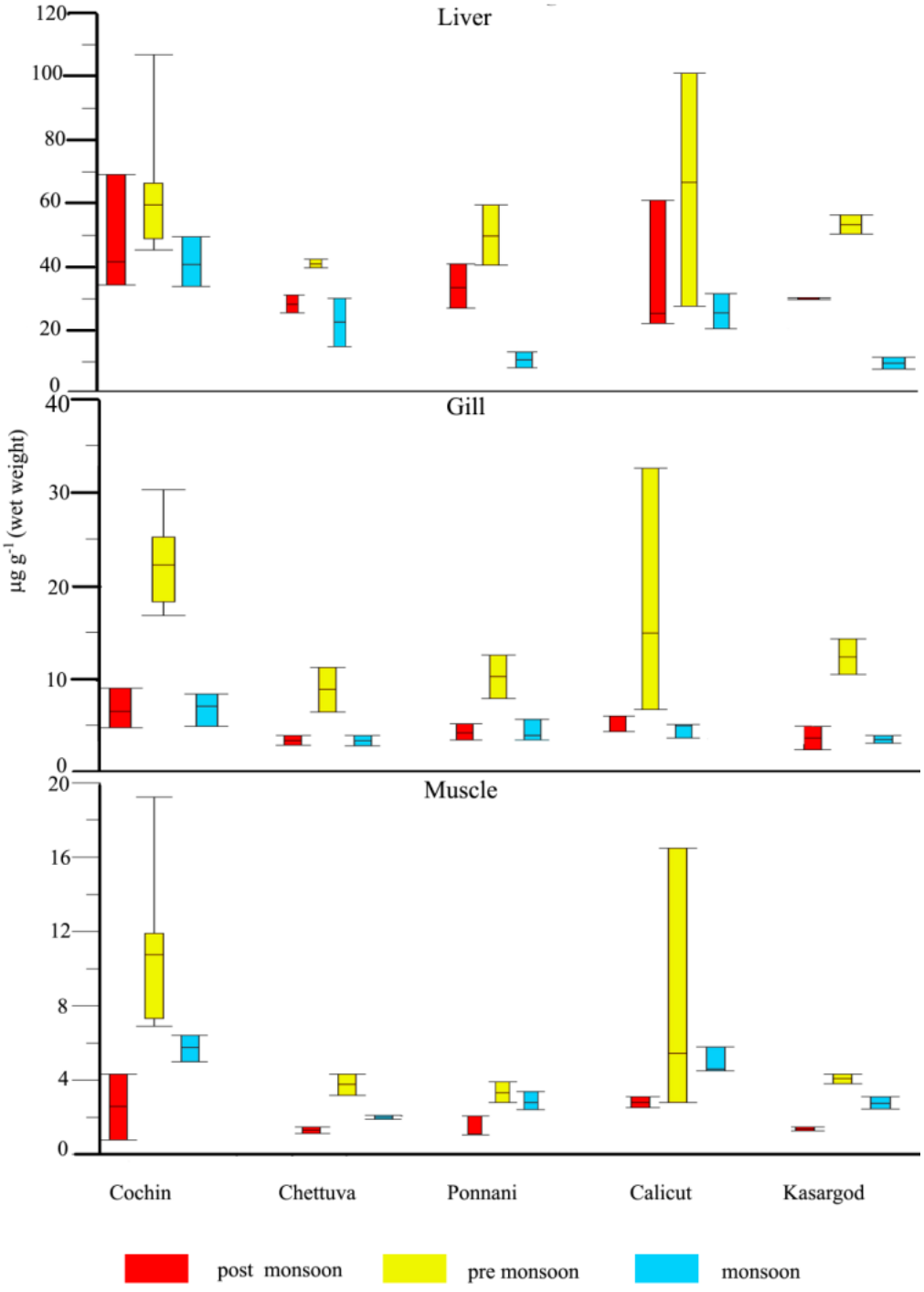


Figure 7A. Seasonal Variation of Copper (Cu) in different organs of flatfish among different transects.

7.2.2.2 Lead (Pb)

Lead belongs to the group of non-essential and toxic metals, which implies that it has no known function in biochemical processes. It is generally acknowledged that human activities influence the lead content of marine fishes. Lead is known to induce reduced cognitive development and intellectual performance in children and increased blood pressure and cardiovascular disease in adults (Commission of the European Communities, 2001). Lead was found to in the tissues in detectable levels and was found to vary in its accumulation in the organs of flatfish among the transects (Fig. 7B).

At Cochin, the range and average values (in brackets) of Pb concentration for liver, gill and muscle of flatfish were 0.98 – 1.49 (1.25 ± 0.21), 0.96 - 4.18 (2.16 ± 1.40), 0.07 – 0.41 (0.23 ±0.15) µg g^{-1} wet weight respectively in post monsoon. In pre monsoon, the levels were in the range 1.35 – 2.34 (1.71 ± 0.35), 2.04 - 3.60 (3.70 ± 2.32), 0.16 -0.45 (0.35 ± 0.13) µg g^{-1} wet weight for liver, gill and muscle respectively. In monsoon the levels of Pb (0.18 – 4.54 (1.98 ± 1.92)) was higher in liver compared to other season where the accumulation was high in the gills of flatfish. The concentration for gill and muscle were, 1.04 – 1.37 (1.26 ± 0.16) and BDL –0.44 (0.21± 0.1) µg g^{-1} wet weight respectively.

At Chettuva, the range and average values of Pb concentration for liver, gill and muscle of flatfish were 0.23- 1.05 (0.64 ± 0.58), 0.29 – 0.37(0.33± 0.05), 0.03 – 0.09(0.06 ± 0.04) µg g^{-1} wet weight respectively in post monsoon. In pre monsoon the range and average values for liver (0.62 – 0.98 (0.80 ± 0.25)) were higher compared to gills (0.06 - 0.19 (0.13± 0.09) µg g^{-1} wet weight and in muscles it was below the detectable level. In monsoon, the concentration range of Pb for liver and gill were 0.04 – 0.06 (0.05 ± 0.01) and BDL – 0.09 (0.05± 0.06) µg g^{-1} wet weight respectively and in muscle it was below the detectable level.

At Ponnani, the range and average values of Pb concentration recorded for liver, gill and muscle of flatfish were 0.76– 1.69 (1.15 ± 0.48), 0.37 – 1.30

(0.75± 0.40) ,0.06 – 0.39 (0.19 ± 0.17) and 0.56 –1.69 (1.11 ± 0.57), 0.79 – 0.96 (0.90 ± 0.09), 0.10 – 0.33 (0.18± 0.10) µg g^{-1} wet weight in post monsoon and pre monsoon respectively. In monsoon the value observed in the tissues were 0.51 –1.33 (0.93 ± 0.21), 0.42 – 1.80 (1.09 ± 0.66) and 0.02 – 0.27 (0.24± 0.04) µg g^{-1} wet weight for liver, gill and muscle respectively.

At Calicut, the range and average values of Pb concentration for liver, gill and muscle of flatfish were 0.93 – 1.23 (1.13± 0.17), 0.48 – 1.17(0.85 ± 0.35), 0.13 – 0.28(0.23± 0.08) and 2.31 – 2.49 (2.43 ± 0.08), 0.10– 3.70 (1.72 ± 1.72), 0.22 - 0.45 (0.23 ± 0.23) µg g^{-1} wet weight in post monsoon and pre monsoon respectively. In monsoon, the average Pb concentration for liver; 2.20 – 3.00 (2.60± 0.40) µg g^{-1} wet weight was higher compared to other seasons and in gill and muscle it was in the range, 0.90 – 1.34 (1.14± 0.22) and 0.36– 0.47 (0.40 ± 0.06) µg g^{-1} wet weight respectively.

At Kasargod, the range and average values of Pb concentration for liver, gill and muscle of flat fish were 0.27 –0.87 (0.57 ± 0.42), 0.34 – 0.42 (0.38 ± 0.06), 0.12 – 0.13(0.13 ± 0.01) µg g^{-1} wet weight respectively in post monsoon. In pre monsoon and monsoon it was in the range 0.10 – 0.14 (0.12 ± 0.03), 0.10– 0.22(0.16 ± 0.08), below detectable limit – 0.11 and 0 .03 – 0.08 (0.06 ± 0.03), 0.04 – 0.05 (0.04 ± 0.01) µg g^{-1} wet weight, below detectable limit for liver, gill and muscle respectively.

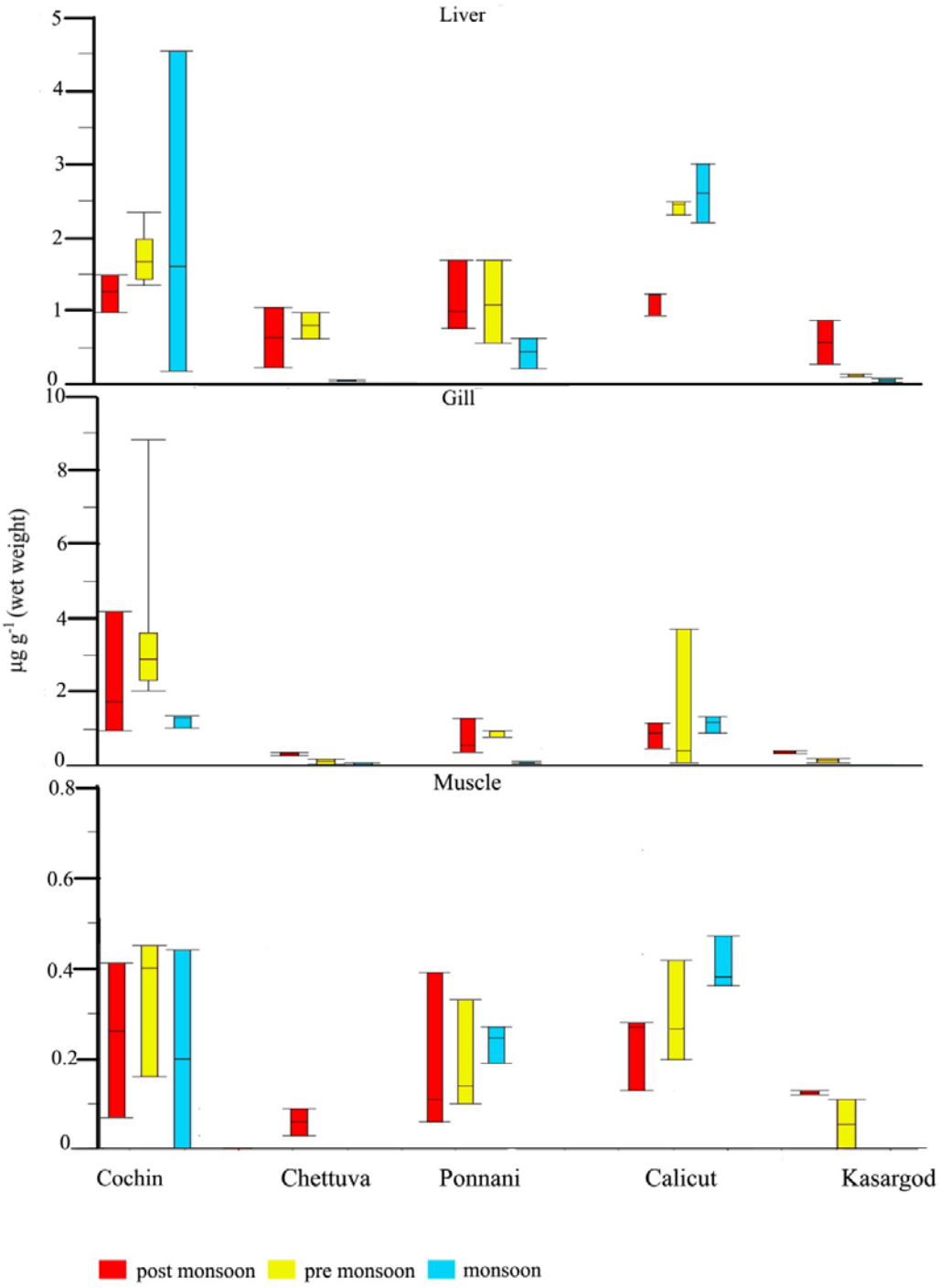


Figure 7B. Seasonal variation of Lead (Pb) in different organs of flatfish among different transects.

7.2.2.3 Chromium (Cr)

Chromium is an essential element, that potentate's insulin action and thus influences carbohydrate, lipid and protein metabolism and it is also harmful at higher levels (Eisler, 1986; Tuzen and Soylak, 2007). Human potential of absorbing this metal is very weak, so that only 3% of the exposure dose ends up in the human body. The greatest chromium share is found in the spleen, kidneys and testicles. Even the exposure to low chromium concentrations can lead to skin irritations and tissue lesions, while higher concentrations cause kidney and liver damage and damages to the cardiovascular and nervous system in humans. In marine organisms it can inhibit several metalloenzyme systems (Sadiq, 1992). The levels of Cr in the tissues of flatfish showed marked fluctuation among the transects (Fig. 7C).

At Cochin, the range and average values of Cr concentration for liver, gill and muscle of flat fish were 1.20 - 6.00 (3.60 ± 1.96), 0.87- 1.19 (1.03 ±0.13), 0.70 - 1.02 (0.89± 0.14) and 1.39 – 4.49 (2.30 ± 1.10), 0.89 - 2.16 (1.53 ± 0.52), 0.28 - 1.09 (0.69 ± 0.29) µg g^{-1} wet weight in post monsoon and pre monsoon respectively. In monsoon, Cr concentration for liver, gill and muscle of flatfish were in the range 1.20 – 4.10 (2.18 ± 1.35), 0.71 – 2.09 (1.41± 0.56), 0.37 – 1.19 (0.77± 0.34) µg g^{-1} wet weight respectively. Marked seasonal variation was not observed in its distribution in the tissues.

At Chettuva, the levels of Cr in the tissues were comparable for all the seasons. The range and average values of Cr concentration for liver, gill and muscle of flatfish were 1.20- 2.25 (1.73 ± 0.74), 0.26 – 0.90 (0.58 ± 0.45), 0.32 – 0.48 (0.40 ± 0.11) and 0.80- 1.00 (0.90 ± 0.14), 0.30 - 0.38 (0.34 ± 0.06), 0.12- 0.29 (0.21 ± 0.12) µg g^{-1} wet weight in post monsoon and pre monsoon respectively. In monsoon, the range and average values of Cr concentration for liver, gill and muscle of flatfish were 0.63 – 0.76 (0.70 ± 0.09), 0.39 – 0.46 (0.43± 0.05), 0.35 – 0.38 (0.37± 0.02) µg g^{-1} wet weight respectively.

At Ponnani, the range and average values of Cr concentration for liver, gill and muscle of flatfish were 0.89 - 2.40 (1.61 ± 0.76), 0.76 – 1.28 (1.09 ±

0.23), 0.40– 0.83 (0.60 ± 0.22) and 0.62- 0.93 (0.78 ± 0.16), 0.21- 0.39 (0.32 ± 0.10), 0.18 – 0.33(0.24 ± 0.08) µg g^{-1} wet weight in post monsoon and pre monsoon respectively. In monsoon, the concentration of Cr in the tissues were lower compared to other season and were in the range 0.48 – 0.62 (0.55± 0.07), 0.26 – 0.37(0.33± 0.06) and 0.03 – 0.59 (0.39± 0.32) µg g^{-1} wet weight for liver, gill and muscle respectively.

At Calicut, marked variation was discerned in the accumulation of Cr in the tissues among different season. The range and average values of Cr concentration for liver, gill and muscle of flatfish were 1.80- 2.98 (2.36 ± 0.59), 1.56 – 2.12(1.89 ± 0.29), 0.28 – 1.73(0.94 ± 0.73) and 0.97 – 5.20 (3.16± 1.73), 0.26 – 3.61(1.57 ± 1.47), 0.72- 1.24 (1.10 ± 0.25) µg g^{-1} wet weight in post monsoon and pre monsoon respectively In monsoon the range and average values of Cr concentration for liver, gill and muscle of flatfish were 1.99 – 4.53 (2.95 ± 1.38), 1.06 – 2.15(1.56 ± 0.55) and 1.02 – 1.34 (1.21 ± 0.17) µg g^{-1} wet weight respectively.

At Kasargod, the accumulation of Cr in the tissues was comparable for three seasons. The concentration of Cr in liver, gill and muscle of flatfish were 0.52- 1.33 (0.93 ± 0.57), 0.32 – 0.89 (0.61 ± 0.40) and 0.15 – 0.34(0.25 ± 0.13) µg g^{-1} wet weight respectively in post monsoon. The range and average values for liver, gill and muscle were 0.60 – 0.70 (0.65 ± 0.07), 0.21 – 0.34 (0.28 ± 0.09), 0.15- 0.18(0.17 ± 0.02) and 0.60 – 0.72 (0.66 ± 0.08), 0.29 – 0.33(0.31± 0.03), 0.12 – 0.16 (0.14 ± 0.03) µg g^{-1} wet weight in pre monsoon and monsoon respectively.

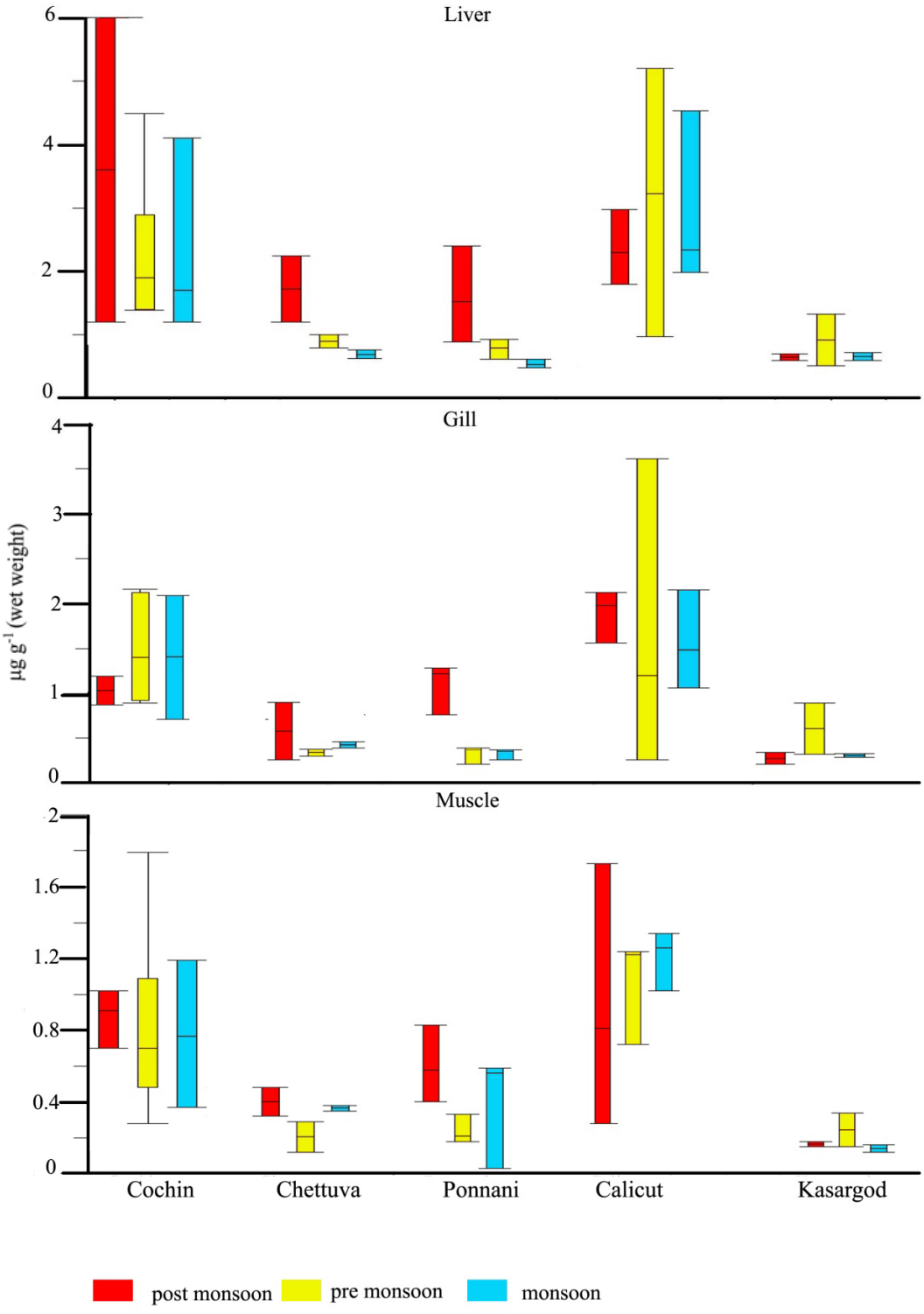


Figure 7C. Seasonal variation of Chromium (Cr) in different organs of flatfish among different transects.

7.2.2.4 Nickel (Ni):

Nickel is a ubiquitous element known for its toxicity, persistence, and affinity for bioaccumulation (Eisler, 1998) but is considered to be essential to various biological functions, often at very low concentrations (Alikhan and Zia, 1989; Muyssen *et al*., 2004). Marked seasonal variation was discerned in its accumulation in the tissues of flatfish in each sampled transect (Fig. **7D**).

At Cochin the range and average values of Ni concentration for liver, gill, muscle of flatfish were 1.67 – 2.84 (2.24 ± 0.48), 0.87- 1.30 (1.06 ± 0.18), 0.20-0.45 (0.27 ± 0.12) and 3.78 – 8.32 (6.09 ± 1.31), 2.86-4.12 (3.45± 0.47), 1.70 - 2.16 (1.93 ± 0.19) µg g^{-1} wet weight in post monsoon and pre monsoon respectively. In monsoon, the concentration Ni in the liver was 4.54 – 6.43 (5.79 ± 0.87) and was discerned the highest among the seasons, while in gill and muscle of flatfish it ranged 1.97 – 2.16 (2.10 ± 0.09) and 1.50 – 2.34 (1.97 ± 0.35) µg g^{-1} wet weight respectively.

At Chettuva, the range and average values of Ni concentration for liver, gill and muscle of flatfish were 1.59 – 2.13(1.86 ± 0.38), 062- 0.89 (0.75± 0.19) and 0.20– 0.32 (0.26 ± 0.08) µg g^{-1} wet weight respectively in post monsoon. In pre monsoon, the accumulation of Ni in the tissues was higher compared to that was observed in other seasons and was in the range 3.82 – 5.74 (4.78 ± 1.36), 1.81- 2.49 (2.15± 0.48) and 0.39 - 0.83 (0.61 ± 0.31) µg g^{-1} wet weight for liver, gill and muscle respectively. In monsoon the range and average values of Ni concentration for liver, gill and muscle of flatfish were 2.30 – 2.90 (2.60 ± 0.42), 1.28 – 2.34 (1.81± 0.75) and 0.18 – 0.24 (0.21± 0.04) µg g^{-1} wet weight respectively.

At Ponnani, the range and average values of Ni concentration for liver, gill , muscle of flatfish were 1.30– 1.96 (1.66 ± 0.33), 0.94 – 1.34 (1.17± 0.17), 0.06 – 0.87(0.51± 0.41) and 2.38 -3.54 (2.94 ± 0.58), 1.85 – 2.39(2.15 ± 0.28), 0.48 – 0.61 (0.53 ± 0.07) µg g^{-1} wet weight in post monsoon and pre monsoon respectively. In monsoon, the accumulation of Ni in the organs was higher compared to that was observed in other seasons. The concentration range

discerned for liver, gill and muscle of flatfish were 2.10 – 8.30 (5.20± 3.10), 2.20 – 4.74(3.24± 1.33) and 2.10 – 2.60(2.37± 0.25) µg g^{-1} wet weight respectively.

At Calicut , marked seasonal variation in the accumulation of Ni in tissues was not observed and the range and average values of Ni concentration for liver, gill, muscle of flatfish were 1.90 – 3.54 (2.71± 0.82), 1.45 – 2.27 (1.80 ± 0.42), 0.52 – 1.21 (0.81± 0.36) and 3.40 – 7.90 (5.68 ± 1.88), 1.80– 2.24 (2.08 ± 0.21) , 0.56 - 0.82 (0.76 ± 1.01) µg g^{-1} wet weight in post monsoon and pre monsoon respectively In monsoon the values of Ni concentration for liver, gill and muscle of flatfish were 2.80 – 3.43 (3.08± 0.32), 1.10 – 2.80(1.73± 0.86) and 0.90– 1.10(1.03 ± 0.12) µg g^{-1} wet weight respectively.

At Kasargod, the range and average values of Ni concentration for liver, gill and muscle of flat fish were 1.24 –2.07 (1.66± 0.59), 0.80 – 0.98 (0.89±0.13) and 0.20 – 0.42 (0.31 ± 0.11) µg g^{-1} wet weight respectively in post monsoon. In pre monsoon the concentration for liver and muscle were generally higher compared to other seasons and was in the range 2.40 – 5.20 (3.80 ± 1.98), and 0.62- 1.23 (0.93± 0.23) µg g^{-1} wet weight respectively. In gill it was in the range1.80– 2.12 (1.96 ± 0.23) µg g^{-1} wet weight. In monsoon, the range and average values of Ni concentration for liver, gill and muscle of flatfish were 1.90– 2.08 (1.99 ± 0.13), 1.34 – 1.78 (1.56± 0.31) and 0.47 – 0.54 (0.51± 0.05) µg g^{-1} wet weight respectively.

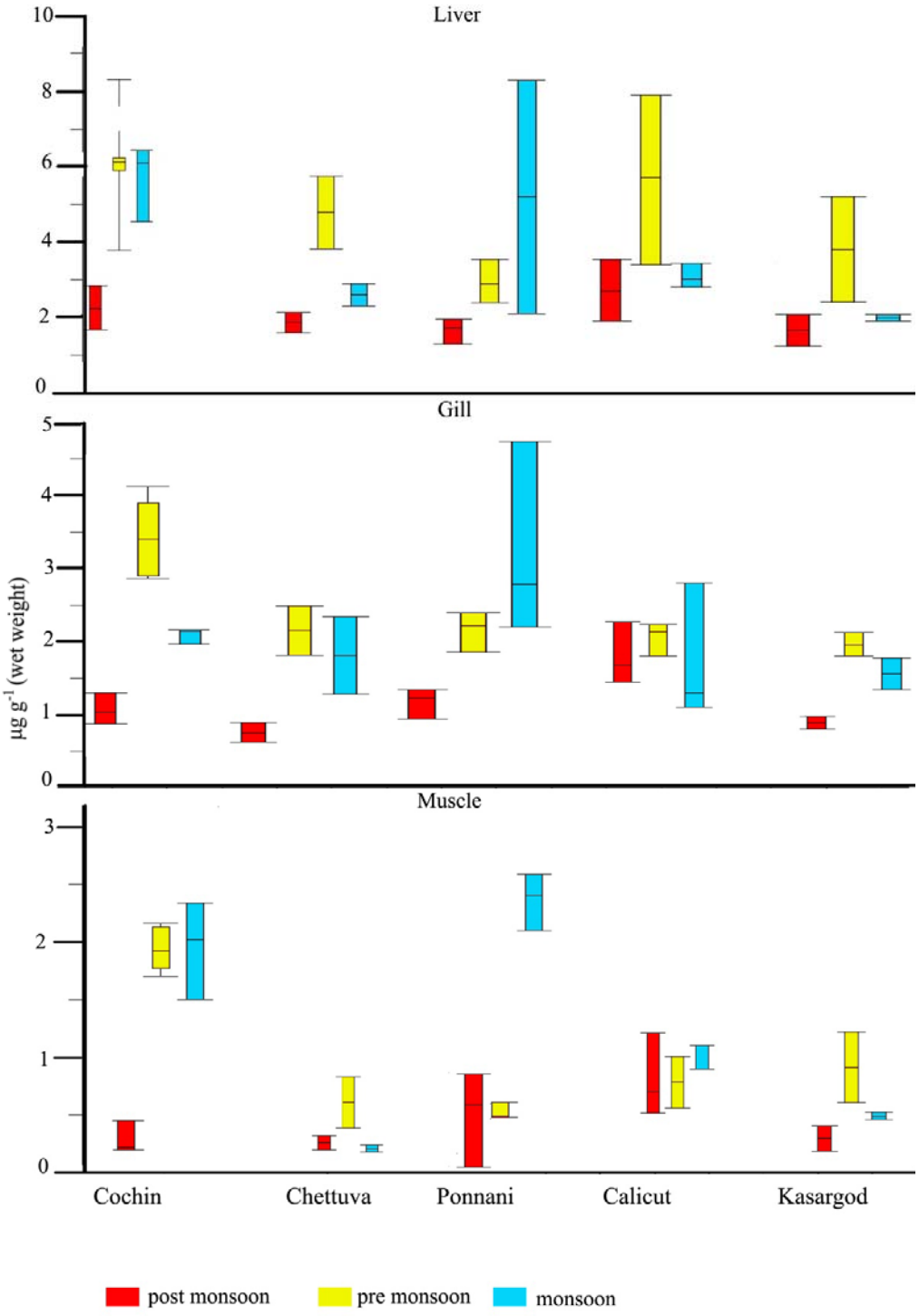


Figure 7D. Seasonal variation of Nickel (Ni) in different organs of flatfish among different transects.

7.2.2.5 Zinc (Zn)

Although zinc is an essential trace element for all living organisms, and is a constituent of more than 200 metalloenzymes and other metabolic compounds ensuring stability of biological molecules such as DNA and structures such as membranes and ribosomes, and excess intake can cause a variety of pathological effects (Eisler, 1993). The content of zinc in the body is regulated until a threshold of exposure is reached, after which it will accumulate in tissues at higher levels (Bryan, 1967; White and Rainbow, 1982; 1984; Vijayram and Geraldine, 1996). This regulation is often mediated by the detoxifying proteins, metallothioneins (Rainbow, 1997). Metallothioneins are non-enzymatic proteins with a low molecular weight which play a role in the homeostatic control of essential metals such as Zn and Cu (Kagi and Schaffer, 1988; Amiard *et al.*, 2006). Being an essential element, the concentration of Zn in the tissues were detectable in high levels in flatfish pooled from each transect (Fig. **7E)**.

At Cochin, marked seasonal variation in the levels of Zn in the tissues was discerned. The range and average values of Zn concentration for liver, gill, muscle of flatfish were 110.20 – 132.90 (121.50 ± 9.27), 30.40 – 53.46 (40.64 ±10.89), 14.56 – 21.43 (17.91 ± 2.85) and 76.36 – 153.20 (101.32 ± 25.39), 58.98 - 89.57 (69.61 ± 9.66), 28.90 - 44.96 (39.89 ± 5.88) µg g^{-1} wet weight in post monsoon and pre monsoon respectively. In monsoon, Zn levels for liver, gill and muscle of flatfish were 80.30 – 120.80 (100.60 ± 19.12), 41.89 – 54.23 (46.74 ± 5.30), and 27.67 –32.34 (30.43± 2.08) µg g^{-1} wet weight respectively.

At Chettuva, the range and average values of Zn concentration for liver, gill, muscle of flatfish were 87.67- 111.10 (99.39 ± 16.57), 36.60 – 43.90 (40.25 ± 5.16), 19.14 – 21.64 (20.39 ± 1.77) and 77.90 – 94.74 (86.32 ± 11.91), 49.37-59.86 (54.62± 7.42), 32.56 – 36.78 (34.67 ± 2.98) µg g^{-1} wet weight in post monsoon and pre monsoon respectively. In monsoon the levels of Zn in liver, gill and muscle of flatfish was much higher compared to other seasons and were in the range 53.26 – 62.80 (58.03 ± 6.75), 26.78 – 28.40 (27.59 ± 1.15) and 7.89 - 9.45(8.67 ± 1.10) µg g^{-1} wet weight respectively.

At Ponnani, in post monsoon the range and average values of Zn concentration for liver, gill and muscle of flatfish were 56.30 – 114.80 (87.13 ± 29.38), 29.56 – 38.29 (34.25± 3.59) and 12.50 – 18.82 (15.64± 3.16) µg g^{-1} wet weight, while in pre monsoon the range was much high and were 90.34 – 132.00 (112.34 ± 20.93), 39.38 – 51.04 (45.30 ± 5.83) and 23.90 – 34.56 (29.85± 5.44) µg g^{-1} wet weight respectively. In monsoon, Zn concentration for liver, gill and muscle of flatfish were 67.34 – 94.89 (81.81 ± 13.83), 51.90 – 63.22 (59.34 ± 6.45), and 15.60 – 23.45 (19.74 ± 3.94) µg g^{-1} wet weight respectively.

At Calicut, the range and average values of Zn concentration for liver, gill, muscle of flatfish were 71.60 – 122.30 (101.93± 26.78), 17.90 – 33.22 (24.15 ± 8.04), 15.67 – 21.32 (18.81 ± 2.88) and 107.49 – 126.20 (117.50 ± 7.68), 30.40– 64.76 (47.38 ± 15.20) and 21.80 – 62.60 (38.84 ± 18.19) µg g^{-1} wet weight respectively in post monsoon and pre monsoon. In monsoon the levels were 83.46 – 121.90 (102.99 ± 19.23), 40.71 – 56.02 (48.54 ± 7.66) and 24.45– 32.14 (28.81 ± 3.95) µg g^{-1} wet weight for liver, gill and muscle of flatfish respectively.

At Kasargod, the range and average values of Zn concentration for liver, gill, muscle of flatfish were 76.50 –117.60 (97.05 ± 29.06), 19.30 – 37.89 (28.60 ± 13.15) and 13.90 – 15.67(14.79 ± 0.88) and 66.89 – 92.27 (79.58 ± 17.95), 34.56– 44.90 (39.73 ± 7.31) and 27.89 – 33.02 (30.46 ± 3.63) µg g^{-1} wet weight in post monsoon and pre monsoon respectively. In monsoon, the range and average values of Zn concentration for liver, gill and muscle of flatfish were 63.40 – 89.09 (76.25 ± 18.17), 31.88 – 35.60 (33.74± 2.63) and 23.56 – 27.89 (25.73 ± 3.06) µg g^{-1} wet weight respectively.

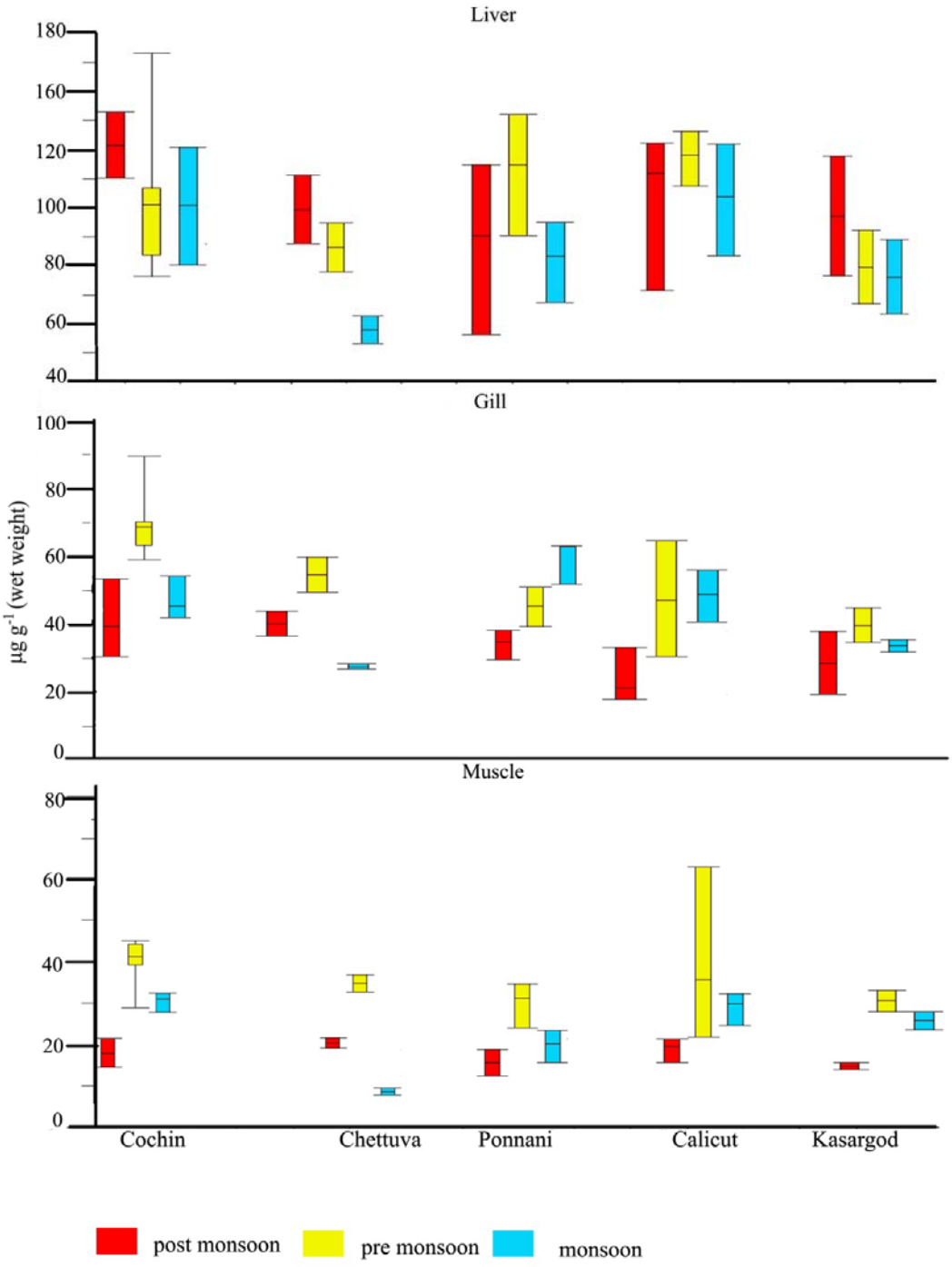


Figure 7E. Seasonal variation of Zinc (Zn) in different organs of flatfish among different transects

7.2.2.6 Cadmium (Cd)

Cadmium is a non-essential toxic metal, and elevated concentrations are often a threat to marine biota. It is also a serious environmental contaminant that is also transported atmospherically. In humans, cadmium may accumulate from food chain magnification and may induce kidney dysfunction, skeletal damage and reproductive deficiencies (Commission of the European Communities, 2001). In a fish, it can cause anameia and vertebral fractures, osmoregulatory problems, decreased digestive efficiency, haematological and biochemical effects, erratic swimming and mortality (Burger *et al.*, 2002). It can also cause teratogenic, carcinogenic and highly nephrotoxic effects on living organisms (Anderson *et al.*, 1978; Eisler, 1985). Cadmium was found to be in detectable levels in the tissues of flatfish and showed varying levels from each transect (Fig. 7F).

At Cochin, the range and average values of Cd concentration for liver, gill, muscle of flatfish were 0.21- 0.69 (0.43 ± 0.24), 0.10 - 0.39 (0.22 ± 0.16),0.01- 0.37 (0.17± 0.18) and 0.10 – 2.36 (0.61 ± 0.79), 0.07-0.21 (0.11 ± 0.05), 0.04 - 0.11(0.08 ± 0.03) µg g^{-1} wet weight in post monsoon and pre monsoon respectively. In monsoon, the levels of the range and average values of Cd concentration for liver, gill, muscle of flatfish were 0.02 – 0.27 (0.12 ± 0.11), 0.07 – 0.09 (0.08± 0.01), and 0.03 – 0.18 (0.08± 0.07) µg g^{-1} wet weight respectively.

At Chettuva, a low level of Cd in the tissues was discerned and marked seasonal variation was not observed. The range and average values of Cd concentration for liver, gill and muscle of flat fish were 0.01- 0.08 (0.04 ± 0.05), BDL – 0.04 (0.02± 0.03) and 0.09 – 0.11(0.10 ± 0.01) µg g^{-1} wet weight respectively in post monsoon. In pre monsoon, the level of Cd in liver and gill were 0.03 - 0.05 (0.04± 0.01) and 0.01- 0.03 (0.02 ± 0.02) µg g^{-1} wet weight and in muscle it was below the detectable limit. In monsoon, Cd concentration in liver, gill and muscle of flatfish ranged 0.01 – 0.05 (0.03 ± 0.02), below detectable limit – 0.07 (0.04± 0.05) and below detectable limit – 0.03 (0.03) µg g^{-1} wet weight respectively.

At Ponnani, Cd was discerned to be in detectable levels in tissues and was comparable for all seasons. The range and average values of Cd concentration for liver, gill, muscle of flatfish were 0.03 - 0.07 (0.05± 0.02), 0.06 – 0.09(0.08 ± 0.01), 0.01– 0.02 (0.01 ± 0.01) and 0.02- 0.04 (0.03± 0.01), 0.01 – 0.05 (0.03 ± 0.02) and below detectable limit – 0.01(0.01) µg g^{-1} wet weight in post monsoon and pre monsoon respectively. In monsoon, the range and average values of Cd concentration for liver, gill and muscle of flatfish were 0.03 – 0.07(0.05 ± 0.02), 0.01 – 0.03 (0.02 ± 0.01) and 0.02 – 0.05 (0.03± 0.02) µg g^{-1} wet weight respectively.

At Calicut, cadmium concentration in the tissues was low and noticeable seasonal variation in its accumulation was not observed. The range and average values of Cd concentration for liver, gill, muscle of flat fish were 0.08- 0.09 (0.08± 0.01), 0.06 – 0.16 (0.10 ± 0.05), 0.04 – 0.06 (0.05± 0.01) and below detectable limit – 0.10 (0.06 ± 0.05), 0.01– 0.04 (0.02 ± 0.01), below detectable limit - 0.04 (0.02 ± 0.02) µg g^{-1} wet weight respectively in post monsoon and pre monsoon. In monsoon, the Cd levels in liver, gill and muscle of flatfish ranged 0.05 – 0.08 (0.06 ± 0.02), 0.03 – 0.07 (0.04 ± 0.02) and 0.01– 0.02 (0.01) µg g^{-1} wet weight respectively.

At Kasargod, the concentration of Cd in the tissues was low in all seasons. In post monsoon, the range and average values of Cd concentration for liver and gill of flatfish were 0.05- 0.06 (0.05± 0.01) and below detectable limit – 0.08 (0.04 ± 0.06) µg g^{-1} wet weight respectively while it was not detectable in muscle. In pre monsoon and monsoon, the levels for liver, gill, muscle ranged 0.02 – 0.03 (0.02± 0.01), below detectable limit – 0.02 (0.02), below detectable limit - 0.01(0.01) and 0.02– 0.03(0.03 ± 0.01), 0.01 – 0.03 (0.02 ± 0.01), below detectable limit – 0.01(0.01) µg g^{-1} wet weight respectively.

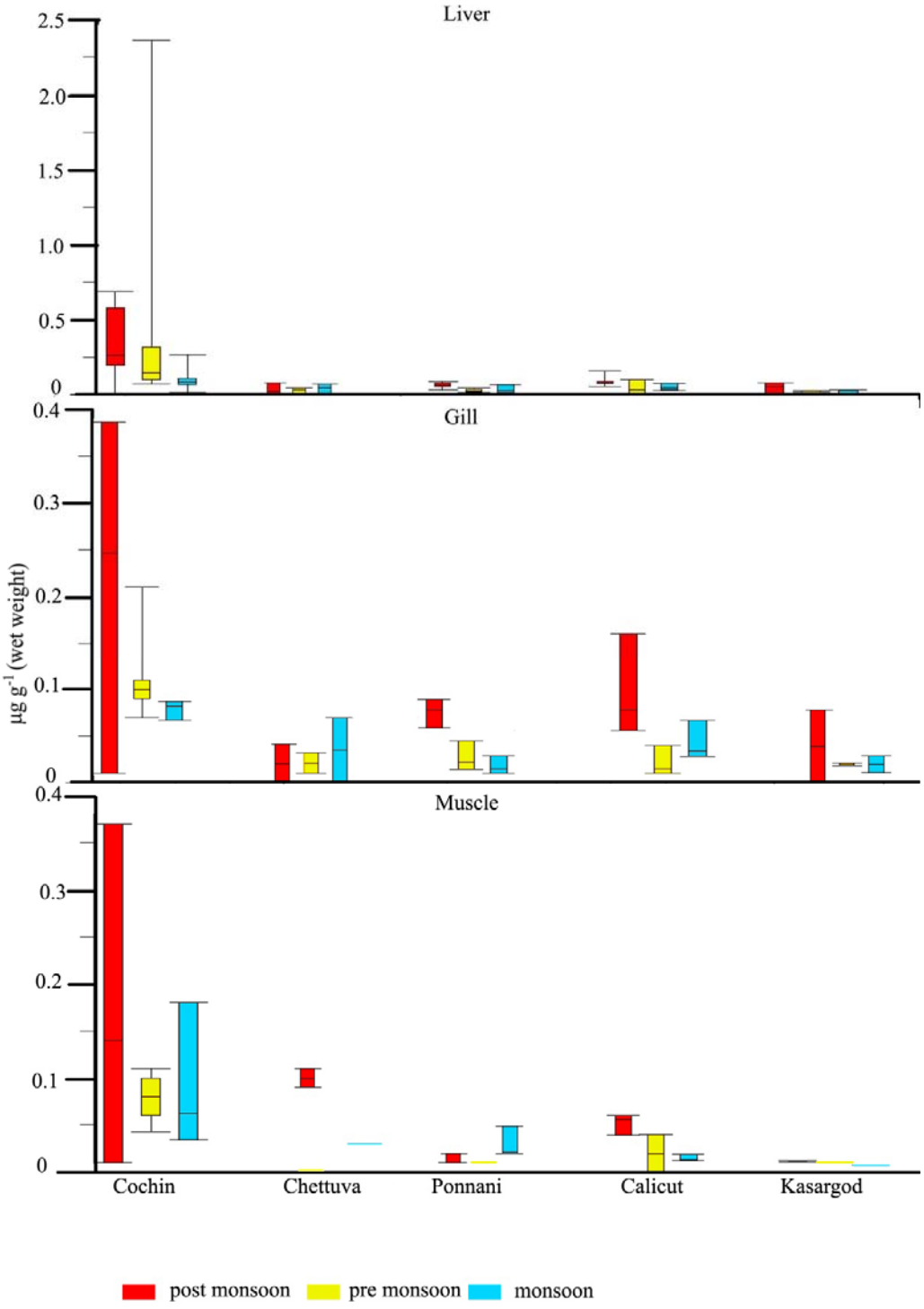


Figure 7F. Seasonal variation of Cadmium (Cd) in different organs of flatfish among different transects.

7.2.2.7 Mercury (Hg)

Mercury is one of the most toxic metals for marine fauna and known to be a latent neurotoxin. It is listed as a priority pollutant by international agencies in charge of marine environmental protection. A high dietary intake of mercury (organic) from consumption of fish has been hypothesized to increase the risk of coronary heart disease (Salonen *et al.*, 1995). Being a non essential element its concentration in the tissues of flatfish was detected low at each transect (Fig. 7G).

At Cochin, the level of Hg in the tissues was detectable and the range and average values of Hg concentration for liver, gill, muscle of flatfish were 0.07 – 0.23 (0.16 ± 0.07), 0.04 – 0.15 (0.11± 0.05), 0.02 – 0.11 (0.04 ± 0.04) and 0.02 – 0.16 (0.06 ± 0.05), 0.02-0.10 (0.05± 0.03), 0.01- 0.06 (0.03 ± 0.02) µg g^{-1} wet weight in post monsoon and pre monsoon respectively. In monsoon the range and average values of Hg concentration for liver, gill and muscle of flatfish were 0.07 – 0.39 (0.18 ± 0.15), 0.01 – 0.07 (0.03 ± 0.04) and 0.09–0.11 (0.10± 0.01) µg g^{-1} wet weight respectively.

At Chettuva, in post monsoon the range and average values of Hg concentration for liver, gill and muscle of flatfish were 0.02 - 0.04 (0.03 ± 0.01), 0.01 – 0.02 (0.02± 0.01) and below detectable limit – 0.03 (0.02 ± 0.01) µg g^{-1} wet weight respectively. In pre monsoon, the concentration was detected low in the tissues and the values ranged from below detectable limit to 0.01 µg g^{-1} wet weight for liver and gill, while in muscle it was not detectable. In monsoon, the level of Hg in the tissues was higher compared to other seasons and the range and average values for liver, gill and muscle of flatfish were 0.03 – 0.04 (0.03 ± 0.01), 0.01 – 0.10 (0.05 ± 0.07) and 0.02 -0.03(0.03 ± 0.01) µg g^{-1} wet weight respectively.

At Ponnani, marked seasonal variation was not observed in the accumulation of Hg in tissues and was found to be comparable. The range and average values of Hg concentration for liver, gill, muscle of flatfish were 0.02 – 0.04 (0.03 ± 0.01), 0.02 – 0.03 (0.03± 0.01), below detectable limit – 0.02(0.01) and

0.01 – 0.03 (0.02 ± 0.01), 0.01 – 0.02(0.02 ± 0.01), below detectable limit – 0.01 µg g^{-1} wet weight in post monsoon and pre monsoon respectively. In monsoon, the range and average values of Hg concentration for liver, gill and muscle of flatfish were 0.01 – 0.02 (0.02 ± 0.01), below detectable limit – 0.02 (0.01) and 0.02 – 0.05 (0.03 ± 0.02) µg g^{-1} wet weight respectively.

At Calicut, the level of Hg in the tissues was detected low in each season. The range and average values of Hg concentration for liver, gill and muscle of flat fish were 0.02 – 0.08 (0.06± 0.10), 0.01 – 0.05 (0.03 ± 0.02) and below detectable limit – 0.02 (0.02) µg g^{-1} wet weight respectively in post monsoon, while in pre monsoon it was in the range 0.03 – 0.04 (0.03 ± 0.01), 0.01 – 0.03 (0.02 ± 0.01) and below detectable limit – 0.01 µg g^{-1} wet weight respectively. In monsoon the range and average values of Hg concentration for liver, gill and muscle of flatfish were 0.03 – 0.04 (0.03), below detectable limit – 0.01, and below detectable limit – 0.02 µg g^{-1} wet weight respectively.

At Kasargod, the range and average values of Hg concentration for liver, gill and muscle of flatfish were below detectable limit – 0.02 (0.01), 0.01 – 0.03 (0.02 ± 0.01) and below detectable limit – 0.02 (0.01) µg g^{-1} wet weight respectively in post monsoon. In pre monsoon the range and average values for liver, gill and muscle of flatfish were 0.01 – 0.03 (0.02 ± 0.01), below detectable limit – 0.01 and below detectable limit – 0.01, µg g^{-1} wet weight respectively, while in monsoon Hg was detected only in liver of flatfish and the average value was discerned to be 0.03 µg g^{-1} wet weight and in gill and muscle it was below the detectable limit.

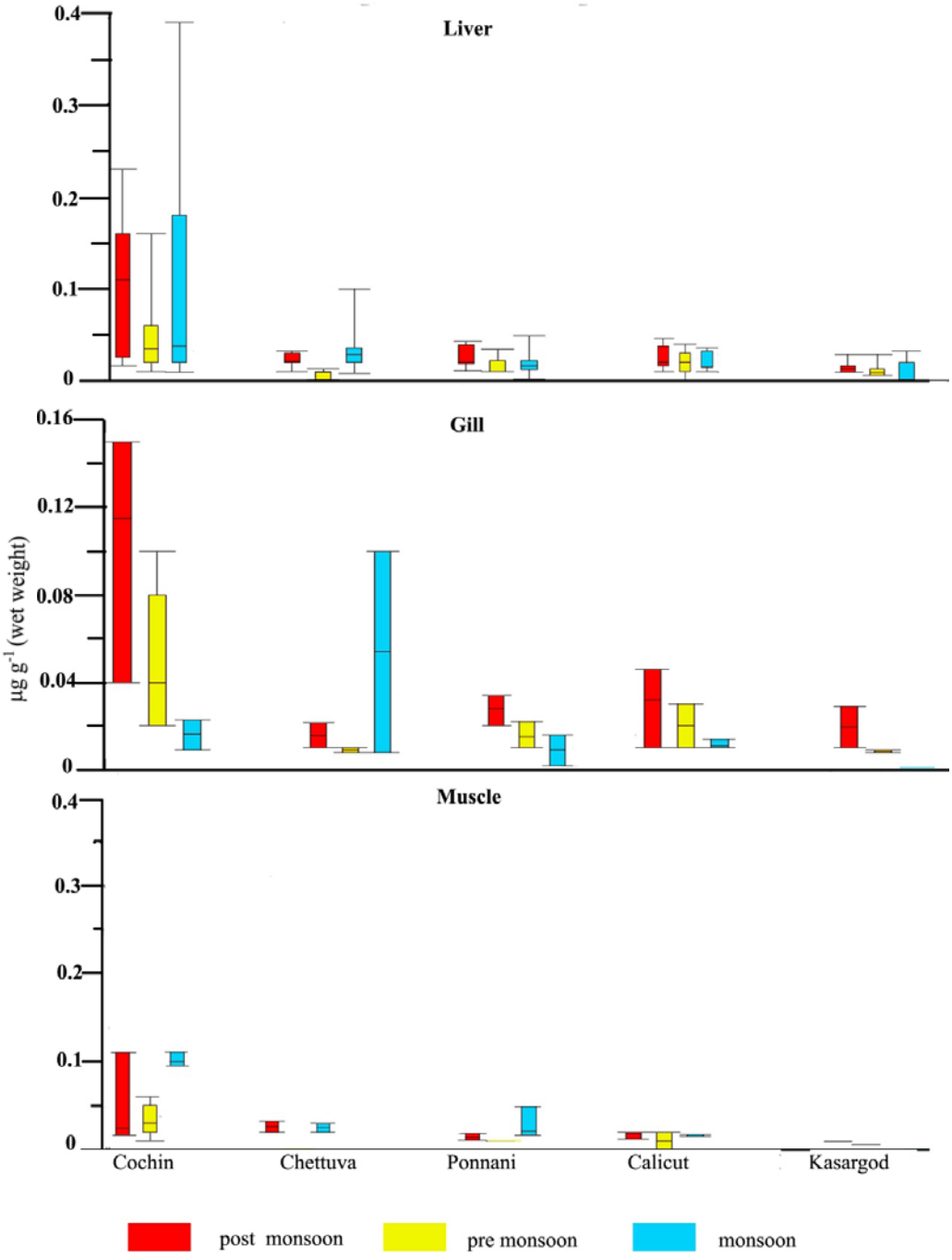


Figure 7G. Seasonal variation of Mercury (Hg) in different organs of flatfish among different transects.

7.2.3 Metal Pollution Index

The overall metal contents of the fishes among transects were compared, using the metal pollution index (MPI) calculated with the following formula (Usero, 1996; 1997):

$$MPI = (M1 \times M2 \times M3 \times \cdots \times Mn)^{1/n},$$

where *Mn* is the concentration of metal *n* expressed in µg g^{-1} of wet weight.

MPI recorded its maximum value for the liver in flatfish, followed by the gill, and finally the muscle (Table 7.1, Fig. 7H**)**. Among transects the maximum MPI value was recorded at Cochin followed by Calicut, Ponnani, Kasargod and finally the lowest at Chettuva.

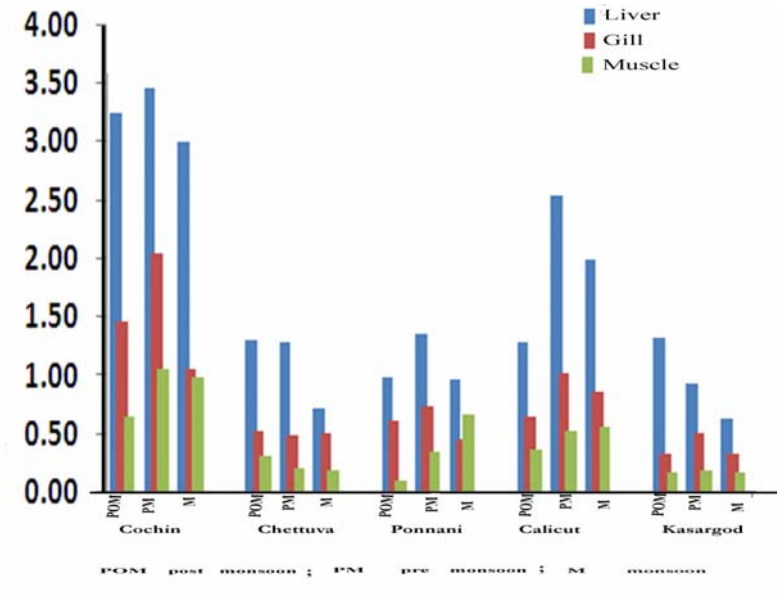


Figure 7H. Seasonal variation in Metal Pollution Index (MPI) of the tissues of flatfish pooled along the central and northern coast of Kerala.

7.2.4 Metal Selectivity Index (MSI) of the Flatfish among Transects.

It is defined as the relative metal – accumulating capacity of a tissue for a particular metal. For each part of the fish, the concentration of metals can be expressed as the metal selectivity index (MSI).

$$MSI = \frac{\text{Absolute concentration of a metal in a tissue}}{\text{Total concentration of all metals in that tissue.}} \times 100$$

The relative percentage contribution of each metal with respect to total metal concentration in each tissue gives the affinity for the species to accumulate a particular metal in that part of the body. The results are presented in Table 7.2. Affinities for non essential metals (Cr,Pb,Cd and Hg) by the tissues showed discrepancy between seasons in each transects as such a wide variation in the order of accumulation of metals in tissues was discerned.

At Cochin, in liver, it ranked in the decreasing order Zn > Cu > Cr > Ni > Pb > Cd > Hg in post monsoon while there was interchange of Cd,Hg in the order of affinity in pre monsoon and monsoon which was discerned as Zn > Cu > Ni > Cr > Pb > Cd > Hg and Zn > Cu > Ni > Cr > Pb > Hg > Cd respectively. In gills the affinity of the metals for tissue were Zn > Cu > Pb > Ni > Cr > Cd >Hg in post monsoon and pre monsoon,while in monsoon Pb showed a weak affinity varying the order as Zn > Cu > Ni > Cr > Pb > Cd >Hg. In muscles the affinity of metals viz.Cr, Pb and Ni differed between seasons leading to discrepancy in the ranking order of metals which was discerned to be Zn > Cu > Cr > Pb > Ni > Cd > Hg, Zn > Cu > Ni > Pb > Cr > Cd > Hg and Zn > Cu > Ni > Cr > Pb > Hg > Cd for post monsoon, pre monsoon and monsoon respectively.

At Chettuva, the order in which each metal contributed with respect to total metal concentration in liver and gill was Zn > Cu > Ni > Cr > Pb > Cd > Hg in post monsoon and pre monsoon. In monsoon, there was slight discrepancy in Cd and Hg relative percentage contribution and the order was Zn > Cu > Ni > Cr > Pb > Cd ~Hg and Zn > Cu > Ni > Cr > Pb >Hg > Cd for liver and gill respectively. A wide variation in the relative percentage contribution of each metal with respect to total metal concentration in muscles was conspicuous, it was discerned to be Zn > Cu > Cr > Ni > Cd >Pb >Hg, Zn > Cu >Ni > Cr > Cd > Pb >Hg and Zn > Cu > Cr > Ni >Cd > Hg > Pb for post monsoon, pre monsoon and monsoon respectively.

At Ponnani, the order in which each metal contributed with respect to total metal concentration in liver and gill was Zn > Cu > Ni > Cr > Pb > Cd

>Hg in post monsoon and monsoon. The order was different in pre monsoon which followed the order Zn > Cu > Ni > Pb > Cr > Cd > Hg. A slight discrepancy in the relative percentage contribution of each metal with respect to total metal concentration in muscles was conspicuous, it was discerned to be Zn > Cu > Cr > Ni > Cd > Hg in post monsoon, and Zn > Cu > Ni > Pb > Cr >Cd ~ Hg for pre monsoon and monsoon.

At Calicut, there was no disparity in the order in which each metal contributed with respect to total metal concentration in liver and was observed to be Zn > Cu > Ni > Cr > Pb > Cd >Hg in all seasons. In gill the metals followed the order Zn > Cu > Cr >Ni > Pb > Cd > Hg in post monsoon, while in pre monsoon and monsoon the order was Zn > Cu > Ni > Cr > Pb > Cd > Hg. A slight discrepancy in the relative percentage contribution of each metal with respect to total metal concentration in muscles was also evident, it was discerned to be Zn > Cu > Ni > Pb > Cr > Cd > Hg in post monsoon, and Zn > Cu > Cr > Ni > Pb > Cd >Hg for pre monsoon and monsoon.

At Kasargod, there was no disparity in the order in which each metal contributed with respect to total metal concentration in liver and was observed to be Zn > Cu > Ni > Cr > Pb > Cd >Hg in all seasons. In gill the metals followed the order Zn > Cu > Ni > Cr > Pb > Hg in post monsoon, while in pre monsoon and monsoon the order was Zn > Cu > Ni > Cr > Pb > Cd >Hg and Zn > Cu > Ni > Cr > Pb >Hg respectively. A slight discrepancy in the relative percentage contribution of each metal with respect to total metal concentration in muscles was also evident, it was discerned to be Zn > Cu > Ni > Cr > Pb > Cr > Cd >Hg in post monsoon, Zn > Cu > Ni > Cr > Cd >Hg (no contribution from Pb) in pre monsoon and Zn > Cu > Ni > Cr > Cd (no contribution from Pb, Hg) in monsoon.

Table 7.2 The relative metal – accumulating capacity of a tissue (MSI) of flatfish (*Cynoglossus macrostomus*) expressed as %.

			Percentage (%) contribution of each metal in tissue						
Transect	Season	Organ	Cu	Pb	Cr	Ni	Zn	Cd	Hg
Cochin		Liver	26.51	0.71	2.05	1.28	69.13	0.24	0.09
	POM	Gill	12.87	4.16	1.98	2.05	78.30	0.43	0.20
		Muscle	11.45	2.60	3.95	1.22	79.86	0.74	0.19
		Liver	36.44	0.97	1.30	3.45	57.45	0.35	0.03
	PM	Gill	21.91	3.68	1.52	3.44	69.29	0.11	0.05
		Muscle	20.37	1.74	1.26	3.53	72.89	0.14	0.06
		Liver	27.07	1.30	1.43	3.81	66.19	0.08	0.12
	MON	Gill	11.72	2.16	2.40	3.60	79.96	0.14	0.03
		Muscle	14.48	1.06	1.96	4.99	77.04	0.21	0.26
Chettuva	POM	Liver	21.44	0.48	1.31	1.41	75.30	0.03	0.02
		Gill	7.48	0.73	1.28	1.66	88.77	0.05	0.03
		Muscle	5.82	0.27	1.78	1.16	90.42	0.44	0.12
	PM	Liver	30.65	0.60	0.67	3.57	64.47	0.03	0.01
		Gill	13.35	0.19	0.51	3.25	82.64	0.03	0.01
		Muscle	9.56	0.025	0.52	1.55	88.29	0.025	0.025
	MON	Liver	26.84	0.06	0.83	3.10	69.10	0.04	0.04
		Gill	10.03	0.14	1.28	5.44	82.86	0.11	0.16
		Muscle	17.68	0.088	3.23	1.86	76.66	0.27	0.22
Ponnani		Liver	31.21	0.88	1.03	1.51	65.31	0.04	0.02
	POM	Gill	9.68	1.05	2.16	2.68	84.19	0.17	0.06
		Muscle	7.48	0.07	2.85	0.41	89.04	0.07	0.08
		Liver	29.89	0.66	0.47	1.76	67.19	0.02	0.01
	PM	Gill	17.35	1.52	0.55	3.65	76.86	0.05	0.03
		Muscle	9.66	1.42	0.70	1.53	86.63	0.03	0.03
		Liver	10.78	0.94	0.55	5.24	82.43	0.05	0.02
	MON	Gill	6.39	0.84	0.49	4.78	87.47	0.03	0.01
		Muscle	10.69	5.17	1.47	8.83	73.63	0.11	0.11
Calicut		Liver	22.55	0.94	1.83	1.93	72.66	0.08	0.02
	POM	Gill	16.76	1.86	6.05	5.63	69.44	0.22	0.04

		Muscle	12.85	2.21	1.44	2.67	80.56	0.20	0.06
		Liver	33.68	1.25	1.63	2.92	60.47	0.03	0.02
	PM	Gill	24.87	1.68	2.26	2.99	68.16	0.03	0.03
		Muscle	15.56	0.46	2.27	1.62	80.04	0.03	0.02
		Liver	18.83	1.89	2.15	2.24	74.83	0.04	0.02
	MON	Gill	7.97	1.98	2.71	3.01	84.23	0.07	0.02
		Muscle	13.63	1.11	3.31	2.83	79.04	0.04	0.04
		Liver	27.40	0.25	0.48	1.15	70.67	0.04	0.01
	POM	Gill	10.28	1.47	1.38	3.45	83.33	0.04	0.04
		Muscle	8.17	0.77	0.96	1.28	88.70	0.07	0.06
		Liver	38.76	0.09	0.47	2.76	57.89	0.02	0.02
Kasargod	PM	Gill	22.67	0.29	0.50	3.60	72.89	0.04	0.02
		Muscle	11.42	0.03	0.46	2.60	85.45	0.03	0.02
		Liver	10.96	0.06	0.74	2.24	85.94	0.03	0.03
	MON	Gill	8.94	0.11	0.79	3.98	86.10	0.05	0.03
		Muscle	9.51	0.03	0.48	1.73	88.18	0.02	0.03

NOTE: POM - post monsoon, PM - pre monsoon, M - monsoon

7.2.5 Tissue Selectivity Index (TSI)

It is defined as the relative tissue-occupying capacity of a metal in a particular tissue.

$$TSI = \frac{\text{Absolute concentration of a metal in a tissue}}{\text{Total concentration of all metals in that tissue.}} \times 100$$

Relative percentage concentration of each metal with respect to its total concentration in all the tissues, defined as the TSI, showed the affinity of the tissues for the accumulation of a particular metal. The results are presented in Table 7.3. From the results it is conspicuous that in most cases metals are mainly accumulated in the liver followed by gill and muscle of flatfish. In certain cases variation in the usual order of accumulation of metals in tissues were also observed during particular seasons in each transects.

At Cochin, in liver the average TSI ranged between 52.17% (pre monsoon) - 59.10% (post monsoon), in gill it was between 22.98 % (monsoon) - 32.01% (pre monsoon) and 12.46% (post monsoon) - 20.26% (monsoon) in muscle. Non

essential metals like Pb, Cd and Hg showed unique tissue specificity in particular seasons, compared with their usual tissue specificity. In pre monsoon Pb showed an affinity towards gill followed by liver and muscle. In monsoon Cd and Hg showed an affinity for tissue in the order liver > muscle > gill.

At Chettuva, the average TSI range for liver, gill and muscle was between 51.22% (monsoon) - 57.35% (post monsoon), 21.39 % (post monsoon) - 34.57% (monsoon) and 8.95% (pre monsoon) - 20.40% (post monsoon) respectively. In post monsoon Cd and Hg discerned an affinity towards muscle followed by liver and gill. In monsoon Cd affinity for tissue was in the order gill > muscle >liver.

At Ponnani, in liver the average TSI ranged between 44.10 % (monsoon) - 54.61% (post monsoon), in gill it was between 22.83 % (monsoon) - 35.80% (post monsoon) and 10.01% (post monsoon) – 34.93% (monsoon) in muscles. Cadmium showed a seasonal shift in the affinity for tissues, it followed the order gill > liver > muscle in post monsoon and pre monsoon while in monsoon its order of affinity in the tissue was liver > muscle > gill. Chromium and Hg showed affinity for specific tissue as compared to their usual order of affinity. Mercury and Cr followed the order gill > liver > muscle and liver > muscle> gill respectively in monsoon.

At Calicut, in liver the average TSI ranged between 53.97 % (post monsoon) – 61.57% (pre monsoon), in gill it was between 25.35 % (pre monsoon) – 28.04 % (post monsoon) and 13.30% (pre monsoon) – 17.28% (post monsoon) in muscles. In monsoon Cu and Hg followed the tissue order liver > muscle > gill and in post monsoon, Hg affinity towards the tissue followed the order liver > muscle > gill.

At Kasargod, in liver the average TSI ranged between 56.29 % (pre monsoon) – 62.53% (monsoon), in gill it was between 23.48 % (post monsoon) – 31.27 % (pre monsoon) and 10.62% (monsoon) – 14.12% (post monsoon) in muscles. In post monsoon Cd showed affinity towards liver and muscle while it didn't show any affinity towards gill. In post monsoon and pre monsoon Pb showed an affinity for tissues in the order gill > liver > muscle.

Table 7.3 The relative tissue-occupying capacity of a metal (TSI) of flatfish (*Cynoglossus macrostomus*) expressed as %.

			Percentage contribution(%) of metal for tissues						
Transect	Season	Organ	Cu	Pb	Cr	Ni	Zn	Cd	Hg
Cochin		Liver	83.43	31.27	65.28	62.64	67.48	52.78	50.81
	POM	Gill	11.96	54.14	18.68	29.68	22.57	27.44	33.87
		Muscle	4.60	14.60	16.05	7.61	9.95	20.37	14.03
		Liver	65.96	26.91	50.92	53.06	48.06	76.43	43.88
	PM	Gill	22.59	58.11	33.80	30.12	33.02	13.75	32.65
		Muscle	11.44	14.97	15.28	16.86	18.92	9.85	23.81
		Liver	76.60	54.17	49.97	58.70	56.59	41.25	60.08
	MON	Gill	12.75	34.43	32.28	21.32	26.29	28.39	5.38
		Muscle	10.65	11.48	17.75	19.98	17.12	30.27	34.58
Chettuva	POM	Liver	85.73	62.14	63.77	64.58	62.10	26.32	36.79
		Gill	10.28	32.16	21.40	26.17	25.15	12.06	22.50
		Muscle	3.98	5.83	14.83	9.07	12.74	58.82	37.50
	PM	Liver	76.53	86.02	62.28	63.40	49.15	66.67	53.49
		Gill	16.46	13.44	23.53	28.51	31.10	35.00	41.86
		Muscle	7.00	0.00	14.19	8.09	19.74	0.00	4.65
	MON	Liver	80.84	51.50	46.80	56.28	61.54	32.78	28.83
		Gill	11.98	45.00	28.62	39.18	29.26	38.89	49.09
		Muscle	7.17	0.00	24.58	4.55	9.20	33.33	22.73
Ponnani		Liver	85.81	67.26	43.41	56.52	57.24	32.00	40.00
	POM	Gill	10.85	32.74	37.07	40.87	30.05	59.00	40.00
		Muscle	3.35	0.00	19.51	2.48	12.71	10.00	22.00
		Liver	78.66	44.40	58.17	52.31	59.92	44.44	44.00
	PM	Gill	16.10	35.87	24.01	38.32	24.16	45.00	31.33
		Muscle	5.24	19.60	17.82	9.37	15.92	16.67	20.00
		Liver	59.76	22.51	43.04	48.10	50.85	51.11	33.33
	MON	Gill	24.21	4.89	25.98	29.97	36.88	20.00	17.87
		Muscle	16.01	72.60	30.97	21.89	12.27	33.44	57.33
Calicut		Liver	76.52	50.54	49.45	49.10	68.08	44.12	40.00
	POM	Gill	14.88	26.09	42.86	37.47	17.02	32.94	25.00
		Muscle	8.61	23.37	7.69	13.44	14.90	22.94	30.00

		Liver	72.49	63.48	54.21	66.46	57.68	62.50	54.17
	PM	Gill	19.15	30.50	26.91	24.30	23.25	20.00	33.33
		Muscle	8.36	5.89	18.88	9.21	19.07	15.00	16.67
		Liver	73.05	62.65	51.60	52.65	57.11	51.40	53.33
	MON	Gill	12.95	27.55	27.32	29.63	26.92	36.24	19.44
		Muscle	14.00	9.72	21.08	17.66	15.98	12.36	26.11
Kasargod		Liver	89.02	36.99	52.53	55.36	69.74	80.70	40.00
	POM	Gill	7.14	46.58	32.32	35.71	17.59	0.00	25.00
		Muscle	3.84	16.44	15.15	8.93	12.67	19.30	22.50
		Liver	76.44	42.86	59.63	56.80	53.13	46.00	59.15
	PM	Gill	17.72	57.14	25.23	29.30	26.53	39.00	23.94
		Muscle	5.84	0.00	15.14	13.83	20.33	20.00	16.90
		Liver	60.75	56.00	59.46	49.01	56.18	60.00	96.30
	MON	Gill	21.91	42.86	27.93	38.42	24.86	37.04	3.70
		Muscle	17.34	0.00	12.61	12.44	18.96	12.96	0.00
NOTE: POM - post monsoon, PM - pre monsoon, M - monsoon									

7.3 Discussion

The concentration of metals in the tissues of flatfishes pooled from the study area indicated wide variation in its accumulation. Among the seven metals examined the essential elements, Zn and Cu irrespective of transects, contributed 90% to the total metals accumulated in the organs. However on a seasonal cumulative average, pattern of accumulation of different metals in the organs was in the decreasing order Zn > Cu >Ni > Cr > Pb > Cd > Hg. From the figures it is explicit that the accumulation of metals in the tissues was in the order liver > gill > muscle.

Zinc content in the tissues of flatfish showed wide fluctuations, ranged from 58.03 to 121.50, 24.15 to 69.61 and 8.67 to 39.89 μg g^{-1} wet weight for liver, gill and muscle respectively. No definite seasonal trend was noticed in tissues, except in muscles which showed high values in pre monsoon. In this study maximum concentration in liver and gill was reported at Cochin while in muscle it was at Calicut. It is generally believed that fish actively regulate zinc

concentrations in their muscle tissue and as a result they do not reflect to changes in ambient levels of this element in their environment (Phillips, 1980). High ranges (84.30- 120.16 µg g^{-1} wet weight) of zinc concentrations in the tissues of fishes have also been reported from relatively polluted areas of the world (Halcrow *et al.*, 1973; Eustace, 1974; Roth and Hornung, 1977; Plaskett and Potter, 1979), which in turn infers that fish body regulates zinc concentrations at an elevated level when exposed to high ambient zinc concentrations. Zn is an essential micronutrient in all marine organisms, and being a cofactor in nearly 300 enzymes its concentration is generally high in tissues. Therefore, marine animals are able to regulate tissue Zn at the concentrations in sea water and sediment from normal ambient levels to incipient lethal levels. The zinc concentration in different organs can be ordered as follows: liver > gill > muscle.

Copper being an essential trace nutrient, most marine organisms have evolved mechanisms to regulate concentrations of this metal in their tissues in the presence of variable concentrations in the ambient water, sediments, and food (Mohammed, 1991). Liver had accumulated the highest level of Cu, while the muscle had the lowest content. Copper levels, in the tissues of flat fishes ranged from 9.72 to 65.45, 3.34 to 22.01 and 1.31 to 11.15 µg g^{-1} wet weight for liver, gill and muscle respectively. The distribution pattern of Cu in the organs follows the order liver > gill > muscle. Liver had accumulated the highest level of Cu, while the muscle had the lowest content. The maximum mean concentration of Cu in liver was reported from Calicut followed by Cochin, while at other locations there was not much wide variation in the mean value. In muscle and gill maximum mean value was reported at Cochin followed by Calicut while at other transects it was comparable. It generally showed a definite seasonal trend in tissues with high values during pre monsoon and low value in monsoon. The maximum concentrations obtained at the aforementioned transects could be the availability of Cu from diverse source inputs and dietary intake.

Nickel (Ni) generally showed an erratic pattern in its distribution in tissues with high values in liver and gill in pre monsoon and in muscles in monsoon. Low values were observed in all the organs in post monsoon. Nickel concentrations in the liver, gill and muscle tissue ranged from 1.66 to 6.09, 0.75 to 3.45 and 0.21 to 2.37 $\mu g\ g^{-1}$ respectively. The order of accumulation in the organ was liver > gill > muscle. The maximum average concentration of Ni in the case of gill and liver was detected at Cochin, while the minimum average value for gill and liver was observed at Chettuva and Kasargod respectively. Nickel content in muscle was found high at Cochin in both pre monsoon and monsoon and at Ponnani in monsoon. Nickel content in this study is comparable with the reported content of BDL to 1.87 ($\mu g\ g^{-1}$ wet weight) for the tissue in smaller mussels and lower than those reported (6.06 to 13.92 $\mu g\ g^{-1}$ dry weight) for both pelagic and benthic fishes along the southwest coast of India (Geeta *et al.*, 2006, Rejomon *et al.*, 2010). The elevated nickel content in the fish at Cochin and Ponnani could be attributed to anthropogenic influence.

The distribution of Cr, in the liver, gill and muscle tissue ranged from 0.48 to 6.00, 0.76 to 3.61 and 0.03 to 1.19 $\mu g\ g^{-1}$ wet weight respectively. The order of accumulation in the organ was liver > gill > muscle. Liver, gill, kidneys and muscle tissues generally have been found to contain the highest Cr concentrations (Buhler *et al.*, 1977; Calamari *et al.*, 1982). The maximum average concentration of Cr in the organs of fish was detected at Cochin and Calicut in all three seasons, while for other transects it was comparable. The elevated Cr content in the fish at Cochin could be from the metal input from the broadly industrialized watershed and at Calicut could be attributed to the influence of effluents from ceramic industries in which Cr is a main constituent (Sadiq, 1992; Tenholder *et al.*, 1978; Van der Putte *et al.*, 1982). Evidence suggests that, Cr is not biomagnified (Holdway, 1988) in marine environment.

Lead levels, in the tissue of flatfish was detectable and ranged from 0.05 to 2.60, 0.04 to 3.70 and BDL to 0.44 $\mu g\ g^{-1}$ wet weight for liver, gill and muscle respectively. The maximum concentration in muscle and liver was reported at Ponnani, while in gill it was reported from Cochin. In general, the

accumulation of Pb in the organ was in the order liver > gill > muscle for all season. However exception was noted in the accumulation pattern in the organs, at Cochin, Pb showed the maximum accumulation in gill in post monsoon and pre monsoon followed by liver and also at Ponnani in monsoon. The high content of lead in gills is approved by the NRCC (1973), and the lower pH value at the gill surface due to the respired CO_2 may dissolve lead, changing it into a soluble form which could diffuse into the gill tissues. At the beginning of waterborne exposure metal concentrations in the gills rapidly increase, and then usually decline. After the end of exposure, metals are rapidly removed from the gills. The affinity of various metals to fish organs may differ. Lead deposits in liver, kidneys and spleen, digestive tract and gills are well documented (Barbara Jezierska and Malgorzata Witeska, 2006). Lead is introduced from many sources into aquatic environments, where it is rapidly incorporated into suspended and bottom sediments. This element is neither essential nor beneficial to living organisms and is responsible for a large number of adverse effects on biota (Eisler, 1988; Allert *et al.*, 2008). Similarly, levels of lead in fish from the study area were comparable for the values reported in the tissues of mussels which ranged between below detectable limit – 1.39 µg g^{-1} wet weight and slightly higher than those reported for pelagic and benthic fishes of a concentration of 0.23 µg g^{-1} to 0.56 µg g^{-1} dry weight along the southwest coast of India. Increased levels of Pb in the organs of flat fish was discerned at Cochin, Calicut and Ponnani, while at other transects (Chettuva and Kasargod) it was comparable. In the former transects, there are intense boat trafficking (mechanized boats) for fishing activities in addition to the inflow of untreated metal processing effluents from the hinterland leading to the increase in Pb value in the coastal milieu and thus bioavailable to the organism. Combustion of oil and gasoline alone accounts for 50% of all anthropogenic emissions of Pb into the environment (Sadiq, 1992). Luoma (1986) concluded that chemical form affects the biological availability of Pb to marine organism and sediment ingesting organisms was found to bioaccumulate more Pb than other organisms.

Cadmium is a serious environmental contaminant that is also transported atmospherically. In fish, it can cause anaemia and vertebral fractures, osmoregulatory problems, decreased digestive efficiency, haematological and biochemical effects, erratic swimming, and mortality (Burger *et al.*, 2002). Cadmium concentration, in the tissue of flatfish was detectable and ranged from 0.01 to 2.36, 0.01 to 0.69 and 0.01 to 0.17 $\mu g\ g^{-1}$ wet weight for liver, gill and muscle respectively. No definite seasonal trend was noted in its accumulation. The maximum concentration in the organs of the flatfish was reported at Cochin, while in other transects it was comparable. In general, the distribution pattern of cadmium in the tissues followed the descending order liver > gill > muscle for all seasons. The liver recorded the highest concentration of cadmium. This is in agreement with WHO–IPCS–Environmental Health Criteria (1987) for Cd which reported that Cd is stored in the body in various tissues, but the main site of accumulation in aquatic organisms is in the kidney and liver. However exception was noted in the accumulation pattern in the organ, at all transects in different seasons. Cadmium's ability to depurate from marine organism is rapid, once the organisms are moved to cleaner water has been reported elsewhere (Sadiq, 1992). The foregoing findings indicate that dynamics of metal concentrations in various organs during exposure and depuration may be different, could be the reasons for the variations in Cd affinity for particular tissues in the flatfish observed in this study. Similarly, levels of Cd in fish from five locations were much less than that has been reported in the tissues of pelagic and benthic fishes which ranged between 0.001 – 11.35, 0.001 – 15.75 and 0.001 – 3.78 $\mu g\ g^{-1}$ wet weight for liver, gill and muscles respectively along the southwest coast of India (Nair *et al.*, 2006). Increased levels of Cd in the organs of flatfish was discerned at Cochin, a plausible explanation could be the inflow of metal inputs from the heavily industrialized watershed leading to the increase in value in the coastal milieu and thus bioavailability to the organism.

Mercury accumulation in fish is affected by water chemistry (e.g. pH, temperature, turbidity), the chemical form of Hg in the environment and food-

chain structure (Zhou, 2000). Mercury, in the tissue of flatfish was detectable and ranged below detectable limit (BDL) to 0.39, BDL to 0.15 and BDL to 0.11 µg g^{-1} wet weight for liver, gill and muscle respectively. The maximum concentration was discerned at Cochin while at other transects the concentration was below 0.05 µg g^{-1} in the tissues. Highest metal concentrations were found in liver tissue, while the lowest were detected in gill and muscle. High metal concentration in the gills of fishes because of the element complexing with the mucus is documented (Karadede *et al.*, 2004). Pentreath (1976) on his experimental studies on the uptake, accumulation, and elimination of methyl mercury and inorganic Hg in two species of flatfish, concluded that inorganic Hg is taken up slowly from water but eliminated rapidly whereas the reverse is found true for organic Hg compounds in which there is rapid uptake through food. In this study the high accumulation of mercury in the tissues discerned at Cochin could be due to the heavy influence of both untreated domestic and industrial discharges in its coastal milieu.

As the collected fish from these regions were more of unequal size and weight the effect of these factors were also studied in order to ascertain whether this can result in varying accumulation of metals. Correlation study showed that the bioaccumualted metal was not influenced with the length and weight of the fish species. The metal levels in tissues represent a time – integrated response to bioavailable metal in the surrounding medium (Philips and Rainbow, 1988). The resulting bioaccumulation is influenced by numerous environmental and biological factors. Environmental factors involve salinity, temperature, dissolved oxygen, pH, dissolved organic carbon, food availability etc. and biological factors involves seasonal growth cycles, size, sex, sexual maturation, reproduction stages etc (Cossa, 1989; Kramer, 1994).

Seasonal variations of the studied metals did not indicate any consistent pattern, though Cu and Zn were found to make a trend in all the three seasons. Copper, generally showed a definite seasonal trend in tissues with high values in pre monsoon and low in monsoon, and Zn showed high values in muscles in monsoon. The maximum discrepancies were found for

the levels of Cr, Ni, Pb, Cd and Hg in the organs in different season among transects. The bioaccumulation of metals in any organism varies according to the bioavailability, the uptake rate, their threshold limit and physiological efficiency of the organism to excrete metals. Hence, the fish indicated different accumulation of metals in a given organ system at different transects. In this study, though the large variation between minimum and maximum values for the concentration of each metal indicates seasonal variation, as such a unique ranking order could not be figured. Metal concentrations in tissues of marine organisms vary enormously among individual species (Eisler, 1981). Irrespective of the region, from which the fishes were caught, generally the liver showed the highest concentration of any given metal. This is in agreement with the earlier studies made on bioaccumulation of metals in fishes (Ismail and Samin, 1987, Yousuf *et al.*, 2000; Nair *et al.*, 2006). High levels of metals in liver also indicate that most of the metals were accumulated in the fish in a fat soluble form (Qasim and Sengupta, 1988). Similiarly muscle tissue showed uniformly lowest values for metals. Comparatively low metal concentration in fish muscle is well documented (Kureishy *et al.*, 1983; Qasim and Sengupta, 1988; Ismail and Samin, 1987; Yousuf *et al.*, 2000; Nair *et al.*, 2006; Rejomon *et al.*, 2010). It is presumed that total volume of tissue is much higher compared to the organs and this leads to spreading of the accumulated metals resulting in low level of metal concentration in muscles. The bioaccumulation of different metals at higher levels in the liver of fish suggested that the metal accumulation was effective through the food chain rather than by direct contamination. For substantiating the above evaluation, tissue occupying capacity of metals (TSI) was determined for the flatfish collected from the study area. Liver contributed 44.10 - 65.36% of the total metal accumulated in the tissue, while gill and muscle contributed 21.39 – 35.80% and 8.95 – 34.93% respectively.

In general as per the metal pollution index (MPI), fishes from Cochin followed by Calicut indicated higher accumulation of metals than those collected from other transects in which the accumulation was comparable. This increase in bioaccumulation at Cochin and Calicut could be due to increase in metal input

from the broadly industrialized watershed and input of untreated urbanized sewage waste. The levels of metals in sediment matrix from Cochin and Calicut were observed to be higher compared to the values for other transects. Another plausible explanation for the increase of metals in the tissues of flatfish at these polluted transects could be due to their feeding type. Flatfish feeds mainly clams, worms, and crustaceans, including euphausiids (Mito, 1974; Smith *et al.*, 1978; Chuchukalo *et al.*, 1994; Pacunski *et al.*, 1998). They shift diet from mainly crustaceans to ophiuroids with increasing size (Mito, 1974; Smith *et al.*, 1978; Pacunski *et al.*, 1998). Their diet also varies greatly with sediment type (McConnaughey and Smith, 2000). This macro benthos might also have an insidious build up of metals in their tissues in the former mentioned polluted transects, which also can intensify the accumulation in the organs through food and feeding. The maximum accumulation in the two transects was discerned in pre monsoon. Similar increase in metal levels in tissues of some invertebrate and fish species were observed during the summer. These were related to the increased metabolism due to high temperatures (Alliot, 1990). By analyzing the specific tissues, of a region it is thus possible to deduce the bioavailability and, by presumption, the level of environmental pollution by specific metals. However, in the case of zinc and copper, their utility is limited to assessing bioavailability, since its self regulation by rapid depuration renders them less useful for long-term environmental monitoring programs for these two metals.

7.3.1 Hazard Level

There is a lively national discussion about the health benefits and risks from consumption of fish, mainly focused on recreational and subsistence fish. While the definition of subsistence is arguable generally, fish comprise an important part of the diet of the people living in the coastal region. Providing these people with information about contaminants in the fish that they consume are thus an important public health mandates. Exceeding certain values of metal concentration in fish can results in its lethal disturbances.

In most cases, fish from metal-contaminated water are safe for human consumption due to low metal accumulation (except for mercury) in the muscle

tissue. However, such fish may constitute a potential risk for predatory fishes, birds and mammals feeding on contaminated fish. Among the different metals analyzed, lead, cadmium and mercury are classified as toxic metals, which causes chemical hazards and therefore maximum residual levels have been prescribed for human consumption by various agencies of food standards (FAO, 1983; EC, 2001). The permissible level set by the FAO (1983) food standards for fish for Zn, Cu, Cd, Pb and Hg are 40.0, 30.0, 0.5, 0.5, 0.5 μg g^{-1} wet weight respectively. Levels of Zn, Cu, Cd and Hg were well below thresholds of concern at all transects. A comparison with the European food standards (EC, 2001), for fish (Pb: 0.4 μg g^{-1} and Cd: 0.10 μg g^{-1}), show that Cd was slightly above the acceptable limits for human consumption at Cochin in post monsoon. In all other transects it was well below the permissible limit.

Table 7.4 The estimated daily exposure of metals for adults expressed as % through the consumption of flatfish (*Cynoglossus macrostomus*) collected from the central and northern coast of Kerala.

Metal	Detected level in muscle (μg g^{-1} wet weight)	Permissible level (μg g^{-1} wet weight)	Consumption @ 100g of fish meat/day	Reference
Cu	1.31 - 11.15	30.0 (350 μg/day)	3.72 -31.86 %	FAO, 1983; EC, 2001
Pb	BDL - 0.44	0.5 (250 μg/day)	0 -17.60 %	EPA, 1980
Cr	0.14 - 1.21	200 μg/day	7.0 - 60.5 %	Institute of Medicine, 2001
Ni	0.21 -2.37	1.46 (146 μg/day)	1.44 - 16.23 %	EPA, 1980
Zn	8.67 - 29.89	40 (1500 μg/day)	5.78 - 26.59 %	EPA, 1980
Cd	BDL - 0.17	0.5 (60 μg/day)	0 -28.33 %	WHO, 1993
Hg	BDL - 0.10	0.5 (425 μg/day)	0 - 24 %	FAO- WHO, 1972

The dose of a certain metal ingested upon fish consumption, depends on the quantity of fish consumed. Based on a daily consumption of 100 g fish meal, the "permissible concentration", the intake and the risk imposed on humans was calculated and is given in Table 7.4. NRC (National Research Council, 1980) proposed the permissible daily dose of 2–3 mg of Cu for adults, or, in other words, 0.05 mg/kg body mass, which in case of a 70-kg weighing man equals to 3.5 mg. Copper concentration found in the fish originating from

the study area averaged 1.31 µg g^{-1} to 11.15 µg g^{-1}. Provided that a person consumes 100 g of the fish meat coming from the coastal region per day, his/her daily copper intake would not exceed the permitted values in the coastal transects because the concentration presumed to be ingested in this manner equals 3.72 % - 31.86 %.

FAO of the United Nations and WHO (1990) has established a provisional tolerable weekly intake (PTWI) of lead as 25 µg/kg body weight for humans, equaling 1,500 µg/g lead/week for a 60-kg person. Lead is a highly toxic element, released into the natural environment from different sources. Lead is a neurotoxin that causes behavioral deficits in vertebrates (Weber and Dingel, 1997) and can cause decreases in survival, growth rates, learning, and metabolism (Eisler, 1988; Burger and Gochfeld, 2000). Levels of 50 µg g-1 in the diet can cause reproductive effects in some predators (Eisler, 1988). In this study, the levels of lead in whole body of flat fish were well below the adverse effects level, suggesting that predators would not be adversely affected because of lead. Data on permissible Pb shares in the fish meat are indigent, but U.S. EPA (1980) proposed the daily dose of 250 µg. The average value encountered in the meat of the fish originating from this study areas, are between 0 – 0.44 mg/kg. That means that the consumption of 100 g of fish meat results in the intake of 0 % - 17.60% of the permitted dose, which is below the critical level.

According to the Institute of Medicine (2001), in case of an adult the recommended daily dietary allowance (RDA) for chromium equals to 200 µg. As per the results obtained in this study, chromium concentrations in the meat of the fish originating from the Kerala coast, range from 0.14 to 1.21 mg/kg. In case of a 100-g daily consumption, the intake of chromium equal to 14 -121 µg can be expected, which represents only 7% - 60.5 % of the permitted daily dose. Levels of 10 µg g^{-1} of chromium in the diets of birds and mammals are considered to cause adverse effects in some wildlife species (Eisler, 1986). Levels of chromium in flatfish were well below 10 µg g^{-1}, suggesting that predators or scavengers would not be at risk from chromium if they ate them in the wild.

Data on permissible nickel (Ni) shares in the fish meat as prescribed by U.S. EPA (1980), proposed the daily dose of 1.46 mg/kg. The average value encountered in the fish originating from the study area, was in the range 0.21 – 2.37 µg g^{-1}. That means that the consumption of 100 g of fish meat results in the intake of 1.44% - 16.23%of the permitted dose, which is far below the critical level.

Data on permissible Zinc shares in the fish meat are indigent, but U.S. EPA (1980) proposed the daily dose of 15 mg. The average value encountered in the meat of the fish originating from this study areas, are between 8.67 – 39.89 mg/kg. That means that the consumption of 100 g of fish meat results in the intake of 5.78% - 26.59% of the permitted dose, which is far below the critical level.

Cadmium levels in the muscle of flatfish from the five locations were well below the normal range (0. 5 µg g^{-1} wet weight) as prescribed by FAO (1983), but when compared with European guidelines (EC, 2001) which prescribe a concentration of 0.05 - 0.10 µg g^{-1} wet weight, it is slightly exceeded at Cochin in post monsoon. The PTWI of cadmium has been set at 7 µg/kg body weight (FAO-WHO, 1989), equaling to 420 µg cadmium/week for a 60-kg person. According to the 1988, JECFA (Joint Expert Committee on Food Additives) recommendation (WHO, 1993), cadmium intake of 0.42 mg/60 kg a week is safe for adults that means 0.06 mg a day. If we calculate the cadmium concentrations in the muscle of the flatfish originating from the Kerala coast, it was in the range BDL - 0.17 mg/kg, It can be concluded that daily consumption of 100 g fish caught in the coastal region leads to cadmium intake of 0.017 mg, which represents 28.33% of the permitted dose at Cochin while at other transects it represents less than 16.66%. It is obvious that these values are below the permitted ones. Birds may be less sensitive to cadmium in their diet than mammals but are adversely affected at levels of 1.0 µg g^{-1} (Eisler, 1985). There is some evidence that cadmium levels in some seabirds are high enough to cause kidney damage (AMAP, 2002). Thus, there may not be any cause for concern for top level avian predators that eat some of these fish, particularly if

they eat the liver of sole. In this study, the whole body average metal cadmium was between 0.05 μg g^{-1} to 0.81 μg g^{-1} which was below the normal estimated values.

The PTWI (permissible tolerable weekly intake) of mercury has been set at 5 μg/kg body weight (FAO-WHO, 1972), equaling 300 μg mercury/week for a 60-kg person. Mercury concentration in muscle was reported a maximum of 0.10 μg g^{-1}. That means that the consumption of 100 g of fish meat results in the intake of 24 % of the permitted dose, which is far below the critical level. Mercury concentrations of 5 μg g^{-1} (wet weight) in fish muscle can be associated with emaciation, decreased coordination, loss of appetite, and mortality in fish (Eisler,1987), while concentrations of 15 μg g^{-1} are required for adverse effects in predators that eat the fish (Spry and Wiener, 1991; Wiener and Spry, 1996). Sensitive birds that consume fish can exhibit effects at dietary mercury concentrations of 0.05–0.5 μg g^{-1} for sensitive mammals, harmful effects occur at dietary levels of 1.10 μg g^{-1} (Eisler, 1987; WHO, 1990; 1991). In this study, mercury levels in muscle reported a maximum 0.10 μg g^{-1}, suggesting that sensitive species may not be affected, although seabirds are generally less sensitive to high levels than other birds.

On the basis of the recommended daily dietary allowances (RDA) for safe consumption of the fish muscle, the allowed intake was regulated at 50-350 mg of metal per 100 g serving of the muscle (National Research Council, 1980). From the results of this report, the examined fish were not associated with vulnerable metal content in their muscle and were safe within the limits for human consumption.

7.4 Conclusion

Based on the results obtained regarding the levels of metal in fish, wide variation was conspicuous for metals like Ni, Cr, Pb, Cd and Hg in the tissues. The studied metals did not show any consistent trend in its accumulation in tissues, except Cu and Zn which were found to make a trend in all the three seasons. On a seasonal cumulative average, accumulation of metals in the

organs was in the decreasing order Zn > Cu > Ni > Cr > Pb > Cd > Hg. Zinc and Copper being essential trace elements their concentration in tissues was high. The accumulation of metals in the tissues was in the order liver > gill > muscle. Relatively high accumulation of metals was observed in the tissues of flatfish pooled from the heavily urbanized regions like Cochin followed by Calicut, while at other transects the level was comparable. The maximum accumulation of metals in the organs of aforementioned urbanized regions was discerned in pre monsoon. The concentration of metals in specific tissues especially in polluted region, can thus give possible evidence of environmental pollution by specific metals at a given site as such it can prove useful as a biological indicator for the examined metals (except Zn and Cu). The levels of toxic metals are within the safe limits prescribed by various agencies; however Cd was slightly exceeded in the muscles of flatfish pooled from Cochin region which is a cause of concern.

Chapter 8

TROPHIC LINK OF HEAVY METALS IN A BENTHIC FOOD CHAIN

8.1	Introduction
8.2	Data analysis
8.3	Results
8.4	Discussion
8.5	Conclusion

8.1 Introduction

There has been an increasing interest in the trophic transfer of metal contaminants in aquatic invertebrates to its predators (Fisher and Reinfelder, 1995; Reinfelder *et al.*, 1998; Wang and Fisher, 1999) among the ecologists and environmentalists to understand the effects of heavy metals in food web dynamics. These studies have demonstrated that uptake from ingested food can be a significant source for metal uptake in marine invertebrates, especially for animals having a high feeding activity or for metals having a high concentration in food particles. The importance of trophic transfer in the bioaccumulation of several metals, including methyl mercury (CH_3Hg) and Se, in fish is well recognized (Riisgard and Hansen, 1990; Fisher and Reinfelder, 1995; Wiener and Spry, 1996). Although other metals such as Ag, Al, Cd, CO, Cu, Pb, Mn, Ni and Zn are not considered to biomagnify in fish (Amiard *et al.*, 1980; Douben, 1989), their occurrences in contaminated environments and potential toxicity to aquatic life may present an environmental hazard. Interest in metals bioaccumulation originates from concerns regarding the direct impact of metals on organisms accumulating the metal and indirect impacts on their consumers (i.e., trophic transfer). Fish may be exposed to metals via different pathways, including ingestion of prey or sediments and/ or uptake from the water column via gills. Metal may affect fish directly via acute toxicity or indirectly, by reducing conditions and/ or reproductive output thus potentially altering population dynamics (Heath, 1995) and consequently humans can be affected through the food chain.

This chapter deals with the metal concentrations in sediments, their bioaccumulation in the polychaetes, which is found to be one of the major selective food item consumed by the flatfish, *C. macrostomus* along the central and northern coast of Kerala, southwest of India. The specific aim is to determine whether any link exist for heavy metal concentrations in flatfish with those of polychaetes and sediment metal concentration through food and feeding and risk of trophic transfer (biotransference).

8.2 Data analysis

The question of whether trace elements increase their levels as a function of the trophic level is still a matter of debate (Barwick and Maher, 2003). Bioaccumulation of one metal M (or other substance) is the process that causes an increased concentration of M in an aquatic organism compared to that in surrounding matrix (water/sediment), due to uptake by all exposure routes (dietary absorption, transport across respiratory surfaces, and dermal absorption). Biotransference is the transfer of metals from a food source to consumer while biomagnification is when an increase in metal concentration occurs through at least two trophic levels in a food chain (Barwick and Maher, 2003). Obviously, if the biomagnification of metals is occurring, elevated metal concentrations in higher trophic groups of organisms could pose a threat to organisms themselves or to human consumers. The common approach in biomagnification studies includes the use of whole-body tissues in invertebrates (Gray, 2002); in larger organisms, muscle is commonly used. In fish, muscle tissues were used for analysis, as this is considered to represent the stable pool of trace metals for these organisms (Barwick and Maher, 2003). In this study only one trophic link is studied (polychaetes - flatfish) as such biotransference is considered.

In order to understand the metal dynamics of the present benthic food chain (sediment - polychaetes – flatfish), in addition to food and feeding, its various exposure pathways were also assessed. Flatfish, being the top consumer in the trophic level of the present benthic food chain pyramid, its dietary items was specially studied by means of gut content analysis. The degree of metal accumulation in the flatfish major dietary items (polychaete worms) with respect to the surrounding environment (sediment and overlying water) was also determined. Simple linear regression analyses were used to investigate the relationships between

a) metal concentrations in flatfish and (i) polychaetes and (ii) bottom water

b) metal concentrations in flatfish and (i) polychaetes and (ii) sediment.

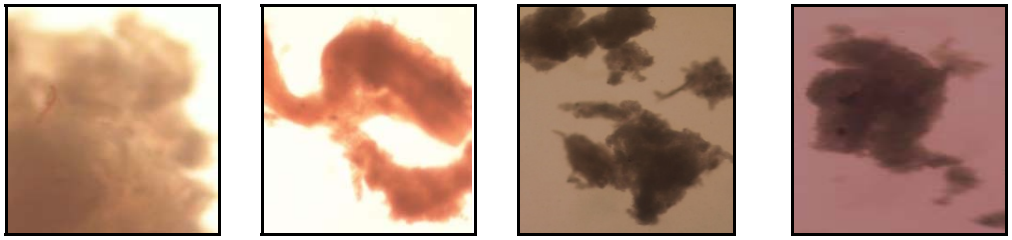
Data that did not meet homogeneity of variance and normality were $\log_e$ transformed.

8.3 Results

8.3.1 Gut Content Analysis of Flatfish (*Cyanoglossus macrostomus*)

The Malabar sole, *Cynoglossus macrostomus* is an important constituent of the fishery along the Malabar and South Kanara coasts. It is highly territorial, marine, benthopelagic and non-migratory. Inhabits shallow muddy and sandy bottoms of the continental shelf, down to 25 m and found in midwaters in certain seasons of the year. It feeds mainly on benthic invertebrates, especially worms (Menon, 1984; http://www.fishbase.us/summary/Cynoglossus-macrostomus.html).

Gut content analysis inferred that the major contents of flatfish diet was dominated by semi digested matter, semi digested polychaetes and polychaetes (Table 8.1, Fig. 8A). This was followed by molluscs and its shell remains. From these observations, the carnivorous feeding habit of this benthic fish is explicit. The presence of plant and animal matter in the gut content analysis concluded that this fish also prefers detritus as a food item from its habitat. Earlier literature in this aspect corroborates the flatfish, Malabar Sole (*C. macrostomus*) under carnivorous/detritivorous feeding habit (Menon, 1984). This finds importance in the metal accumulation study through its food and feeding habits. This also opens a wide scope of research in the field of metal toxicity risk to human, by the consumption of these commercially demanded flatfish in the Indian and foreign market.



Semi digested Polychaete | **Polychaetes** | **Semi digested matter** | **Miscellaneous items**

Figure 8A. Gut contents in magnified view

Table 8.1 Diet content of flatfish (*C. macrostomus*) pooled along the central and northern coast of Kerala.

Cochin					
Season	**Food item**	**% occurrence**	**ABL (cm)**	**ABW (g)**	**Gut content biomass (mL)**
Post monsoon	Bivalve molluscs	17.4	12.37 - 18.53	12.20 - 33.36	1.09 (n = 22)
	Molluscan shell pieces	6.05			
	Semidigested polychaetes	69.17			
	Miscellaneous items	7.38			
Pre monsoon	Crustacean appendage	19.44	21.97 - 23.42	41.80 - 46.77	1.23 (n = 30)
	Molluscan shell pieces	18.46			
	Polychaetes	23.54			
	Semidigested matter	19.33			
	Molluscs	11.03			
	Miscellaneous items	8.2			
Monsoon	Semidigested matter	64.12	12.38	10.97	0.68 (n = 25)
	Semidigested polychaetes	8.07			
	Miscellaneous items	14.21			
	Squilla trunk	0.44			
	Animal matter	13.16			

Note: ABL- Average Body Length; ABW- Average Body Weight; n - no. of fish species

Chettuva					
Season	**Food item**	**% occurrence**	**ABL (cm)**	**ABW (g)**	**Gut content biomass (mL)**
Post monsoon	Animal matter	39.66	18.8	32.55	1.00 (n = 20)
	Molluscan shell pieces	19.03			
	Semidigested polychaetes	35.5			
	Miscellaneous items	5.81			
Pre monsoon	Crustacean appendage	4.23	31.68	202.07	1.44 (n = 18)
	Molluscan shell pieces	37.54			
	Polychaetes	43.14			
	Semidigested matter	13.02			
	Miscellaneous items	2.07			
Monsoon	Semidigested matter	60.84	31.47	201.97	1.08 (n = 22)
	Semidigested polychaetes	33.02			
	Miscellaneous items	6.14			

Note: ABL- Average Body Length; ABW- Average Body Weight; n - no. of fish species

Ponnani					
Season	**Food item**	**% occurrence**	**ABL (cm)**	**ABW (g)**	**Gut content biomass (mL)**
Post monsoon	Animal matter	37.44	16.95	28.68	1.00 (n = 22)
	Molluscan shell pieces	16.03			
	Semidigested polychaetes	41.44			
	Miscellaneous items	5.09			
Pre monsoon	Crustacean appendage	12.28	23.9	102.19	0.95 (n = 25)
	Molluscan shell pieces	29.54			
	Polychaetes	51.74			
	Semidigested matter	2.06			
	Molluscs	1.97			
	Miscellaneous items	2.41			
Monsoon	Semidigested matter	45.21	16.77	30.7	0.85 (n = 20)
	Semidigested polychaetes	34.28			
	Miscellaneous items	12.66			
	Plant matter	2.81			
	Animal matter	5.04			

Note: ABL- Average Body Length; ABW- Average Body Weight; n - no. of fish species

Calicut					
Season	**Food item**	**% occurrence**	**ABL (cm)**	**ABW (g)**	**Gut content biomass (mL)**
Post monsoon	Semidigested items	37.79	31.31	202.23	1.00 (n = 30)
	Molluscan shell pieces	19.04			
	Semidigested polychaetes	41.06			
	Miscellaneous items	2.11			
Pre monsoon	Crustacean appendage	18.14	31.89	202.59	1.20 (n = 30)
	Polychaetes	37.11			
	Semidigested matter	40.36			
	Animal matter	2.31			
	Miscellaneous items	2.08			
Monsoon	Semidigested matter	58.06	31.56	202.35	1.05 (n = 30)
	Semidigested polychaetes	33.89			
	Miscellaneous items	7.17			
	Animal matter	0.88			

Note: ABL- Average Body Length; ABW- Average Body Weight; n - no. of fish species

Kasargod					
Season	**Food item**	**% occurrence**	**ABL (cm)**	**ABW (g)**	**Gut content biomass (mL)**
Post monsoon	Fish head remains	2.39	16.7	27.4	0.85 (n = 30)
	Molluscan shell pieces	22.03			
	Semidigested polychaetes	62.04			
	Miscellaneous items	13.54			
Pre monsoon	Crustacean appendage	11.09	16.86	29.8	1.25 (n = 25)
	Molluscan shell pieces	24.79			
	Semidigested polychaetes	52.03			
	Semidigested matter	4.96			
	Plant matter	4.26			
	Miscellaneous items	2.87			
Monsoon	Semidigested matter	81.59	16.5 - 23.5	31.6 - 102	0.90 (n = 30)
	Miscellaneous items	16.08			
	Animal matter	2.33			

Note: ABL- Average Body Length; ABW- Average Body Weight; n - no. of fish species

8.3.2 Dissolved Metals in Bottom water

The overlying surface water is another potentially important metal exposure pathway for many sediment dwelling biotic communities. Mean concentration of dissolved metals in the bottom water at each transects is presented in Table 8.2. The mean concentration for dissolved metals in bottom water along the study area varied in the range Cu : 3.10 – 9.85 µg l^{-1}, Pb : below detectable limit (BDL) – 4.52 µg l^{-1}, Cr : BDL, Ni : BDL – 14.64 µg l^{-1}, Zn : 2.93 – 29.80 µg l^{-1}, Cd : BDL – 4.72 µg l^{-1} and Hg : 0.01 – 0.18 µg l^{-1}. A concentration of 10 µg l^{-1} for Cu, 10 µg l^{-1} for Pb, 50 µg l^{-1} for Cr, 2 µg l^{-1} for Ni, 20 µg l^{-1} for Zn, 10 µg l^{-1} for Cd, 0.10 µg l^{-1} for Hg represents minimal risk of deleterious effect (WQC, 1972). Results of this study were compared with the aforementioned metals limit for water quality criteria for ecotoxicological risk on marine organisms. It envisaged Ni and Hg having high chances for bioaccumulation at the polluted transect Cochin and Calicut. Ni tend to exceed the limit prescribed for water quality at Cochin and Calicut throughout the season, while in monsoon it will tend to have an impact/ ecotoxicological risks

on the benthic species at Chettuva and Kasargod. In the case of Hg, it tend to have an impact on the benthic species at the polluted transects Cochin and Calicut in post monsoon and Chettuva in monsoon. Zinc will have an impact on the benthic species at Ponnani and Kasargod in monsoon.

Results of Pearson's correlation of dissolved metal concentration, flatfish tissue and polychaetes is presented in Table 8.3. Significant positive correlation was discerned between dissolved lead in water and polychates and dissolved mercury in water with Hg in flatfish muscle.

Table 8.2 Mean concentration of dissolved metals (µg l^{-1}) in bottom water along the central and northern coast of Kerala.

		Heavy Metals						
Transect	Season	Cu	Pb	Cr	Ni	Zn	Cd	Hg
	POM	6.30	4.52	BDL	5.60	5.61	1.87	0.18
Cochin	PM	6.00	3.11	BDL	8.69	6.24	3.57	0.03
	M	4.48	BDL	BDL	2.99	18.55	0.80	0.09
	POM	3.75	2.05	BDL	3.74	2.93	1.94	0.10
Chettuva	PM	6.31	2.27	BDL	14.64	4.16	4.72	0.10
	M	4.08	BDL	BDL	BDL	18.69	0.17	0.11
	POM	3.10	1.60	BDL	BDL	3.57	BDL	0.03
Ponnani	PM	4.80	1.81	BDL	1.65	3.63	0.40	0.01
	M	9.85	0.37	BDL	BDL	29.80	2.67	0.02
	POM	3.65	2.66	BDL	11.36	6.19	0.03	0.15
Calicut	PM	3.17	2.39	BDL	3.32	6.97	3.00	0.02
	M	4.17	BDL	BDL	3.57	16.63	2.47	0.03
	POM	3.70	2.12	BDL	9.49	5.57	0.17	0.03
Kasargod	PM	4.67	2.09	BDL	3.69	4.71	2.82	0.09
	M	9.03	BDL	BDL	BDL	23.72	4.20	0.02

NOTE: POM - post monsoon, PM - pre monsoon, M - monsoon, BDL- below detectable limit

Table 8.3 Results of Pearson correlation coefficient among metal concentration in flatfish muscle, polychaete sp. and bottom water.

	WCu	WPb	WCr	WNi	WZn	WCd	WHg	PCu	PPb	PCr	PNi	PZn	PCd	PHg	FCu	FPb	FCr	FNi	FZn	FCd	FHg
WCu	1																				
WPb	-0.184	1																			
WCr	.530(*)	-0.342	1																		
WNi	-0.145	.557(*)	-0.279	1																	
WZn	.693(**)	-.664(**)	.826(**)	-0.472	1																
WCd	.580(*)	0.048	0.395	0.197	0.324	1															
WHg	-0.152	0.424	-0.245	0.37	-0.288	-0.169	1														
PCu	-0.313	.688(**)	-0.336	0.295	-.566(*)	0.161	-0.093	1													
PPb	-0.314	**.558(*)**	-0.325	0.292	-0.47	-0.017	0.01	.703(**)	1												
PCr	-0.045	-0.206	-0.14	-0.075	0.152	-0.216	0.222	-0.293	0.185	1											
PNi	-0.161	.538(*)	-0.231	0.162	-0.398	0.2	-0.032	.644(**)	.775(**)	-0.095	1										
PZn	-0.078	.534(*)	-0.266	0.333	-0.475	0.391	-0.125	.832(**)	.596(*)	-0.426	.584(*)	1									
PCd	-0.107	.546(*)	-0.214	0.236	-0.355	0.219	-0.131	.790(**)	.892(**)	-0.06	.871(**)	.769(**)	1								
PHg	0.032	-0.063	-0.011	-0.092	0.125	-0.044	0.203	-0.14	0.305	.759(**)	0.098	-0.161	0.167	1							
FCu	0.086	-0.002	-0.154	0.246	-0.044	.550(*)	-0.115	0.348	0.215	-0.022	0.234	.579(*)	0.431	0.041	1						
FPb	-0.086	0.29	-0.39	0.063	-0.272	-0.027	-0.216	0.428	.692(**)	0.481	.600(*)	0.329	.704(**)	0.451	0.309	1					
FCr	-0.368	.617(*)	-0.265	0.33	-0.403	-0.133	0.412	0.442	.645(**)	0.398	0.488	0.153	0.472	0.143	0.026	0.508	1				
FNi	0.382	-0.246	-0.161	-0.057	0.207	0.208	-0.261	0.063	0.273	0.446	0.121	0.153	0.251	0.297	0.234	0.444	-0.033	1			
FZn	0.085	0.055	-0.069	0.138	-0.087	.636(*)	-0.302	.553(*)	0.422	-0.176	0.496	.778(**)	.621(*)	0.085	.796(**)	0.302	-0.082	0.396	1		
FCd	-0.079	.599(*)	-0.223	0.182	-0.283	-0.142	0.455	0.36	.730(**)	0.471	0.465	0.21	.568(*)	.621(*)	-0.082	.562(*)	.663(**)	0.175	-0.014	1	
FHg	0.098	0.287	-0.173	-0.088	-0.037	-0.187	**.562(*)**	-0.105	0.189	.517(*)	0.154	-0.262	0.086	.715(**)	-0.201	0.28	0.281	0.021	-0.26	.722(**)	1

Note:- *Correlation significant atp $<$ 0.05 (two-tailed). **Correlation is significant atp $<$ 0.01 (two-tailed);W: bottom water metal concentration;P#: Polychaete sp. metal concentration; F: Flatfish muscle metal concentration

8.3.3 Sediment Characteristics and Heavy Metals in Surficial Sediment

Sediment composition (sand, silt and clay) was not significantly varied among sites seasonally (Table 8.4). Silt was discerned the dominant fraction (33.31 – 70.62%) followed by clay (10.95% -50.11%) and sand (1.19% - 28.85%). The mean concentration for heavy metals (Table 8.4) in surficial sediment along the study area varied in the range Cu : 19.10 – 69.96 µg g^{-1}, Pb : 12.76 – 41.25 µg g^{-1}, Cr : 37.71 – 283.42 µg g^{-1}, Ni : 28.10 – 121.25 µg g^{-1}, Zn : 42.18 – 148.13 µg g^{-1}, Cd : 0.20 – 2.80 µg g^{-1} and Hg : 0.08 – 0.56 µg g^{-1}. The concentrations of Cu, Cr, Hg in sediments at all transects exceeds the lower sediment quality guideline values (Long *et al.*, 1995), with Ni greater than the higher sediment quality guideline value mostly in monsoon . It is expected that Cu, Cr, Hg can increase the incidence of adverse negative effects on living resources from rare to occasional in the study area. In monsoon, nickel concentrations was observed to be above the ERM value and will represent a probable-effects range within which effects would frequently occur in benthic organisms (Long *et al.*, 1995). At Cochin in addition to the aforementioned metals, Cd concentration in sediments exceeded the lower sediment quality guideline, which is expected to increase the incidence of adverse negative effects on living resources from rare to occasional in the benthic species thriving in this region.

Table 8.4 Mean heavy metal concentration (µg g^{-1} dry weight) and general characteristics of sediments along the central and northern coast of Kerala.

Heavy Metal	Season	Transect					Sediment quality guidelines	
		Cochin	Chettuva	Ponnani	Calicut	Kasargod	ERL	ERM
Cu	POM	27.60	19.10	**45.67**	23.60	21.56	34	270
	PM	**63.21**	**35.00**	**69.96**	**49.52**	40.89		
	Mon	**48.44**	27.50	**45.10**	**39.68**	30.76		
Pb	POM	24.21	14.20	12.76	20.00	18.44	47	218
	PM	36.18	21.15	22.11	28.41	21.56		
	Mon	41.25	28.50	25.50	34.70	21.09		
Cr	POM	**125.57**	**102.30**	37.71	**141.50**	**84.56**	81	370
	PM	**107.40**	**81.92**	**135.96**	**123.30**	**85.76**		
	Mon	**216.45**	**142.30**	**209.50**	**283.42**	**163.50**		
Ni	POM	**52.36**	**31.22**	**38.14**	**47.28**	**28.10**	21	52
	PM	**47.65**	**32.70**	***64.02***	**46.23**	**35.40**		
	Mon	***121.25***	***61.35***	***120.60***	*90.78*	*77.40*		
Zn	POM	75.44	59.70	95.50	61.42	48.78	150	410
	PM	131.41	91.50	110.00	109.50	84.90		
	Mon	148.13	94.75	88.20	66.80	42.18		
Cd	POM	**1.15**	0.24	0.49	0.57	0.20	1.2	9.6
	PM	**2.80**	0.66	0.42	1.12	0.56		
	Mon	**1.90**	0.18	0.41	0.74	0.47		
Hg	POM	**0.56**	0.08	0.13	0.26	0.19	0.15	0.71
	PM	**0.35**	0.11	0.17	0.21	0.25		
	Mon	**0.48**	0.13	0.25	0.28	0.19		
Sediment Characteristics*								
Sand (%)	POM	12.53	7.20	3.88	18.43	13.33		
	PM	28.85	14.66	7.05	19.91	5.96		
	Mon	1.19	19.92	12.56	10.96	5.44		
Silt (%)	POM	46.24	47.99	63.30	70.62	57.25		
	PM	48.11	40.98	52.00	60.01	62.22		
	Mon	50.27	33.31	36.51	48.42	44.35		
Clay (%)	POM	41.24	44.82	32.81	10.95	29.43		
	PM	23.05	44.33	40.95	20.09	31.82		
	Mon	48.55	46.78	50.92	41.10	50.11		
Organic Matter (%)	POM	6.77	4.97	3.61	3.69	4.79		
	PM	4.74	4.16	4.49	2.57	2.60		
	Mon	6.30	4.10	3.78	3.02	2.73		

Note: ERL: Sediment quality guideline value below which there is low probability of biological effect(Long et al., 1995). Values shown in bold exceed this guideline value

ERM : Sediment quality guideline value above which there is high probability of biological effect (Long et al., 1995). Values shown in bold italics exceed this guideline value.

*Sediment fractions and organic matter were measured as a proportion of total dry sediment weight.

POM - post monsoon, PM - pre monsoon, M – monsoon.

8.3.4 Heavy Metal Concentration in Polychaetes and Flatfish

Heavy metal concentration in polychaetes pooled along the study area showed detectable levels in their tissues (Table 8.5). The mean concentration of heavy metals in this major dietary item of flatfish were found to in the range Cu : 2.21 – 29.26 µg g^{-1}, Pb : 0.14 – 4.92 µg g^{-1}, Cr : 0.23 – 13.24 µg g^{-1}, Ni : 0.16 – 2.61 µg g^{-1}, Zn : 14.40 – 68.60 µg g^{-1}, Cd : 0.10 – 2.18 µg g^{-1} and Hg : 0.08 – 0.46 µg g^{-1}.

Table 8.5 Mean metal concentrations (µg g^{-1} dry weight) in flatfish major dietary item (polychaetes) along the central and northern coast of Kerala.

		Heavy Metals						
Transect	**Season**	**Cu**	**Pb**	**Cr**	**Ni**	**Zn**	**Cd**	**Hg**
	POM	24.64	4.92	3.10	2.61	68.60	2.18	0.22
Cochin	PM	5.40	2.48	12.72	0.56	18.80	0.41	0.46
	M	14.24	2.40	8.76	1.02	29.60	0.76	0.36
	POM	10.08	1.14	0.23	0.33	52.60	0.32	0.08
Chettuva	PM	3.20	0.16	2.28	0.21	16.87	0.11	0.10
	M	8.07	1.13	2.24	1.69	19.28	0.29	0.09
	POM	14.62	1.83	0.91	0.97	53.90	0.86	0.16
Ponnani	PM	5.20	0.28	6.56	0.28	20.13	0.12	0.10
	M	10.86	2.59	4.36	0.52	26.80	0.37	0.11
	POM	29.26	3.32	3.82	1.46	58.20	1.31	0.12
Calicut	PM	4.40	1.06	13.24	0.42	16.78	0.27	0.32
	M	12.80	2.60	9.22	0.68	28.60	0.58	0.12
	POM	20.21	0.84	0.31	0.48	55.00	0.38	0.11
Kasargod	PM	2.21	0.14	2.64	0.20	14.72	0.11	0.17
	M	12.40	0.80	1.80	0.16	14.40	0.10	0.10

NOTE: POM - post monsoon, PM - pre monsoon, M - monsoon

The range of metal concentrations in muscle (µg g^{-1} dry weight) of flatfish pooled along the study area were as follows Cu: 2.37 – 6.99 µg g^{-1} ; Pb: BDL – 1.26 µg g^{-1} ; Cr: 0.12 – 1.20 µg g^{-1} ; Ni: 1.08 – 9.75 µg g^{-1} ; Zn: 13.48 – 40.16 µg g^{-1} ; Cd: 0.12 – 1.07 µg g^{-1} ; Hg, 0.01 – 0.43 µg g^{-1} (Table 8.6).

Table 8.6 Mean metal concentrations (µg g^{-1} dry weight) in muscle of flatfish (*C. macrostomus*) pooled along the central and northern coast of Kerala.

		Heavy Metals							Metal Pollution Index
Transect	Season	Cu	Pb	Cr	Ni	Zn	Cd	Hg	(MPI)
	POM	3.97	0.81	0.97	1.68	17.20	1.07	0.43	1.7
Cochin	PM	5.68	1.26	0.71	7.23	39.57	0.78	0.13	2.04
	M	4.35	0.55	0.22	7.80	30.01	0.61	0.16	1.52
	POM	3.28	0.30	0.57	1.31	22.30	0.15	0.13	0.85
Chettuva	PM	6.72	0.10	0.21	3.05	34.80	0.12	0.01	0.57
	M	5.12	0.10	0.17	1.08	19.51	0.15	0.14	0.63
	POM	2.37	0.45	0.61	3.17	15.81	0.48	0.06	0.99
Ponnani	PM	4.99	0.80	0.17	2.73	29.60	0.25	0.05	0.9
	M	4.58	0.66	0.15	9.75	23.66	0.16	0.12	1.1
	POM	4.05	0.59	1.20	4.78	17.10	0.59	0.07	1.38
Calicut	PM	6.99	0.83	0.88	3.95	40.16	0.35	0.05	1.46
	M	5.73	1.07	0.57	5.00	26.20	0.26	0.10	1.42
	POM	2.85	0.36	0.23	1.55	13.48	0.16	0.09	0.68
Kasargod	PM	4.34	0.11	0.17	4.63	32.08	0.25	0.05	0.76
	M	3.86	BDL	0.12	2.52	23.56	0.14	0.05	0.78

NOTE: POM - post monsoon, PM - pre monsoon, M - monsoon, BDL- below detectable limit

Inorder to evaluate the metal dynamics or to understand the process of bioaccumulation in the study area, the concentration of heavy metals have been compared between areas that are polluted to areas that are less polluted by an evaluation based on Metal Pollution Index (MPI) which signifies greater availability of metals for accumulation from the environment. Each transect of the study area was categorized as polluted (MPI >1) and less polluted (MPI < 1) zones based on the MPI tabulated (Table 8.6). Flatfish pooled from Cochin, Calicut in all seasons and Ponnani in monsoon contained the highest metal concentration in tissue, relative to flatfish from Chettuva and Kasargod region. Correlation between heavy metals in sediment, polychate sp. (major prey item of flatfish) and in muscle of flatfish was determined for both polluted and less polluted transect (Table 8.7, Table 8.8). Metals like Cr, Cd, in sediment showed positive correlation with those accumulated in polychaetes in the polluted transect. Significant correlation was also obtained for Hg in sediments and with those in polychaetes and flatfish. In the less polluted transects, Pb in

the polychaetes was positively correlated with those in flatfish and significant positive correlations was obtained for Zn in polychaetes and those in flatfish.

Table 8.7 Significant relationships between metal concentrations in flatfish muscle tissue, and their dietary items (polychaetes) and with sediment (N =7) in polluted transect.

	S# Cu	**P# Cu**	**F#Cu**
S#Cu	1	0.37	0.596
P#Cu	0.37	1	0.614
	S# Pb	P# Pb	F#Pb
S#Pb	1	0.238	0.331
P#Pb	0.238	1	0.449
	S# Cr	P# Cr	F#Cr
S#Cr	1	**0.763(*)**	-0.619
P#Cr	**0.763(*)**	1	-0.227
	S# Ni	P# Ni	F#Ni
S#Ni	1	-0.694	0.699
P#Ni	-0.653	1	-0.119
	S# Zn	P# Zn	F#Zn
S#Zn	1	0.399	0.699
P#Zn	-0.694	1	0.685
	S# Cd	P# Cd	F#Cd
S#Cd	1	**0.772(*)**	0.508
P#Cd	**0.772(*)**	1	0.424
	S# Hg	P# Hg	F#Hg
S#Hg	1	**0.816(*)**	**0.960(**)**
P#Hg	**0.816(*)**	1	0.703

* Correlation significant at $p < 0.05$ (two-tailed). ** Correlation is significant at $p < 0.01$ (two-tailed).
S#: Sediment metal concentration; P#: Polychaetes metal concentration;
F#: Flatfish muscle metal concentration

Table 8.8 Significant relationships between metal concentrations in flatfish muscle tissue, and their dietary items (polychaetes) and with sediment (N =8) in unpolluted transect.

	S# Cu	P# Cu	F#Cu
S#Cu	1	0.463	0.225
P#Cu	0.463	1	-0.023
	S# Pb	P# Pb	F#Pb
S#Pb	1	-0.641	-0.069
P#Pb	-0.641	1	**0.722(*)**
	S# Cr	P# Cr	F#Cr
S#Cr	1	-0.195	-0.661
P#Cr	-0.195	1	0.632
	S# Ni	P# Ni	F#Ni
S#Ni	1	0.664	-0.115
P#Ni	0.214	1	-0.164
	S# Zn	P# Zn	F#Zn
S#Zn	1	0.664	0.387
P#Zn	0.664	1	**0.848(**)**
	S# Cd	P# Cd	F#Cd
S#Cd	1	0.34	0.244
P#Cd	0.34	1	0.375
	S# Hg	P# Hg	F#Hg
S#Hg	1	0.45	-0.328
P#Hg	0.45	1	-0.258

*Correlation significant at $p < 0.05$ (two-tailed). **Correlation is significant at $p < 0.01$ (two-tailed).

S#: Sediment metal concentration; P#: Polychaetes metal concentration;

F# Flatfish muscle metal concentration

8.3.5 Biotransference of Heavy Metals

Biotransference is the transfer of metals from a food source to consumer while biomagnification is the increase in metal concentration occuring through at least two trophic levels in a food chain (Barwick and Maher, 2003). In this study only one trophic link is studied (polychaetes - flatfish) as such biotransference is considered. In order to have an idea of the degree of metal accumulation in the analyzed species with respect to the surrounding environment, the concentration factor was calculated according to the following formula (Szefer, 1998): $CF = C_1/C_2$, where C_1 represents the average concentration of the metal of interest in biota and C_2 is the average concentration of the element in the surrounding surficial sediment and is presented in Table 8.9.

Table 8.9 Concentration factor (CF) and Biotransference factor (TF) of heavy metals in benthic components (sediment –polychaetes- flatfish muscle) of the study area.

Metals	Season	Cochin		Chettuva		Ponnani		Calicut		Kasargod	
		CF	TF	CF	TF	CF	TF	CF	TF	CF	TF
Cu	POM	0.89	0.16	0.53	0.33	0.32	0.16	1.24	0.14	0.94	0.14
	PM	0.09	1.05	0.09	2.10	0.07	0.96	0.09	1.59	0.05	1.96
	Mon	0.29	0.31	0.29	0.63	0.24	0.42	0.32	0.45	0.40	0.31
Pb	POM	0.20	0.16	0.08	0.26	0.14	0.25	0.17	0.18	0.05	0.43
	PM	0.07	0.51	0.01	0.63	0.01	2.86	0.04	0.78	0.01	0.79
	Mon	0.06	0.23	0.04	0.09	0.10	0.25	0.07	0.41	0.04	0.00
Cr	POM	0.02	0.31	0.00	2.48	0.02	0.67	0.03	0.31	0.00	0.74
	PM	0.12	0.06	0.03	0.09	0.05	0.03	0.11	0.07	0.03	0.06
	Mon	0.04	0.03	0.02	0.08	0.02	0.03	0.03	0.06	0.01	0.07
Ni	POM	0.05	0.64	0.01	3.97	0.03	3.27	0.03	3.27	0.02	3.23
	PM	0.01	12.91	0.01	14.52	0.00	9.75	0.01	9.40	0.01	23.15
	Mon	0.01	7.65	0.03	0.64	0.00	18.75	0.01	7.35	0.00	15.75
Zn	POM	0.91	0.25	0.88	0.42	0.56	0.29	0.95	0.29	1.13	0.25
	PM	0.14	2.10	0.18	2.06	0.18	1.47	0.15	2.39	0.17	2.18
	Mon	0.20	1.01	0.20	1.01	0.30	0.88	0.43	0.92	0.34	1.64
Cd	POM	1.90	0.49	1.33	0.47	1.76	0.56	2.30	0.45	1.90	0.42
	PM	0.15	1.90	0.17	1.09	0.29	2.08	0.24	1.30	0.20	2.27
	Mon	0.40	0.80	1.61	0.52	0.90	0.43	0.78	0.45	0.21	1.40
Hg	POM	0.39	1.95	1.00	1.63	1.23	0.38	0.46	0.58	0.58	0.82
	PM	1.31	0.28	0.91	0.10	0.59	0.50	1.52	0.16	0.68	0.29
	Mon	0.75	0.44	0.69	1.56	0.44	1.09	0.43	0.83	0.53	0.50
NOTE: POM - post monsoon, PM - pre monsoon, M - monsoon											

Average concentrations of metals in the analyzed species were used to calculate transference factor (TF) according to Mackay and Fraser (2000): TF = C_C/C_p, where C_C represents the concentration of metal (expressed on a dry weight basis) of interest in the consumer (predator) and C_p is the concentration of metal in the food (potential prey) and the value determined is given in Table 8.9. If the transference factor (TF) is greater than 1, then the metal is biomagnified (Gray, 2002).

The transference factor (TF) of metals among the trophic link examined is shown in Fig 8B. From 15 calculated transference rates (polychaetes – flatfish) for each metal in all transects,4 cases for Cu (26.66 %) showed transference rate greater than 1, 1 case for Pb (6.66 %), 1 case for Cr (6.67%), 13 cases for Ni (86.67%),8 cases for Zn (53.33%), 6 cases for Cd (40 %) and 4 cases for Hg (40%). Among the heavy metals the transference factor (3.23 – 23.15) was found greatest for nickel.

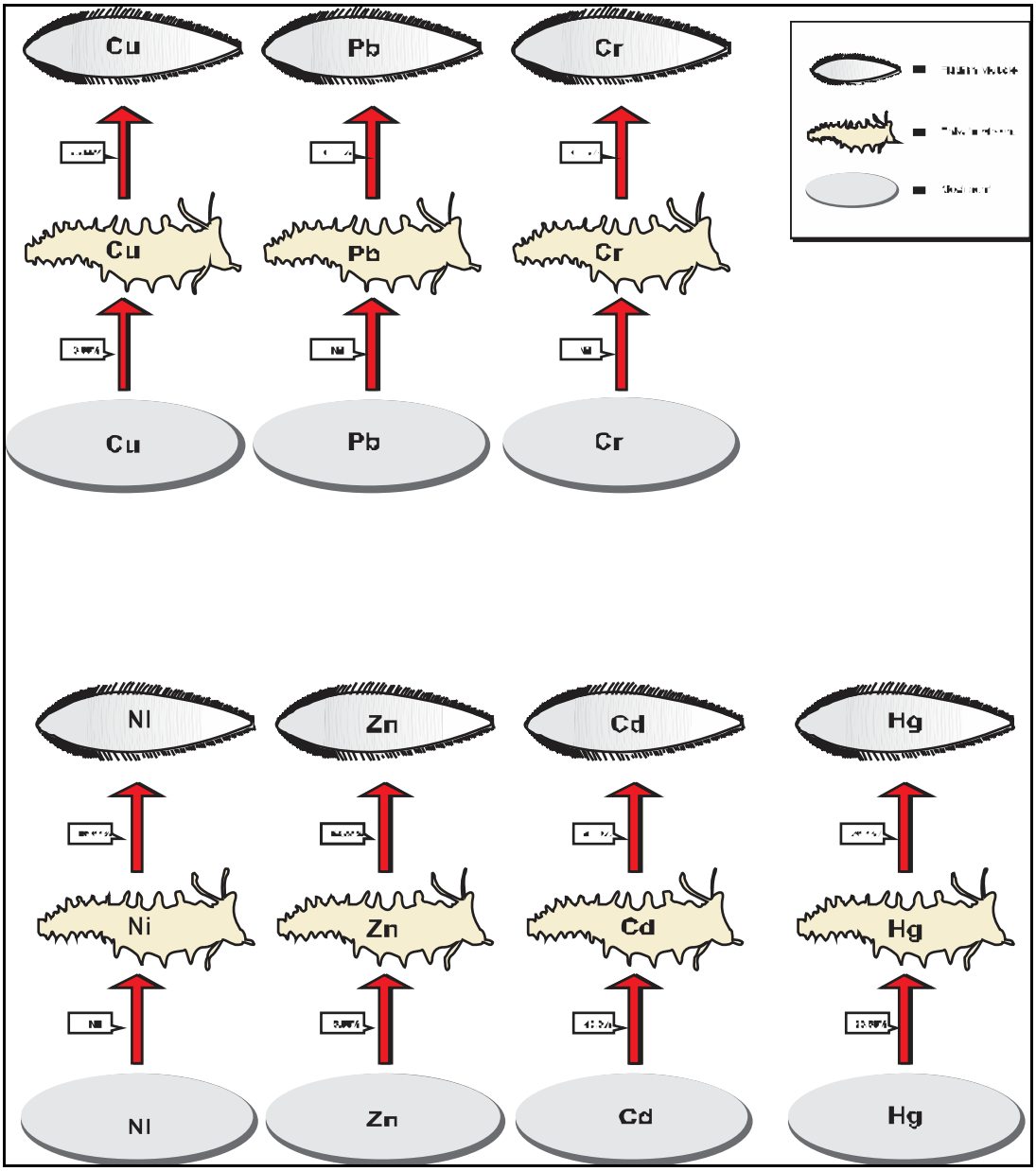


Figure 8B Biotransference in benthic ecosystem (sediment – polychaetes – flatfish) components of the study area. Values on lines are no. of cases resulted in transference factors (TF) > 1 expressed as %.

8.4 Discussion

The gut content analysis of flatfish (Malabar Sole; *C. macrostomus*) results primarily inferred that it is a carnivore. However, the presence of plant and animal matter in the gut also confirmed its detritivorous nature. Polychaetes represented the majority part of the diet. This voracious feeding habit of this particular fish finds its importance in the present metal accumulation study.

The overall metal content of the fish collected from each transects were compared by an evaluation based on MPI (Metal pollution index) which signifies greater availability of metal for accumulation from the environment. Flatfish pooled from Cochin, Calicut during all seasons and Ponnani in monsoon contained high metal concentration in tissue, relative to flatfish from Chettuva and Kasargod region. Transects were thus categorized as polluted (MPI >1) and less polluted (MPI <1) zones based on the MPI tabulated. A number of researchers have found greater concentrations of heavy metals in organisms from polluted compared to non polluted areas (Bryan *et al.*, 1980; Mackey *et al.*, 1992; Campbell, 1994; Locarnini and Presley, 1996; Taylor, 1998; Scanes and Roach, 1999; De Wolf *et al.*, 2000). The link between heavy metals in sediment, polychaetes and in muscles of flatfish for both polluted and less polluted transects showed differed kinship. In the polluted transects, the concentration of metals in sediments like Cr, and Cd were positively related to those in polychaetes (a major part in flatfish diet), but not reflected in flatfish tissue, while Hg in sediment was significantly related with polychaetes and flatfish. This result corroborate with the findings of Alam *et al.*, (2010), according to which Cd and Cr in the tissues of polychaetes were positively related with sediment metal (Cr and Cd) concentration in region of intense metal pollution in sediments. The authors also explain the possibility of channeling these metals to higher trophic level (fish) which is not discerned here. A plausible explanation could be that flatfish from the most contaminated site may have genetically and or physiologically adapted to long term exposure of elevated metal concentration in sediment and associated prey items and thus may be internally regulating its accumulation by different expelling

mechanisms. Similar explanation was given by Alquezar and Markich (2006) in the case of toadfish thriving in metal contaminated sediment elsewhere. The presence of detrital matter in flatfish gut may explain the concentration of Hg in sediments being positively related to those in flatfish. Significant positive correlation was observed between dissolved Hg in bottom water and flatfish in the study area as such exposure route through overlying water cannot be ruled out. Further, the concentration of dissolved Hg in bottom water in polluted transects are above the limits prescribed for water quality criteria as such, it can have an impact on the benthic species in terms of accumulation or other ecotoxicological risk.

In the less polluted transects, Pb in the polychaetes was positively correlated with those in flatfish and significant positive correlations was obtained for Zn in polychaetes and those in flatfish. The trophic transfer models through different food chains (autotrophs, planktivores, herbivores, detritivores, omnivores and carnivores) for essential and non essential metals was investigated by Barwick and Maher (2003). They concluded that metals like Cd, Zn and Pb at a lesser extend were transferred and biomagnified to higher trophic levels via diet. Similar positively correlation between the concentrations of metals in sediments and toad fish prey items were also related to those in toadfish, suggesting multiple exposure pathways; direct ingestion of sediments and/or ingestion of prey items that may have accumulated metals from sediments (Alquezar and Markich, 2006). This study corroborates with the above findings as Pb and Zn in polychaetes is significantly related with that of flatfish. This signifies that in less polluted transect or where there is no intense metal contamination, exposure pathways of Pb and Zn facilitated through prey-predatory relationships, in which the polychaetes should have accumulated from its surrounding environment. The overlying surface water can be another potentially important metal exposure pathway for many sediment dwelling biotic communities. Significant positive correlation was observed between dissolved Pb in bottom water and polychaetes in the study area.

From the above results, metal concentrations in flatfish tissue were linearly and positively related to metal concentrations in both sediments and polychaetes, indicating that sediment and infauna is an important metal exposure pathway. In the polluted site and less polluted site metal toxicity and associated accumulation through food and feeding is site specific occurring on a local population level.

8.4.1 Biotransference of Heavy Metals in Benthic Food Chain

To understand which all metals are undergoing biotransference (transfer of metals from a food source to consumer) i.e from aquatic invertebrates (polychaetes) to its predators (flatfish), transference factor (TF) and concentration factor (CF) were determined for each metal to ascertain whether any metals has a possibility to get biomagnified (TF >1).

The transference factor (TF) associated with the trophic interactions of polychaetes and flatfish in the case of essential metals like Cu and Zn are 26.66 % and 53.33% respectively while the transfer from sediment to polychaetes is 6.66% each. Zinc and Cu being essential metals is often regulated in organisms of lower and higher trophic levels. This can be inferred as the reason for low biotransference factors or transference factor (TF) for Cu, but for Zn there is evidence for biotransference, probably its accumulation and regulation mechanism may be different in higher trophic levels. This conclusion is consistent with the findings of Inzunza and Osuna (2008) in food web of SE Gulf Of California, Barwick and Maher (2003) in a temperate seagrass ecosystem from the lake Macquarie estuary in Australia and with data reported by Szefer (1998) in biota from a southern Baltic ecosystem.

In the case of Pb, there were only a few evident trends (6.66%) in the magnitude of biotransference factor between polychaetes and flatfish. In the present case it shows that Pb is an element with negligible potential for biotransference. From the number of cases having biotransference factor from sediment to polychaetes (nil) and polychaetes to flatfish (6.66 %) and considering that Pb usually accumulates more markedly in sediments than in biota, it can be

said that this element is comparatively less likely to undergo biotransference. Dietz *et al.*, (2000) have mentioned that Pb does not bioaccumulate towards higher trophic levels in the terrestrial or the marine ecosystem; a similar pattern of metal accumulation was found in diverse organisms from a souther Baltic ecosystem (Szefer, 1991) – the authors concluded that Pb is not biomagnified along the successive trophic levels of the food chain.

For Cr, there was no marked positive biotransference factor (6.66 %) in the trophic interactions or food link, it can be concluded that there is no Cr biotransference. Considering Ni element, the number of trophic interactions with transference factor values greater than 1 is found to be 86.66%, though there was no bioavailability from sediment to polychaetes (CF= 0%) but transference factors were relatively elevated between polychaetes and flatfish, which can be interpreted as evidence of Ni biotransference in flatfish. This finding contrasts with previous reports in the literature, in which the biomagnification is non - existing in the case of Ni (Amirad *et al.*, 1980; Szefer, 1991). In the study area, nickel concentrations in sediments was observed to be above the ERM value for sediment quality and will represent a probable-effects range within which effects would frequently occur in benthic organisms (Long *et al.*, 1995).

From the calculated transference factors for Cd, six cases each indicated tranference of metal from sediment to polychaetes (CF=40 %) and through food link from polychaetes to flatfish (TF = 40%). Bargagli (1998) studied metal concentrations in a food web in the Mediterranean Sea and found that at high trophic levels, Cd concentrations are lower than at the bottom of the food chain, concluding that there is no evidence of biomagnification of Cd in this marine food chain. Similarly, Barwick and Maher (2003) found no evidence of magnification of Cd in a temperate estuarine ecosystem from NSW Australia; only in 5 of the 35 trophic interactions examined did they observe increases in Cd concentrations. Within the Greenland part of the Arctic, Dietz *et al.*, (2000) found a general pattern of Cd biomagnification, but the authors concluded that metal transfer in successive trophic levels is influenced by the comparisons

being made among the different species. On the other hand, in a study of TF in a southern Baltic ecosystem, it was found that values for Cd were usually less than 1 (Szefer, 1991). In this study, it can be concluded that there is a small potential for biotransference of Cd in this marine benthic food chain.

Concerning Hg, four cases, each were found in the transference of metal from sediment to polychaetes (CF = 26.66 %), and through food link from polychaetes to flatfish (TF = 26.66%), concluding that there is little or small biotransference potential for Hg in this marine food chain. Typically, it has been stated that mercury is subjected to bioaccumulation and biomagnifications (Castilhos and Bidone, 2000; Dietz *et al.*, 2000).

In this study of benthic food chain and from the number of cases of trophic interaction (polychaetes – flatfish) for the studied metal, Ni and Zn showed evidence of biotransference, while Cd and Hg showed small potential for biotransference.

8.5 Conclusion

As per the sediment quality guidelines, metals like Cu, Cr and Hg in sediments are in a level that can be available to the living resources occasionally while the levels of Ni can be bioavailable frequently. Wide seasonal variation was conspicuous in the accumulation of metals in polychaete worms and flatfish irrespective of transects. The levels of examined metals in water, sediment and biota was high at polluted transects. The gut content analysis of flatfish (*C. macrostomus*) revealed that, diet constituted mostly of polychaete worms. This finds importance in the metal accumulation study through its food and feeding habits. Metal concentrations in flatfish tissues were linearly and positively related to metal concentrations in both sediments and polychaetes, which highlight the relative importance of sediment's decisive role as a vector in the metal uptake pathway in flatfish and their foraging items. No significant correlation between metals from the overlying water and flatfish was obtained, though it contained levels of metal which can cause ecotoxicological risk. In the polluted site and less polluted site metal toxicity and associated

accumulation through food and feeding is site specific occurring on a local population level. In this study of benthic food chain and from the number of cases of trophic interaction (polychaetes – flatfish) for the studied metal, Ni and Zn showed evidence of biotransference, while Cd and Hg showed small potential for biotransference.

Chapter 9

SUMMARY OF THE RESULTS

9.1 Summary

9.2 Recommendations for Future Research

9.1 Summary

The spatial and temporal variation of nutrients in water column, metals in water, sediment and benthic biota of five transects along the central and northern coast of Kerala was investigated in this study. The concentration of heavy metal (persistent pollutant) in organism in relation to those in sediment and to trophic level was also studied to assess the ecological risk. The selection of locations was based on the inflow of pollutants from different sources. Cochin [major port, fishing harbors, densely populated zone, busy waterways, tourist destination, major industrial center], Chettuva [agricultural region, river estuary, fishing village], Ponnani [fishing harbor, densely populated area, agricultural region, small scale industries], Calicut [commercial port, fishing harbor, densely populated area, industrial city] and Kasargod [fishing harbor, small scale industries, agricultural region]. The spatio-temporal variation of the nutrient inventory is controlled by a complex mixture of anthropogenic and natural sources and processes. Among the nutrients; dissolved Inorganic phosphate concentration was higher than dissolved inorganic nitrogen forms leading to N: P ratios of an average of less than 10, while Si: N ratios were greater than unity indicating that $Si(OH)_4$ is not a limiting nutrient in the surface coastal water. A comparison of ambient nutrient ratios with the Redfield ratio (N: P: Si = 16:1:16) showed "potential stoichiometric N limitation" in the factors that regulate phytoplankton biomass. Most plankton variability along the coast appears to be driven by species of diatoms; Si supply being a driving force. Addition of nutrient load in which rivers act as vectors reinforced by seasonal upwelling is augmenting the productivity in terms of phytoplankton biomass. The consistency in Chlorophyll *a* concentration maintaining its mesotrophic to eutrophic state regardless of seasonal trends suggests that coastal region along the central and northern Kerala is a biologically active zone. A definite gradient was conspicuous between the surface and bottom waters for the physico chemical variables highlighting the dynamic environment of the study area. Principal component analysis of the datasets revealed riverine, phosphorus, upwelling, aeration processes in surface water

and in addition diagenetic process in bottom water as the factors influencing or creating an ecological change in the waters of central and northern coast of Kerala.

Seasonal variability plays an important role in accentuating the distribution of dissolved metals in coastal waters. Metals like Cu, Zn and Cd received by the coastal water, varied seasonally, with minimum distribution occurring in post monsoon and maximum in monsoon seasons. This minimum, most likely reflects the reduced input of these metals from non-point sources together with the lack of freshwater inflow and maximum concentration due to heavy rainfall and subsequent river runoff, bringing much industrial and land derived materials into the coastal waters. Concentration of Pb showed a relatively restricted range of variability and Ni showed increased concentration in pre monsoon reflecting its involvement in biological production. Both Pb and Ni showed low distribution in monsoon which could have been scavenged by organic matter through deposition brought by monsoonal flushing. Chromium was not detectable in all transects though low concentration was observed in the water column at Cochin and Calicut and its meager presence in coastal water could be the removal of Cr by precipitation and deposition in sediments. Mercury did not show any seasonal trend; its concentration being relatively uniform in surface and bottom waters at all transects. The distribution of dissolved metals in bottom water showed similar seasonal variation as that of surface water due to the shallowness and vertical mixing of the water column. There were cases in which bottom water showed higher concentration of dissolved metal compared to surface layer. It reveals the propensity of these metal reserves in sediments by organic matter deposition to be remobilized; as a result of digenesis at the sediment water interface. Concentrations of the dissolved metals measured in the coastal waters of central and northern coast of Kerala were comparable with other worldwide ranges and the region is not as much polluted as the other coastal waters of India. A definite shore to offshore concentration gradient in the distribution of metals was not distinct could be possibly due to a balance between sedimentation processes, incorporation by

organisms, advection and diffusion. As per the quality criteria used to assess the heavy metal contamination in the investigated area, revealed contamination of dissolved metals in coastal water in the order Cu > Ni > Cd > Pb > Zn in all the transects. Contamination due to Hg in the coastal water was discerned only at Cochin. Among the transects increased heavy metal contamination noticed along the coast at Cochin which could be attributed mainly to changes in land use, disposal of industrial and urban waste water in combination with hydrological alterations might certainly turn it as a hotspot location in terms of land based heavy metal pollution in future. It was followed by Kasargod, Chettuva, Calicut and Ponnani. In the former two transects contamination by metals may be mainly resulting from the metal residue brought through increased agricultural runoff and contribution from sewage pollution. Given that there is no industrial development within the catchments, the most likely anthropogenic sources for these metals are non-point sources such as storm water runoff and atmospheric deposition of combusted fuels. In the latter two transects, in addition to the agricultural runoff, effluents from small scale industries situated in the hinterland which impinges into the coastal water through freshwater bodies also lead to metal enrichment. The levels of Cu, Ni, Zn and Hg exceeded the limits furnished for minimal risk concentration for heavy metals in all transects and as such these metals can pose ecotoxicological risk to organism inhabiting the waters of the central and northern coast of Kerala.

The dominancy of fine fraction in sediment, with contribution from clay forming a principal part, signifies the susceptibility of sediments for sorption of metal content. The average percentage of organic matter reported at each transects for all seasons were above the world average of 2.5 % for near shore sediments due to enhanced productivity in the overlying water. A definite seasonal trend with high accumulation of organic matter in sediment in post monsoon and low in pre monsoon was conspicuous at Ponnani, Calicut and Kasargod. In the central coast (Cochin and Chettuva) a definite seasonal trend was not noticed and the sediment was highly enriched with organic matter due

to the heavy input of domestic wastes. The sediments at Cochin was highly enriched with organic matter content in monsoon due to the heavy inflow of organic rich domestic wastes in to the coastal water which is estimated to be 34,000 m^3 per day. The wide variation in metal distribution in sediments among seasons supports the view that anthropogenic activity contributes significantly to the contamination of marine sediments due to industry and urban activities in the study area. On the basis of highest concentration of metal reported along the study area it followed the order Zn > Cr > Ni > Cu > Pb > Cd > Hg. The maximum concentration of all studied metals was found at Cochin in different seasons presumed to be due to the input of contaminants from the broader heavily industrialized catchment area. There was much spatial variation in the concentration of Cr, Ni, Zn and Cu among seasons, as such a definite order in the distribution of metals in sediments both spatially and temporally could not be figured. Metals like Cr, Ni showed enrichment at all transects in monsoon signifying the monsoonal flushing of terrestrial inputs into coastal water enhancing its concentration in sediments. Contamination due to Cr was discerned at Calicut all throughout the season presumed to be the effect of effluent released from the contiguous ceramic industries in which Cr forms a main constituent. The sediments collected during post monsoon reflected low metal enrichment throughout the study sites, probably due to coastal currents averting their deposition in sediments and biogenic association. On moving towards offshore in all transects, heavy metal concentration was higher compared to near shore due to fine sediment composition facilitating easy adsorption of heavy metals. On the basis of PLI (Pollution Load Index) which shows the magnitude and extent of the heavy metals deposition in sediment, regional contamination followed the order Cochin > Calicut > Ponnani > Chettuva > Kasargod. Thus, Cochin has the highest anthropogenic activities while Kasargod the lowest in terms of metal contamination in sediments. The geo-accumulation index (I_{geo}) , a pollution indicator which accounts for anthropogenic inputs of heavy metals in the study area, depicted Cd being moderately to strongly polluting sediments at Cochin. The enrichment of Cd in

the sediment matrix is mainly due to quantum of metal input from the contiguous industrial establishments situated along the coast. Sediments in Cochin region was moderately to strongly polluted with Cd in monsoon, presumed to be effected by monsoonal flushing of pollutants from the urban city into the coast. For all the other transects, Cd and Cr were the metals which fell into class 1 (unpolluted to moderately polluted) , except at Kasargod where the overall average I_{geo} values of all metals fall into class 0 which can be categorized as unpolluted. Overall average of I_{geo} values of for all metals in sediments from central and northern coast of Kerala fall into class 0 and 1 which is categorized as unpolluted to moderately polluted environment except at Cochin where it is moderately to strongly polluted with Cd. Based on comparisons to the effect-range classification of sediment quality guidelines, in monsoon the distribution of Ni in sediment is such that there is a propensity of Ni metal to enhance the incidence of adverse negative effects on living resources frequently at all transects. The total metal concentrations in this study were comparable to other studies reported in the literature; however concentrations of Ni and Zn found in this study were higher than other coastal regions of India and other regions of the world but much lower than those reported for polluted coasts. High values of Ni (134 $\mu g\ g^{-1}$) and Zn (219 $\mu g\ g^{-1}$) were recorded at Cochin in monsoon, could have emanated from industrial effluent input. Results of PCA analysis reflected anthropogenic activities, biogenic association and its diagentic reaction driven by its degradation, regulating the behavior of reactive metals especially Cu, Zn and Cd in all transects. Positive values of mercury and its association with fine sediments were discerned at all transects except at Ponnani, revealing alternative natural source of this metals or from a diffuse anthropogenic source. Since agriculture is the major economy of the study region, Hg source can be traced to its increased use in pesticides and fungicides. An assessment of PLI among seasons revealed PLI < 1 at all transects in post monsoon, suggestive of region having less input from metal contaminants. In general, though the region is being influenced by metal contamination through anthropogenic forces, with high input in monsoon, local hydrodynamic conditions especially coastal

currents and biogenic association are playing a vital role to negate this enrichment of metals in the sediments.

Heavy metal accumulation in the selected biota (polychaete *Glycera longipinnis*) in this study signified that it is being influenced by an increasing number of diverse sources such as urbanisation, industrial activities and agricultural run-off. Results of Pearson's correlation shows a positive correlation between Cd and Cr in sediments to Cd and Cr in the organisms. Cr content (1.73 - 29.20 µg g^{-1}) recorded for *G. longipinnis* during this study is considerably higher than that reported from other coastal regions of the world. The bioconcentration factor revealed the ability of this organism to accumulate Hg and Cd more than in sediments in both polluted and unpolluted transects. Organic carbon was found to play a pivotal role in the availability of mercury in sediments. Thus, the results of this study strongly suggest that the polychaete *G. longipinnis* is a useful indicator for contamination of heavy metals such as Cd, Hg and Cr (in a long run) due to anthropogenic sources along the southwest coast of India.

Based on the results obtained regarding the levels of metal in fish, wide variation was conspicuous for metals like Ni, Cr, Pb, Cd and Hg in the tissues. Relatively high accumulation of metals was observed in the tissues of flatfish pooled from the heavily urbanized regions like Cochin followed by Calicut, while at other transects the level was comparable. The concentration of metal in specific tissues, can give possible evidence of environmental pollution by specific metals at a given site as such it can prove useful as a biological indicator for the examined metals (except Zn and Cu). The levels of toxic metals are within the safe limits prescribed by various agencies; however Cd slightly exceeded in the muscles of flatfish pooled from Cochin region which is a matter of concern.

The trophic transfer of metals in the benthic food chain (sediment – polychaetes - flatfish) was assessed. Polychaete worms constituting the major dietary item of flatfish (*C. macrostomus*) was established by the gut content

analysis, which also revealed its carnivorous/detritivorous feeding habit. This finds importance in the metal accumulation study through its food and feeding habits. Metal concentrations in flatfish tissues were linearly and positively related to metal concentrations in both sediments and polychaetes which highlight the relative importance of sediment's decisive role as a vector in the metal uptake pathway in flatfish and their foraging items. In the polluted site and less polluted site, results revealed metal toxicity and associated accumulation through food and feeding is site specific occurring on a local population level. From the number of cases of potential trophic interactions with Transference Factor (TF) > 1, Ni and Zn showed evidence of biotransference (transfer of metals from a food source to consumer), while Cd and Hg showed small potential for biotransference.

The results of the present observations clearly indicate the intricate pattern of relationship existing among the abiotic and biotic components of a benthic ecosystem, and can very well be regarded as an ecological model for future investigations aimed at developing measures for the effective management of the coastal zone of Kerala.

9.2 Recommendations for Future Research

This study has served as an introduction to metals research in the coastal environment of Kerala and will hopefully provide a platform from which future research can be conducted.

1) Assessment of bioavailability of metals:

   The most logical progression from this study is to assess the bioavailability of metals within the sediments. As bioavailability of metals is inseparably linked with metal uptake in many benthic organisms and its flow in benthic food chain, benthic organism's analysis can be trusted compared to chemical analysis and can very well provide a measure of the presence of the heavy metals averaged over a time.

2) Integrated environment quality approach to assess coastal health:

Most countries have well established coastal monitoring programs and India is of no exception, and it is imperative that such long term monitoring programs includes integrated approach to better assess ecosystem health. Chemical monitoring alone cannot, however, be used to assess the environmental risks imposed by chemical contamination. Ecotoxicology and use of bioindicators and biomarkers has emerged as a powerful means of assessing the effects of contaminants on living organisms and ecosystem health, and a combination of chemical and biological monitoring allows scientists to better assess environmental risk. It is advised that future research focuses on identifying the most suitable bioindicators, and to characterize and assess the impact of metals speciation (in this study total metal concentration was taken into consideration) on ecological receptors that can be used alongside chemical monitoring to assess ecosystem health.

3) Studies on heavy metal distribution in offshore environment:

It was found that the concentrations and enrichment of several metals in the sediment increased significantly in a seaward direction especially nickel (Ni) in monsoon in the study area, possibly suggesting a chance of input from the marine environment. It can be hypothesized that this pattern of enrichment can be due to upwelling events. It would thus be interesting to conduct spatial and temporal studies on metal concentrations in the offshore environment coupled with nutrient and phytoplankton analysis to identify if upwelling is having an influencing effect.

4) Cycling of metals in the coastal environment:

In this study wide variation was discerned in the distribution of metals in water and sediment and biota both seasonally and also among the transects. It would be thus pertinent to investigate the processes that impact the cycling and toxicity of heavy metals including the influence of

fresh water discharge, sediment/ water exchange, redox behavior of metals, atmospheric and geological input etc., for the increased understanding of metal chemistry in the coastal environment

5) Trophic distribution of metals in food web:

To extend this type of trophic transfer models to other pelagic, benthic and bacteria based food chains in the coastal environment in order to understand the dynamics of metal flow through food and feeding and related risks to resident organisms and human consumers.

6) Acclimation and adaptation to metals:

In this study, organism thriving in polluted environment showed absence of additional metal bioaccumulation in the presence of very high metal concentration in sediments. It can be hypothesized that physiological acclimation or acquired genetic resistance of sediment dwelling organisms through generations of continuous metal exposure results in the absence of metals in their tissues in relation to their host sediments. Additional research is necessary to understand the cost of tolerance and adaptation to metals and the potential consequences with regard to exposure to multiple stressors.

REFERENCES

Abdallah, M. A. M., & Abdallah, A. M. A., 2008. Biomonitoring study of heavy metals in biota and sediments in the South Eastern coast of Mediterranean sea, Egypt. *Environmental Monitoring and Assessment*, 146, 139–145.

Accornero, Manfra, L., Salluzzo, A., Modestia, F., 2004. Trace metal pollution in surface marine waters: nearshore concentrations along Apulia and Albania. *Chemistry and Ecology*, 20 (1), 195– 203.

Adeyeye, E. I., Akinyugha, N. J., Fesobi, M. E., Tenabe, V. O., 1996. Determination of some metals in *Clarias gariepinus* (Cuvier and Valenciennes), *Cyprino Carpio* (L) and *Oreochromis niloticus* (L) fishes in a Polyculture Freshwater Pond and their Environments. *Aquaculture*, 47, 205– 214.

Agency for Toxic Substances and Disease Registry, 2005. *Agency for Toxic Substances and Disease Registry*. Division of Toxicology, Clifton Road, Atlanta, available at http*://www.atsdr.cdc.gov/toxprofiles*.

Agnihotri, R., Sarin M. M., Somayajulu, B. L. K., Jull, A. J. T., Burr, G. S., 2003. Late – Quaternary biogenic productivity and organic carbon deposition in the eastern Arabian Sea. *Paleogeography, Palaeoclimatology, Palaeoecology*, 197, 43 – 60.

Ahumada, R., Lorena, G., Iris, S., Eduardo, F., 2008. Trace metals in the coastal waters and organisms of the austral Chilean channels and fjords, In: *Progress in the oceanographic knowledge of Chilean interior waters, from Puerto Montt to Cape Horn*, Silva, N., Palma, S. (Eds.), Comité Oceanográfico Nacional - Pontificia Universidad Católica de Valparaíso, Valparaíso, pp. 45- 49.

Alam, M. A., Gomes, A., Sarkar, S. K., Shuvaeva, O. V., Vishnevetskaya, N. S., Gustaytis, M. A., Bhattacharya, B. D., Godhantaraman, N., 2010. Trace Metal Bioaccumulation by Soft-bottom Polychaetes (Annelida) of Sundarban Mangrove Wetland, India and Their Potential Use as Contamination Indicator. *Bulletin of Environmental Contamination and Toxicololgy*, 85, 492–496.

Alemdaroglu, T., Onur, E., Erkakan, F., 2003. Trace metal levels in surface sediments of Lake Manyas, Turkey and tributary rivers. *International Journal of Environmental Studies*, 60, 287–298.

Alikhan, M. A., & Zia, S., 1989. Nickel uptake and regulation in a copper-tolerant decapod, *Cambarus bartoni* (Fabricus) (Decapoda, Crustacea). *Bulletin of Environmental Contamination and Toxicology*, 42, 94–102.

Allert, A. L., Fairchild, J. F., DiStefano, R. J., Schmitt, C. J., Brumbaugh, W. G., Besser, J. M., 2009. Ecological effects of lead mining on Ozark streams: In-situ toxicity to woodland crayfish (*Orconectes hylas*). *Ecotoxicology and Environmental Safety*, 72(4), 1207–1219.

Alliot, A., & Piron, M. F., 1990. Relationship between metals in sea-water and metal accumulation in shrimps. *Marine Pollution Bulletin*, 21, 30–33.

Aloup, M., Angelidis, M.O., Gabriel, A., Karantanelli, M., Koulousaris, M., Nikolaou, A., Petsas, A., Tsirtsis, G., Vagi, M., Vlatsiotou, F., 2007. Marine monitoring along the eastern coastal area of the island of Lesvos, Greece during 2004 in the framework of Medpol III. *Global NEST Journal*, 9(2), 83– 97.

Alquezar Ralph, & Markich, J. S., 2006. Accumulation of metals by toadfish from sediment and infauna: are fish what they eat. *Australasian Journal of Ecotoxicology*, 12, 95– 106.

AMAP (Arctic Monitoring and Assessment Programme), 2002. *Arctic Pollution 2002*. available at http://www.amap.no/homepage.htm.

Amiard, J. C., Amiard-Triquet, C., Barka, S., Pellerin, J., Rainbow, P. S., 2006. Metallothioneins in aquatic invertebrates:Their role in metal detoxification and their use as biomarkers. *Aquatic Toxicology*, 76, 160–202.

Amiard, J. C., Amiard-Triquet, C., Metayer, C., Marchand, J., Ferre, R., 1980. Study on the transfer of Cd, Pb, Cu and Zn in neritic and estuarine trophic chains. I. The inner estuary of the Loire (France) in the summer of 1978. *Water Research*, 14, 665–673.

Amin Bintal, Ahmad Ismail, Aziz Arshad, Chee Kong Yap, Mohd Salleh Kamarudin, 2009. Gastropod Assemblages as Indicators of Sediment Metal Contamination in Mangroves of Dumai, Sumatra, Indonesia. *Water Air Soil and Pollution*, 201, 9–18.

Amin, B., Ahmed, I., Aziz, A., Yap, C. K., Kamarudin, M. S., 2009. Anthropogenic impacts on heavy metal concentrations in the coastal sediments of Dumai, Indonesia. *Environmental Monitoring and Assessment*, 148, 291 – 305.

Anabela, O., Carla, P., Manuela, V., Aurora, R., 2007. Maderia Island- SW coastal sediments Geochemistry. *Thalassas*, 23(2), 9– 16.

Anand, S. P., & Jayaraman, R., 1972. Distribution of Inorganic phosphate in the upper hundred- metre column in different regions of the northern Indian ocean. *Indian Journal of Marine Sciences*, 1 (1), 79–84.

Anderson, K. B., Sparks, R. E., Paparo, A. A., 1978. *Rapid assessment of water quality using the fingernail clam, Musculiwn transversum*. Research Report No. 133, University of Illinois Water Resources Center, USA.

Ansari, T. M., Marr, L. L., Tariq, N., 2004. Heavy metals in marine pollution perspective – A Mini Review. *Journal of Applied Sciences*, 4 (1), 1– 20.

Anu, G., Nair, S. M., Kumar, N. C., Jayalakshmi, K. V., Padmalal. D., 2010. A baseline study of trace metals in a coral reef sedimentary environment, Lakshadweep Archipelago. *Environmental Earth Science*, 59, 1245 – 1266.

APHA (American Public Health Association), 1998. *Standard Methods for the Examination of Water and Wastewater- 20th edition*. Technology and Engineering, University of California, USA.

Arellano, J. M., Ortiz, J. B., Capeta Da Silva, D., Gonzalez De Canales, M. L., Sarasquete, C., Blasco, J., 1999. Levels of copper, zinc, manganese and iron in two fish species from salt marshes of Cadiz Bay (southwest Iberian Peninsula). *Boletino Del Instituto Espanol De Oceanografia*, 15, 485 – 488.

Arrigo, K., 2005. Marine microorganisms and global nutrient cycles. *Nature*, 437, 349 – 355.

Asha, J. K., & Vijayalakshmi, R. N., 1999. Concentration of metals in fishes from Thane and Bassein creeks of Bombay, India. *Indian Journal of Marine Sciences*, 28, 39 – 44.

Ashokkumar, S., Mayavu, P., Sampathkumar, P., Manivasagam, P., Rajaram, G., 2009. Seasonal Distribution of Heavy Metals in the Mullipallam Creek of Muthupettai Mangroves (Southeast Coast of India). *American-Eurasian Journal of Scientific Research*, 4 (4), 308– 312.

Aston, S. R., 1980. Nutrients, dissolved gases and general biochemistry in estuaries, In: *Chemistry and biogeochemistry of estuaries*, Olausson, E., Cato, I. (Eds.), John Wiley and Sons, New York, pp. 233 – 262.

Atchison, G. J., Henry, M. G., Sadheinrich, M. B., 1987. Effects of metals on fish behavior: a review. *Environmental Biology of Fishes*, 18, 11 –25.

Auernheimer, C., & Chinchon, S., 1997. Calcareous skeletons of sea urchins as indicators of heavy metals pollution. Portman Bay, Spain. *Environmental Geology*, 29 (1-2), 78– 83.

Babu, C. P., Brumsack, H. J., Schnetger, B., 1999. Distribution of organic carbon in surface sediments along the eastern Arabian Sea: a revisit. *Marine Geology*, 162, 91 – 103.

Badarudeen, A., Padamlal, D., Sajan, K., 1998. Organiccarbon and total phosphorous in the sediments of some selected mangrove echo systems of Kerala, southwest coast of India. *Journal of Geological Society of India*, 52(5), 679–684.

Bakun, A., Roy, C., Lluch Cota, S., 1998. Coastal upwelling and other processes regulating ecosystem productivity and fish production in the western Indian Ocean, In: *Large Marine Ecosystems of the Indian Ocean: Assessment, Sustainability and Management*, Sherman, K., Okemwa, E., Nitiba, E. M. (Eds.), Blackwell Sciences Inc., Massachusettes, pp.103 –141.

Balachandran, K. K., Laluraj, C. M., Martin, G. D., Srinivas, K., Venugopal, P., 2006. Environmental analysis of heavy metal deposition in a flow-restricted tropical estuary and its adjacent shelf. *Environmental Forensics*, 7, 345–351.

Balachandran, K. K., Laluraj, C. M., Nair, M., Joseph, T., Sheeba, P., Venugopal, P., 2005. Heavy metal accumulation in a flow restricted tropical estuary. *Estuarine Coastal Shelf Science*, 65, 361–370.

Balachandran, K.K., Joseph, T., Nair, M., Sankaranarayanan, V. N., Kesavadas, V., Sheeba, P., 2003. Geochemistry of surficial sediments along the centralsouthwest coast of India – Seasonal changes in regional distribution. *Journal of Coastal Research*, 19, 664– 683.

Balachandran, V. K., Rajagopalan, M. S., Pillai, V. K., 1989. Chlorophyll 'a' and pheopigment as indices of biological productvity in the inshore surface waters off Cochin. *Indian Journal of Fisheries*, 36, 227– 237.

Balls, P. W., Hull, S., Miller, B. S., Pirie, J. M., Proctor, W., 1997. Trace metal in Scottish estuarine and coastal sediments. *Marine Pollution Bulletin*, 34, 42–50.

Barbara Jezierska, & Maágorzata Witeska, 2006. The Metal uptake and accumulation in fish living in polluted waters, In: *Soil and Water Pollution Monitoring- Protection and Remediation*, Twardowska, I. (Ed.), Springer, pp. 3–23.

Bargagli, R., 1998. Cadmium in marine organisms from the Tyrrhenian Sea: no evidence of pollution or biomagnification. *Oebalia*, 19, 13–25.

Barwick, M., & Maher, W., 2003. Biotransference and biomagnification of selenium copper, cadmium, zinc, arsenic andlead in a temperate seagrass ecosystem from Lake Macquarie Estuary, NSW, Australia. *Marine Environmental Research*, 56, 471–502.

Bettinetti, R., Giarei, C., Provini, A., 2003. Chemical analysis and sediment toxicity bioassays to assess the contamination of the River Lambro (Northern Italy). *Archives of Environmental Contamination and Toxicology,* 45, 72–78.

Bhosale, U. R., & Sahu, K. C., 1991. Distribution of heavy metals between water,suspended particles and sediments in a polluted aquatic regime. *Chemical Geology*, 90, 285 – 305.

Blake, A. C., Chadwick, D. B., Zirino, A., Rivera- Duarte, I., 2004. Spatial and temporal variations in copper speciation in San Diego Bay. *Estuaries,* 27, 437 – 447.

Blaxter, J. H. S., & Tjabbes, T. H., 1992.The effect of pollutants on sensory systems and behaviour of aquatic animals. *Aquatic Ecology*, 26 (1), 43–58.

Blinda, M., Sabhi, Y., El Quessar, S., Fekhaoui, M., Brahim, L., 2009. Dynamics of heavy-metal transfer between biotic (*Cytheria chione* and *Cerastoderma edule*) and abiotic (water and sediment) components in marine environment (Bay of Martil, Moroccan Mediterranean coast). *Chemistry and Ecology*, 21(4), 279–301.

Bonsdorff , E., Blomquist, E. M., Mattila, J., Norkko, A., 1997. Coastal eutrophication: Causes, consequences and perspectives in the archipelago areas of the Northern Baltic Sea. *Estuarine Coastal Shelf Science*, 44, 63– 72.

Bowen, H. J. M., 1979. *Environmental Chemistry of the Elements,* Academic Press, London.

Boyd, P. W., & Hurd, C. L., 2010. Ocean Nutrients, In: *Surface Ocean – Lower Atmosphere Processes,* Corinne, L. Q., Eric, S. S. (Eds.), American Geophysical union, Florida, pp. 139 –161.

Boyle, A. E., Sclater, F., Edmond, J. M., 1976. On the marine geochemistry of cadmium. *Nature*, 263, 42 – 44.

Brooks, R. R., Presley, B. J., Kaplan, I. R., 1967. APDC-MIBK extraction system for the determination of trace elements in saline waters by atomic-absorption spectrophotometry. *Talanta*, 14, 809– 816.

Bruland, K. W., Knauer, G. A., Martin, J. H., 1978. Zinc in northeast Pacific water. *Nature*, 271, 741–743.

Bruland, K. W., 1983. Trace elements in seawater, In: *Chemical Oceanography*, Riley, J. P., Chester, R. (Eds.), Academic Press, London, pp. 157 – 220.

Bryan, G. W., 1967. Zinc concentrations of fast and slow contracting muscles in the lobster. *Nature*, 213, 1043 – 1044.

Bryan, G. W., Langston, W. J., Hummerstone, L. G., 1980. The use of biological indicators of heavy metal contamination in estuaries. *Marine Biological Association- UK*, 1, 1– 73.

Bryan, G.W., 1984. Pollution due to heavy metals and their compounds, In: *Marine Ecology*, Kinne, O. (Ed.), Wiley, London, pp. 1289–1431.

Buhler, D. R., Stokes, R. M., Caldwell, R. S., 1977. Tissue accumulation and enzymatic effects of hexavalent chromium in rainbow trout (*Salmo gairdneri*). *Journal of the Fisheries Research Board of Canada*, 34, 9 – 18.

Burger, J., Gaines, K. F., Boring, C. S., Stephens, W. L., Snodgrass, J., Dixon, C., McMahon, M., Shukla, S., Shukla, T., Gochfeld, M., 2002. Metal levels in fish from the Savannah River: potential hazards to fish and other receptors. *Environmental Research*, 89, 85–97.

Burger, J., & Gochfeld, M., 2000. Heavy metals in commercial fish in New Jersey. *Environmental Research*, 99, 403–412.

Burgera, J., Michael, G., Christian, J., Sean, B., Timothy, S., 2007. Metal levels in flathead sole (*Hippoglossoides elassodon*) and greatsculpin (*Myoxocephalus polyacanthocephalus*) from Adak Island, Alaska: Potential risk to predators and fishermen. *Environmental Research*, 103, 62–69.

Cain, D. J., & Luoma, S. N., 1990. Influence of seasonal growth, age and environmental exposure on Cu and Ag in a bivalve indicator, Macomabalthica, San Francisco bay. *Marine Biology Progress Series*, 60, 45–55.

Calamari, D., Gaggino, G. F., Pacchetti, G., 1982. Toxicokinetics of low level of Cd, Cr, Ni and their mixture in long term treatment on Salmogairdneri. *Chemosphere*, 11, 59 – 70.

Campbell, K. R., 1994. Concentrations of heavy metals associated with urban runoff in fish living in storm water treatment ponds. *Archives of Environmental Contamination and* Toxicology, 27, 352–356.

Campbell, P. G. C., Lewis, A. G., Chapman, P. M., Crowder, A. A., Fletcher, W. K., Imber, B., Luoma, S. N., Stokes, P. M., Winfrey, M., 1988. *Biologically Available Metals in Sediments*. NRCC No.27694, National Research Council of Canada, Ottawa, Canada.

Cantillo, A.Y., 1998. Comparison of results of Mussel Watch programs of the United States and France with worldwide Mussel Watch studies. *Marine Pollution Bulletin*, 36, 712–717.

Castilhos, Z. C., & Bidone, E. D., 2000. Hg biomagnification in the ichthyofauna of the Tapajo´s river region, Amazonia, Brazil. *Bulletin of Environmental Contamination and Toxicology*, 64,693–700.

Chakraborty, R., Zaman, S., Mukhopadhyay, N., Banerjee, K., Mitra, A., 2009. Seasonal Variation of Zn,Cu and Pb in the estuarine stretch of West Bengal. *Indian Journal of Marine Science*, 38 (1), 104– 109.

Chandran, R., & Ramamurthy, K., 1984. Hydrobiological studies in the gradient zone of Vellar estuary: 1. Physico chemical parameters. *Mahasagar*, 17, 69– 77.

Chaoudhary, S., & Panigrahy, R. C., 1991. Seasonal distribution and behavior of nutrients in creek and coastal waters of Gopalpur East coast of India. *Mahasagar*, 24, 81 – 83.

Chen, C.W., Kao, C. M., Chen, C. F., Dong, C. D., 2007. Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan. *Chemosphere*, 66(8), 1431-1440.

Cho, Y. G., Lee, C. B., Choi, M. S., 1999. Geochemistry of surface sediments off the Southern and Western coast of Korea. *Marine Geology*, 159, 111–129.

Chuchukalo, V. I., Nadtochij, V. A., Kobilikov, V. N., 1994. Food habits of soles on the western Kamchatka shelf. *Ehkologiya*, 116, 193–198.

Cloern, J. E., 1987. Turbidity as a Control on Phytoplankton Biomass and Productivity in Estuaries. *Continental Shelf Research*, 7(11), 1367–1381.

CMFRI (Central Marine Fisheries Research Institute), 2008. *Central Marine Fisheries Research Institute Research Highlight 2007- 2008*. CMFRI, Kochi.

Cohen, T., Hee, S., Ambrose, R., 2001. Trace metals in fish and invertebrates of three California coastal wetlands. *Marine Pollution Bulletin*, 42, 232–242.

Commission of the European Communities, 2001. *Commission Regulation (EC) No. 221/2002 of 6 February 2002 amending regulation (EC) No. 466/2002 setting maximum levels for certain contaminants in foodstuffs, 2002*. Official Journal of the European Communities, Brussels.

Committee for Inland Fisheries of Africa, 1991. Report of the third session of the Working Party on Pollution and Fisheries: review of heavy metals in the African aquatic environment. *FAO Fisheries Report*, 471, 1–43.

Cossa, D., 1989. A review of the use of Mytilus spp. as quantitative indicators of cadmium and mercury contamination in coastal waters. *Oceanologica Acta*, 12(4), 417– 432.

Da Cunha, L. C., Wasserman, J. C., 2003. Relationships between nutrients and macroalgal biomass in a Brazilian coastal lagoon: The impact of a lock construction. *Chemistry and Ecology*, 19, 283 – 298.

Damotharan, P., Vengadesh Perumal, N., Arumugam, M., Vijayalakshmi, S., Balasubramanian, T., 2010. Seasonal Variation of Physico Chemical Characteristics in Point Calimere Coastal Waters (South East Coast of India). *Middle East Journal of Scientific Research*, 6(4), 333– 339.

Danielson, L. G., 1980. Cadmium, cobalt, copper, iron, lead, nickel and zinc in Indian Ocean water. *Marine Chemistry*, 8, 199–215.

Das, J., Das, S. N., Sahoo, R. K., 1997. Semidiurnal variation of some physico-chemical parameters in the Mahanadi estuary, East coast of India. *Indian Journal of Marine Sciences*, 26, 323 – 326.

Dassenakis, M. I., Kloukiniotou, M. A., Pavlidou, A. S., 1996. The influence of long existing pollution on trace metal levels in a small tidal Mediterranean bay. *Marine Pollution Bulletin*, 32, 275–282.

Dassenakis, M., Scoullos, M., Gaitis, A., 1997. Trace metals transport and behaviour in the Mediterranean estuary of Acheloos river. *Marine Pollution Bulletin*, 34, 103–111.

De Souza, S. N., 1983. Study on the behavior of nutrients in the Mandovi estuary during pre monsoon. *Estuarine Coastal Shelf Science*, 16, 299 – 308.

De Wolf, H., Backeljau, T., Blust, R., 2001. Heavy metal accumulation in the periwinkle Littorina littorea, along a pollution gradient in the Scheldt estuary. *Science of the Total Environment*, 262,111 –121.

Dean, H. K., 2008. The use of polychaete (Annelida) as indicator species of marine pollution: a review. *Revista de Biologia Tropical*, 56, 171–185.

Demayo, A., Taylor, M. C., Taylor K.W., Hodson, P.V., 1984. Toxic effects of lead and lead compounds on human health, aquatic life, wildlife, and livestock. *Critical Reviews in Environmental Control*, 12, 257 – 305.

Demayo, A., Taylor, M. C., Taylor, K. W., Hudson, P. V., 1984. Toxic effects of lead and lead compounds on human health, aquatic life, wildlife, and livestock. *Critical Review of Environment Control*, 12, 257–305.

Devassy, V. P., 1987. Trichodesmium red tides in the Arabian Sea, In: *Contribution to Marine Sciences,* Rao, T. S. S., Natarajan, R., Desai, B. N., Narayanaswamy, G., Bhatt, S. R. (Eds.), National Institute of Oceanography, Goa, pp. 60 – 61.

Diaz, M. A. H., Hinojosa, F. D., Ayon, M. H., Zavala, J. A. S., Esquivel, Z. G., Zarate, H. L., Valencia, A. S., Bect, S. G., 2008. Diagnosis of trace metal contamination in sediments: The example of Ensenada and El Sauzal, two harbors in Baja California, Mexico. *Marine Environmental Research*, 66, 345 – 358.

Diez, R., Riget, F., Cleeman, M., Aarkrog, A., Johansen, P., Hansen, J.C., 2000. Comparison of contaminants from different trophic levels and ecosystems. *Science of the Total Environment*, 245, 221–231.

Diez, G., Soto, M., Canton, L., Carmen Vaquero, M., Marigomez, I., 2000. Hediste (Nereis) diversicoloras bioindicator of metal and organic chemical bioavailability: a field study. *Ecotoxicology and Environmental Restoration*, 3, 7–15.

Dilli, K., 1986. Geochronology and geochemistry of a sediment core from Bombay coast. *Mahasagar*, 19, 87– 95.

Douben, P. E., 1989. Lead and cadmium in stone loach (Noemacheilus barbatulus L.) from three rivers in Derbyshire. *Ecotoxicology and Environmental Safety*, 18, 35–58.

Duinker, J. C., & Nolting, R. F., 1982. Dissolved Copper, Zinc and Cadmium in the Southern Bight of the North Sea. *Marine Pollution Bulletin*, 13(3), 93–96.

Duinker. J. C., & Nolting, R. F., 1977. Dissolved and Particulate trace metals in the Rhine estuary and the Southern Bight. *Marine Pollution Bulletin*, 8 (3), 65–70.

EC, (2001). *European Commision Regulation (EC) No. 466/2001 of 8 March 2001*. Official Journal of the European Communities, Brussels.

Eisler, R., 1981. *Trace metal concentration in marine organisms*, Pergamon Press, Oxford.

Eisler, R., 1985. *Cadmium hazards to fish, wildlife, and invertebrates: a synoptic review*. US Fish and Wildlife Service Report, 85, Washington, DC, USA.

Eisler, R., 1986. *Chromium hazards to fish, wildlife, and invertebrates: a synoptic review*. US Fish and Wildlife Service Report, 85(1.6), Washington DC, USA.

Eisler, R., 1987. *Mercury hazards to fish, wildlife, and invertebrates: a synoptic review*. US Fish and Wildlife Service Report, 85(1.10), Washington DC, USA.

Eisler, R., 1988. *Lead hazards to fish, wildlife, and invertebrates: a synoptic review*. US Fish and Wildlife Service, Washington DC, USA.

Eisler, R., 1993. *Zinc hazards to fish, wildlife, and invertebrates: a synoptic review*. US Fish and Wildlife Service Biological Report, 10, Washington, DC, USA.

Eisler, R., 1998. *Copper hazards to fish, wildlife, and invertebrates: a synoptic review*. US Fish and Wildlife Service Biological Report, 33, Washington, DC, USA.

El Nemr, A. M., Khaled, A., Sikaily, A., 2006. Distribution and Statistical Analysis of Leachable and Total Heavy metals in the sediments of the Suez gulf. *Environmental Monitoring and Assessment,* 118, 89 – 112.

El Nemr, A. M., Sikaily, A., Khaled, A., 2007. Total and Leachable Heavy metals in muddy and sandy sediments of Egyptian Coast along Mediterranean Sea. *Environmental Monitoring and Assessment,* 129, 151 – 168.

Eleftheriadou, M., & Skoullos, M., 2003. Nutrient and Trace metal distribution in the Gulf of Astakos, Aetoloakarnania, Greece. *Global Nest,* 5(3), 27–133.

El wakeel, S. K., & Riley, J. P., 1957. Determination of organic carbon in the marine muds. J*ournal du Conseil International Pouri Exploration de Lamar*, 22, 180–183.

Environment Canada, 2005. *Inorganic mercury and methyl mercury*. National Guidelines and Standards Office, Environment Canada, available at: http://www. Gaag_mercury_wqg_e.pdf.

EPA (US Environmental Protective Agency), 1980. *Experimental/ Engineering support for EPA'S FBC Program: Final Report- Vol II. Pariculate, Nitrogen Oxide and Trace Element Control.* US Environmental Protection Agency, EPA- 600/7-80-015b, Research Triangle Park, NC.

Eustace, I. J., 1974. Zinc, Cadmium, copper, and manganese in species of finfish and shellfish caught in the Derwant Estuary, Tasmania. *Australian Journal of Marine and Freshwater Research*, 25, 209 – 220.

Evans, D. W., Doodo, D. K., Hanson, P. J., 1993. Trace elements concentrations in fish livers -Implications of variations with fish size in pollution monitoring. *Marine Pollution Bulletin*, 26, 329 – 334.

Everaarts, J. M., & Fischer, C. V., 1992. The distribution of heavy metals (Cu, Zn, Cd, Pb) in the fine fraction of surface sediments of the North Sea. *Netherlands Journal of Sea Research*, 29(4), 323 – 331.

Faganeli, J., 1983. Organic nitrogen and phosphorus in the Gulf of Trieste (N. Adriatic). *Archives Oceanography* and *Limnology*, 20, 153–177.

Falkowski, P. G., Richards, T., Smetacek, V., 1998. Biogeochemical controls and feedbacks on ocean primary production. *Science*, 281, 200–206.

Falusi, B. A., & Olanipekun, E. O., 2007. Bioconcentration factors of heavy metals in tropical crab (Carcinussp) from river Aponwe, Ado-Ekiti, Nigeria, *Journal of Applied Sciences and Environmental Management,* 11, 51–54.

FAO, 1983. Compilation of legal limits for hazardous substances in fish and fishery products. *Food and Agriculture Organisation (FAO),* Fishery Circular No. 464, 5–100.

FAO-WHO, 1972. *Evaluation of certain food additives and the contaminants mercury, lead, and cadmium (Sixteenth report of the Joint FAO/WHO Expert Committee on Food Additives)*. WHO Technical Report Series No. 505, Hague.

FAO-WHO, 1989. *Evaluation of certain food additives and contaminants (Thirty-third report of the Joint FAO/WHO Expert Committee on Food Additives)*. WHO Technical Report Series No. 776, Hague.

FAO-WHO, 1990. *Evaluation of certain food additives and contaminants (Thirty-fifth report of the Joint FAO/WHO Expert Committee on Food Additives)*. WHO Technical Report Series No. 789, Hague.

Fatoki, O. S., & Mathabatha, S., 2001. An assessment of heavy metal pollution in the East London and Port Elizabeth harbours. *Water SA*, 27(2), 233–240.

Fauchald, K., 1977. *The Polychaete Worms- Definitions and Keys to the Orders, Families and Genera*. Science Series. Natural History Museum, Los Angeles.

Fauchland, K., & Jumars, P. A., 1979. The diet of worms: a study of polychaete feeding guilds, *Oceanography and Marine Biology: Annual Review*, 17, 193–284.

Fauvel, P., 1953.The *fauna of India including Pakistan, Ceylon, Burma and Malaya*. Indian Press, Allahabad.

Fevzi Yilmaz, 2009. The Comparison of Heavy Metal Concentrations (Cd, Cu, Mn, Pb, and Zn) in Tissues of Three Economically Important Fish (*Anguilla anguilla*, *Mugilcephalus* and *Oreochromis niloticus*) Inhabiting Köycegiz Lake-Mugla(Turkey). *Turkish Journal of Science and Technology*, 4(1), 7–15.

Fisher, N. S., & Reinfelder, J. R., 1995. The trophic transfer of metals in marine systems, In: *Metal speciation and bioavailability in aquatic systems*, Tessier, A., Turner, D. R. (Eds.), Wiley, pp. 363–406.

Folk, R. L., 1974, *Petrology of Sedimentary Rocks*. Hemphill Press, Austin, TX.

Forstner, U., & Muller, G., 1973. Heavy metal accumulation in river sediments a response to environment pollution. *Geoforum*, 14, 83.

Forstner, U., & Wittman, G. T. W., 1981. *Metal pollution in the Aquatic Environment*. Springer, Berlin, Germany.

Fowler, S.W., Readman, J. W., Oregioni, B., Villeneure, J. P., McKay, K., 1993. Petroleum hydrocarbons and trace metals in near shore Gulf sediments and biota before and after the 1991 War: An assessment of temporal and spatial trends. *Marine Pollution Bulletin*, 27, 171 – 182.

Furness, R. W., & Rainbow, P. S., 1990. *Heavy Metals in the Marine Environment*. CRS Press, Florida, USA.

Galanopoulos, S., Vgenopoulos, A., Conispoliatis, N., 2009. Anthropogenic Heavy Metal Pollution in the Surficial Sediments of the Keratsini Harbor, Saronikos Gulf, Greece. *Water Air Soil and Pollution,* 202, 121–130.

Gallegos, C. L., & Jordon, T. E., 1997. Seasonal progression of factors limiting phytoplankton pigment biomass in Rhode river estuary- Maryland (USA) II- Modeling N versus P limitation. *Marine Ecology Progress Series*, 161, 199 – 212.

Garnier, J., Billen, G., Palfner, L., 2000. Understanding the oxygen budget and related ecological processes in the river Mosel: The Riverstrahler approach. *Hydrobiologia*, 410, 151 – 166.

Garrett, R.G., 2007. Natural sources of metals in the environment. *Human and Ecological Risk Assessment*, 6(6), 945–963.

Gaspic, Z., Ujevic, I., Zvonaric, T., Baric, A., 2007. Biomonitoring of trace metals (Cu, Cd, Cr, Hg, Pb, Zn) in Mali Ston Bay (eastern Adriatic) using the Mediterranean blue mussel (1998-2005), *Acta Adriatic*, 48 (1), 73–88.

Gattuso, J. P., & Smith, S. V., 2007. Coastal zone, In: *Encyclopedia of Earth*, Cleveland C. J. (Ed.), National Council for Science and the Environment Washington DC, available at http://www.eoearth.org/article/Coastal_zone.

Gattuso, J. P., Frankignoulle. M., Wollast, R., 1998. Carbon and carbonate metabolism in coastal aquatic systems. *Annual Review of Ecology, Evolution, and Systematics*, 29, 405 – 434.

Geetha Sasikumar, Krishnakumar, P. K., Bhat, G. S., 2006. Monitoring Trace Metal Contaminants in Green Mussel, Perna viridis from the Coastal Waters of Karnataka, Southwest Coast of India. *Archives of Environmental Contamination and Toxicology*, 51, 206–214.

GESAMP (Joint group of experts on the scientific aspects of marine pollution), 1982. *Protecting the Oceans from land based activities, land based sources and activities affecting the quality and uses of the marine, coastal and associated fresh water environment.* Report and studies no.71, pp.162.

GESAMP (Joint group of experts on the scientific aspects of marine pollution), 2001. *The evaluation of the hazards of harmful substances carried by ships*, Report and studies no.17, pp. 50.

Gesteira, G. J. L., & Dauvin, J. C., 2005. Impact of the Aegean Sea oil spill on the subtidal fine sand macrobenthic community of the Ares-BetanzosRia, Northwest Spain, *Marine Environmental Research*, 60, 289–316.

Gilbert, P. M., Biggs, D. C., McCarthy, J. J., 1982. Utilization of ammonium and nitrate during austral summer in the Scotia Sea. *Deep Sea Research*, 29, 837 – 850.

Glibert, P.M., Magnien, R., Lomas, M.W., Alexander, J., Fan, C., Haramoto, E., Tice, M., Kana, T.M., 2001. Harmful algal blooms in the Chesapeake and coastal bays of Maryland, USA: comparison of 1997, 1998 and 1999 events. *Estuaries*, 24, 875–883.

Goldberg, E. D., 1992. Marine metal pollutants. *Marine Pollution Bulletin*, 14, 45 – 47.

Goldberg, E. D., 1995. Emerging problems in the coastal zone for the twenty-first century. *MarinePollution Bulletin*, 31, 152–158.

Gopinath, A., Neema Joseph, Sujatha, C.H., Nair, S.M., 2002. Forms of Nitrogen (NO_3-N; NO_2-N and NH_2CONH_2-N) and their relations to A.O.U. in the Indian Coastal waters of Arabian Sea. *Chemistry and Ecology*, 18, 233–244.

Gopinath, A., Nair, S. M., Kumar, N. C., Jayalakshmy, K.V., Pamalal, D., 2010. A baseline study of trace metals in a coral reef sedimentary environment, Lakshadweep Archipelago. *Environmental Earth Sciences*, 59(6), 1245–1266.

Govindasamy, C., & Kannan, L., 1996. Ecology of rotifers of pichavaram mangroves, southeast coast of India. *India Hydrobiologia*, 1, 69 – 76.

Govindasamy, C., & Azariah, J., 1999. Seasonal variation of heavy metals in coastal water of the Coromandel coast,Bay of Bengal, India. *Indian Journal of Marine Sciences,* 28, 249–256.

Govindasamy, C., Kannan, L., Azariah, J., 2000. Seasonal variation in physico- chemical properties and primary production in the coastal water biotopes of Coromandel Coast, India. *Journal of Environmental Biology*, 21(1), 1 – 7.

Govindasamy, C., Viji, R. G., Azariah, J., 1997. Seasonal variation of heavy metals in water and zooplankton of Pondicherry coast, Bay of Bengal. *International Journal* of *Environmental Science and Technology,* 23, 10–16.

Gowda, G., Gupta, T. R. C., Rajesh, K. M., Gowda, H., Lingadhal, C., Ramesh, A. M., 2001. Seasonal distribution of phytoplankton in Nethravathi estuary, Mangalore. *Journal of Marine Biological Association of India,* 43 (1, 2), 31– 40.

Grasshoff, K., 1999. *Methods of seawater analyses*.Verlag Chemie, Weinheim.

Grathwohl, P., 1990. Influence of organic matter from soils and sediments from various of the sorption of some chlorinated aliphatic hydrocarbons. *Environmental Science and Technology*, 24, 1687–1693.

Gray, J. S., 2002. Biomagnification in marine systems: The perspective of an ecologist. *Marine Pollution Bulletin*, 45, 46–52.

Greenpeace, 2003. *Status of Periyar's health at the Eloor industrial estate, Kerala India*. Greenpeace Research Laboratories, University of Exeter.

Groot, A., Zshuppe, K., Salomons, W., 1982. Standardization of methods of analysis for heavy metals in sediments. *Hydrobiologia*, 92, 689– 695.

Halcrow, W., Mackay, D. W., Thornton, I., 1973. The distribution of trace metals and fauna in the firth of Clyde in relation to the disposal of sewage sludge. *Journal of the Marine Biological Association of the United Kingdom*, 53, 721– 739.

Hall, L., & Chang- Yen, I., 1986. Metals in Seawater off Trinidad, West Indies. *Marine Pollution Bulletin*, 17(7), 332–333.

Hammond, A., 1971. Mercury in the environment: natural and human factors. *Science*, 171, 788.

Hanninen, J., Vuorinen, I., Helminen, H., Kirkkala, T., Lehtila, 2000. Trends and gradients in nutrient concentrations and loading in the archipelago sea, Northern Baltic, in 1997. *Coastal and Shelf Science*, 50, 153 – 171.

Harrison, P. J., Hu, M. H., Yang, Y. P., Lu, X., 1990. Phosphate limitation in estuarine and coastal waters of China. *Journal of Experimental Marine Biology and Ecology*, 140, 79– 87.

Heath, A. G., 1995. *Water Pollution and Fish Physiology*. CRC Press, Boca Raton, Florida, USA.

Heyvaert, A. C., Reuter, J. E., Sloton, D. G., Goldman, C. R., 2000. Paleo-limnological reconstruction of historical atmospheric lead and mercury deposition at Lake Tahoe, California–Nevada. *Environmental Science and Technology*, 34, 3588–3597.

Hildebrand, M., 2000. Silicic acid transport and its control during cell wall silicification in diatoms, In: *Biomineralization: From Biology to Biotechnology and Medical Application*, Baeuerlein, E. (Ed.), Wiley-VCH, New York, pp. 176 –188.

Hoare, K., Davenport, J., Beaumont, A. R., 1995. Effects of exposure and previous exposure to copper on growth of veligar larvae and survivorship of Mytilus edulis juveniles. *Marine Ecology Progress Series*, 120, 163 –168.

Hobbie, J. E., 2000. Estuarine science: the key to progress in coastal ecological research, In: *Estuarine Science: a synthetic approach to research and practice,* Hobbie, J. E. (Ed.), Island Press,Washington DC, pp. 1–11.

Holdway, D. A., 1988. The toxicity of Chromium to Fish, In: *Chromium in the Natural and Human Environments*, Nriagu, J.O., Nieboer, E. (Eds.), John Wiley and Sons, New York, pp. 369 – 397.

Hudson, R. J. M., Covault, D. T., Morel, F. M. M., 1992. Investigations of iron coordination and redox reactions in seawater using 59Fe radiometry and ion-pair solvent extraction of amphiphilic iron complexes. *Marine Chemistry*, 38, 209–235.

Hursthouse Andrew, S., Matthews Joy, M., Figures Julie, E., Iqbal-Zahid Parveen, Davies Ian, M., Vaughan D. H., 2003. Chromiumin intertidal sediments of the Clyde, UK: Potentialfor remobilisation and bioaccumulation. *Environmental Geochemistry and Health*, 25,171–203.

ICMAM (Integrated Coastal and Marine Area Management), 2010. Report on Assessment of pollution in Coastal waters of India, MoES, Chennai, pp. 289.

Idardare, Z., Chiffoleau, J. F., Moukrim, A., AitAlla, A., Auger, D., Lefrere, L., Rozuel, E., 2008. Metal concentration in sediment and Nereisdiversicolor in two Moroccan lagoons: Khnifiss and Oualidia. *Chemistry and Ecology*, 24, 329–340.

Imeri, A., Mullaj, A., Babani, F., Yill, A., 2008. Evaluation of trophic state in Bishtaraka Lagoon. *BALWOIS, 27*, 1–7.

Institute of Medicine, 2001. *Dietary Reference Intakes for Vitamin A, Vitamin K, Arsenic, Boron, Chromium, Copper, Iodine Iron, Manganese, Molybdenum, Nickel, Silicon, Vanadium, and Zinc*. National Academic Press, Washington DC, USA.

Inzunza, J. R., & Osuna, F., 2008.Trophic Distribution of Cd, Pb, and Zn in a Food Web from Altata-Ensenada del Pabello´n Subtropical Lagoon, SE Gulf of California. *Archives of Environmental Contamination and Toxicology*, 54,584 – 596.

Ismail, P., & Samin, K., 1987. Heavy metal content in fish from Sarawak waters, In: *A study on the offshore waters of the Malayasian EEZ*, Mohsin, A. K. H., Mohammed, M. I. H. (Eds.), Universiti Pertanian, Malaysia, pp. 157– 161.

Iyer, C. S., Sindhu, M., Kulkarni, S. G., Tambe, S. S., Kulkarni, B. D., 2003. Statistical analysis of the physico chemical data on the coastal waters of Cochin. *Journal of Environmental Monitoring*, 5, 324 – 327.

Janicki, K., Dobrowolski, J., Krasnicki, K., 1987. Correlation between contamination of the rural environment with mercury and occurrence of leukaemia in men and cattle. *Chemosphere*, 16, 253 – 257.

Jargensen, L. A., & Pedersen, B., 1994. Trace metals in fish used for time trend analysis and as environmental Indicators. *Marine Pollution Bulletin*, 28 (4), 235 – 243.

Jickells, T. D., 1988. Nutrient biogeochemistry of the coastal zone. *Science*, 281, 217–222.

Joice Thomas, V., Sreedevi, C., MadhusoodanaKurup, 2006. Variations on the infaunal polychaetes due to bottom trawling along the inshore waters of Kerala (south-west coast of India). *Indian Journal of Marine Sciences*, 35, 249–256.

Kagi, J. H., & Schaffer, A., 1988. Biochemistry of Metallothionein. *Biochemistry,* 27, 8509–8515.

Kaladharan, P., Pillai, V. K., Nandakumar, A., Krishnakumar, P. K., 1999. Mercury in seawater along the west coast of India. *Indian Journal of Marine Sciences*, 28, 338–340.

Kaladharan, P., Krishnakumar, P. K., Prema, D., Nandakumar, A., Khambadkar, L. R., Valsala, K. K., 2011. Assimilative capacity of Cochin inshore waters with reference to contaminants received from the backwaters and the upstream areas. *Indian Journal of Fisheries*, 58(2), 75– 83.

Kalimurthy, M., 1973. Observations on the transparency of the waters of the Pulicat Lake with particular reference to plankton production. *Hydrobiologia*, 41, 3– 11.

Karadede, H., Seyit, A., Erhan, U., 2004. Heavy metals in mullet, *Liza abu*, *catfish* and *Silurustriostegus*from the Atatürk Dam Lake (Euphrates), Turkey. *Environment International*, 30, 183–188.

Kemp, W. M., Boynton, W. R., Adolf, J. E., Boesch, D. F., Boiciurt, W. C., 2005. Eutrophication of Chesapeake Bay: historical trends and ecological interactions. *Marine Ecology Progress Series*, 303, 1–29.

Khan, A. T., & Weis, J. S., 1993. Bioaccumulation of heavy metals in two populations of mummichog (*Fundulus heteroclitus*). *Bulletin of Environmental Contamination and Toxicology*, 51, 1–5.

Khan, Y. S. A., Hossain, M. S., Hossain, S. M. G., Halimuzzaman, A. H. M., 1998. An Environmental assessment of trace metals in the Ganges-Brahmaputra- Meghna estuary. *Journal of Remote Sensing and Environment*, 2,103–117.

Kissao, G., Seunghee, H., Hassan R. B. M., Magali, P., Dimitri D. D., 2011. Increased Bioavailability of Mercury in the Lagoons of Lome´, Togo: The Possible Role of Dredging. *AMBIO*, 40, 26–42.

Kramer, K., 1994. Selecting a model to predict the onset of growth of *Fagus Sylvatica*. *Journal of Applied Ecology*, 31, 172–182.

Krishna Kumari, L., Sujata Kaisary, Veera Rodrigues, 2006. Bioaccumulation of some trace metals in the short- neck clam *Paphia malabarica* from Mandovi estuary, Goa. *Environment International*, 32, 229 – 234.

Krishnakumar, P.K., & Bhat, G.S., 2008. Seasonal and interannual variations of oceanographic conditions off Mangalore coast (Karnataka, India) in the Malabar upwelling system during 1995- 2004 and their influences on the pelagic fishery. *Fisheries Oceanography*, 17, 45 – 60.

Krishnakumar, P.K., & Pillai, V. K., 1990. Mercury near a caustic soda plant at Karwar, India. *Marine Pollution Bulletin*, 21, 304– 307.

Krishnamurti, A. J., & Vijayalakshmi R. Nair, 1999. Concentration of metals in fishes from Thane and Bassein creeks of Bombay, India. *Indian Journal of Marine Sciences*, 28, 39 – 44.

Kronvang, B., Ertebjerg, G., Grant, R., Kristensen, P., Hovmand, M., Kirkegaard, J., 1993. Nationwide monitoring of nutrients and their ecological effects: State of the Danish aquatic environment. *Ambio*, 22, 176 – 187.

Kulkarni, V. V., & Desai, M. U. M., 1980. *Pollution studies on Ulhas River*. International seminar on Management of Environment, BARC, Bombay.

Kureishy, T. W., Sanzgiry, S., Braganca, A., 1981. Some heavy metals in fishes from the Andaman Sea. *Indian Journal of Marine Sciences*, 10, 303–307.

Kureishy, T. W., Sanzgiry, S., George, M. D., Braganca, A., 1983. Mercury, Cadmium and Lead in different tissues of fishes and in zooplankton from the Andaman Sea. *Indian Journal of Marine Sciences*, 12, 60 – 63.

Kurland, L., 1960. The outbreak of neurologic disorder in Minamata, Japan and its relationship to the ingestion of seafood contamination by mercuric compounds. *World Neurology*, 1, 370 – 395.

Kuwabara, J.S., Chang, C.C.Y., Cloern, J.E., Fries, T.L., Davis, J.A., Louma, S.N., 1989. Trace metal association in the water column of southern San Francisco bay, California. *Estuarine Coastal and Shelf Science,* 28, 307–325.

Kwon, Y. T., & Lee, C. W., 2001. Ecological risk assessment of sediment in waste water discharging area by means of metal speciation. *Microchemical Journal,* 70, 255 – 264.

Lakshmanan, P. T., Shynamma, C.S., Balchand, A. N., Nambisan, P. N., 1987. Distribution and variability of nutrients in Cochin backwaters, southwest coast of India. *Indian Journal of Marine Sciences,* 16, 99 – 102.

Lal, D., 1978. Transfer of Chemical species through estuaries to Oceans, In: *Proceedings of a UNESCO/SCOR workshop on Biogeochemistry of estuarine sediments*, Melreus, Belgium, pp. 166–170.

Lapedes, D.N., 1974. *Dictionary of Scientific and Technical Terms*, McGraw Hill, New York.

Lawson, T. B., 1995. *Fundamentals of Aquacultural Engineering*. Chapman and Hall, New York.

Le Jeune, A. H., Charpin, M., Sargos, D., Lenain, J. F., Deluchat, V., Ngayila, N., Baudu, M., Amblard, C., 2007. Planktonic microbial community responses to added copper. *Aquatic Toxicology,* 83, 223–237.

Lesaca, R. M., 1977. *Monitoring of heavy metals in Phillippine rivers, bay waters and lakes*. Symposium proceedings on International conference of Heavy Metals- Environment, Toronto.

Li, Y. H., & Schoonmaker, J. E., 2005. Chemical composition and mineralogy of marine sediments, In: *Sediments, Diagenesis, and sedimentary Rocks, volume 7, First Edition: Treatise on Geochemistry*, Mackenzie, F.T., Holland, H. D., Turekian, K. K. (Eds.), Elsevier- Pergamon, Oxford, pp. 1– 35.

Liss, P. S., & Spencer, C. P., 1970. A biological process in the removal of silicate from sea water. *Geochimica Cosmochimica Acta*, 34, 1073 – 1088.

Liu, C.W., Lin, K. H., Kuo, Y. M., 2003. Application of factor analysis in the assessment of groundwater quality in a black foot disease area in Taiwan. *Science of the Total Environment*, 313, 77 – 89.

Locarnini, S. J. P., & Presley, B. J., 1996. Mercury concentrations in benthic organisms from a contaminated estuary. *Marine Environmental Research*, 41, 225–239.

Long, E. R., MacDonald, D. D., Smith, S. C., Calder, F. D., 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental Management*, 19(1), 81– 97.

Long, E. R., Field, L. J., MacDonald, D. D., 1997. Predicting toxicity in marine sediments with numerical sediment quality guidelines. *Environmental Toxicology Chemistry*, 17 (4), 714 – 727.

Lorenzen, C. J., 1967. Determination of chlorophyll and phaeopigments spectrophotometric equations. *Limnology Oceanography*, 12, 343 – 347.

Loring, D. H., & Prosi, F., 1986. Cadmium and lead cycling between water, sediments, and biota in an artificially contaminated mud flat on Borkum (F.R.G.). *Water Science*, 18,131 – 139.

Loring, D. H., & Rantala, R. T. T., 1992. Manual for geochemical analysis, *Earth Science Reviews*, 32, 235–283.

Luo, W., Yonglong, L., Tieyu, W., Wenyou, H., Wentao, J., Jonathan, N., Jong, S. K., John, G., 2010. Ecological risk assessment of arsenic and metals in sediments of coastal areas of northern Bohai and Yellow Seas, China. *AMBIO*, 39,367–375.

Luoma, S. N., & Bryan, G. W., 1982. A Statistical study of Environmental factors controlling concentrations of heavy metals in the burrowing bivalve Scrobicularia plana and the polychaete Nereis diversicolor. *Estuarine coastal and Shelf science*, 15, 95 – 108.

Luoma, S. N., & Rainbow, P. S., 2008. *Metal*. Cambridge University Press, New York.

Luoma, S.N., 1986. *Cycling of Pb into food webs in aquatic environments*. Report for the commission on Lead in the Environment, The Royal Society of Canada, Toronto.

Mackay, D., & Fraser, A., 2000. Bioaccumulation of persistent organic chemicals: mechanisms and models. *Environment Pollution*, 110, 375–391.

Mackey, A. P., Hodgkinson, M., Nardella, R., 1992. Nutrient levels and heavy metals in mangrove sediments from the Brisbane River, Australia. *Marine Pollution Bulletin*, 24,418 – 420.

Madhupratap, M., 1987. Status of zooplankton of tropical Indian estuaries - A review. *Bulletin of Plankton Society of Japan*, 34, 65 – 81.

Madhupratap, M., Nair, K. N. V., Gopalakrishnan, T. C., Haridas, P., Nair, K. K. C., Venugopal, P., Gauns, M., 2001. Arabian Sea oceanography and fisheries off the west coast of India. *Current Science*, 81, 355 – 361.

Magalhaes, M. C., Costa, V., Menezes, G. M., Pinho, M. R., Santos, R. S., Monteiro, L. R., 2007. Intra and inter specific variability in total and methylmercury bioaccumulation by eight marine fish species from the Azores. *Marine Pollution Bulletin*, 54, 1654 – 1662.

Maheswari, N., Balachandran, K. K., Sankaranarayanan, V. N., Joseph, T., 1997. Heavy metals in fishes from coastal waters off Cochin, southwest coast of India. *Indian Journal of Marine Sciences*, 26, 98– 100.

Maheswari, N., Jayalakshmy, K.V., Balachandran, K. K., Joseph, T., 2006. Bioaccumulation of Toxic Metals by Fish in a Semi-Enclosed Tropical Ecosystem. *Environmental Forensics*, 7, 197– 206.

Mahloch, J. L., 1974. Multivariate Techniques for Water Quality Analysis. *Journal of Environmental Engineering*, 5, 1119–1132.

Mamdouh, A. F., 2003. Water quality in the Red sea coastal waters (Egypt): Analysis of Spatial and Temporal variability. *Chemistry and Ecology*, 19, 67–77.

Mance, G., 1984. *Proposed environmental quality standards for chromium in waters and associated materials*. Water Research Center Technical Report- 268-M, Stevenage.

Manjunatha, B. R., Yeats, P. A., Smith, J. N., Shankar, R., Narayana, A. C., Prakash, T. N., 1998. Accumulation of heavy metals in sediments of marine environments along the SW coast of India. *Proceedings of Internaional Atomic Energy Agency*, IAEA-SM-534/51.

Mansour, S. A., & Sidky, M. M., 2002. Ecotoxicological studies - Heavy metals contaminating water and fish from Fayoum Governorate, Egypt. *Food Chemistry*, 78, 15– 22.

Maria, J. B., Oihana, S., Victoriano, V., Victor, P., 2004. Contaminants in estuarine and coastal water, In: *Oceanography and Marine Environment of The Basque Country*, Borja, A., Collins, M. (Eds.), Elsevier Oceanography Series, Amsterdam, pp. 312– 326.

Mart, L., & Nurnberg, H. W., 1986. Cd, Pb, Cu, Ni and Co distribution in the German Bight. *Marine Chemistry*, 18, 197–213.

Martin, D.F. (1970). *Marine Chemistry*. Marcel Dekker Inc., New York.

Martin, G. D., Vijay, J. G., Laluraj, C. M., Madhu, N. V., Joseph, T., Nair, M., Gupta, G. V. M., Balachandran, K. K., 2006. Fresh water influence on nutrient stoichiometry in a tropical estuary, southwest coast of India. *Applied Ecology and Environment Research*, 6(1), 57–64.

Martincic, D., Kwokal, Z., Branica, M., 1986. Distribution of zinc, lead,cadmium and copper between different size fractions of sediments I. The Limski Canal (North Adriatic Sea). *Science of the Total Environment*, 95, 201 – 215.

Martincic, D., Nurnberg, H. W., Branica, M., 1986. Bioaccumulation of heavy metals by bivalves from Limski Kanal. *Marine Chemistry*, 18, 299–319.

Maurer, D., Gerlinger, T., Robertson, G., Nguyen H., 1997. Trace metal bioaccumulation in soft-bottom macro benthos from the San Pedro Shelf, California. *Internationale Revue der gesamten Hydrobiologie und Hydrographie,* 82(2), 225- 245.

Mayer, L. M., 1988. Geochemistry of Chromium in Oceans, In: *Chromium in the natural and human environments*. Nriagu, J. O., Nieboer, E. (Eds.), Wiley, New York, pp. 110 – 173.

McConnaughey, R. A., & Smith, K. R., 2000. Associations between flatfish abundance and surficial sediments in the eastern Bering Sea. *Canadian Journal of Fisheries and Aquatic Sciences*, 57, 2410–2419.

McLusky, D. S., Bryant, V., Campbell, R., 1986. The effects of temperature and salinity on the toxicity of heavy metals to marine and estuarine invertebrates. *Oceanography and Marine Biology Annual Review*, 24, 481 – 520.

Meglen, R. R., 1992. Examining large databases: a chemometric approach using principal component analysis. *Marine Chemistry*, 39, 217– 237.

Menon, A. G. K., 1984. Cynoglossidae, In: *Western Indian Ocean fishing area*, Fischer, W., Bianchi G. (Eds.), FAO species identification sheets for fishery purposes, Rome, pp. 50 - 51.

Menon, N. N., Balchand, A. N., Menon, N. R., 2000. Hydrobiology of the Cochin backwater system- a review. *Hydrobiologia*, 430, 149–183.

Mito, K., 1974. *Food relationships among benthic fish populations in the Bering Sea*, Ms Thesis, Hokkaido University, Hokkaido, Japan.

Mitra, A., Patra K. C., Panigrahy, R. C., 1990. Seasonal variations of some hydrographical parameters in a tidal creek opening in to the Bay of Bengal. *Mahasagar Bulletin National Institute of Oceanography*, 23(1), 55 – 62.

Mohamed, N. I., 1991. *Biological and biochemical studies of some Siganid fishes from the Mediterranean waters off Alexandria*, Doctoral Thesis, Alexandria University, Egypt.

Moore, J. W., & Ramamoorthy, S., 1984. *Heavy metals in Natural waters- Applied monitoring and Impact Assessment*. Springer - Verlag, New York.

Mountouris., Voutsas, E., Tassios, D., 2002. Bioconcentration of heavy metals in aquatic environments: the importance of bioavailability. *Marine Pollution Bulletin*, 44, 1136–1141.

Muller, G., 1979. Schwermetalle in den sedimenten des Rheins – Vera nderungenseitt 1971. *Umschau*, 79, 778 – 783.

Muller, G., 1981. Die Schwermetallbelastung der sediment des Neckars und seiner Nebenflusse: eine Bestandsaufnahme. *Chemical Zeitung*, 105,157 –164.

Mustafa, H. M., & Collins, K. J., 1995. Heavy metal concentrations in sea urchin tissues from Egypt, Ireland and United Kingdom. *Chemistry and Ecology*, 10, 181–190.

Muyssen, B. T. A., Brix, K. B., De Forest, D. K., Janssen, C. R., 2004. Nickel essentiality and homeostasis in aquatic organisms. *Environmental Reviews*, 12,113–131.

Naidu, A. S., & Shankar, R., 1999. Palaeomonsoon history during the last Quaternary: Results of a Pilot study on sediments from the Laccadive trough, Southeastern Arabian Sea. *Journal of Geological Society of India*, 53, 401 – 406.

Naidu, J. R., & Shringarpure, S. G., 1975. Hydrological characteristics of the Bombay harbour bay. *Journal of the Marine Biological Association of India*, 17, 82 – 86.

Nair, M. N. M., & Ramachandran, K. K., 2002. Textural and trace elemental distribution in sediments of the Beypore estuary (SW coast of India) and adjoining inner shelf. *Indian Journal of Marine Sciences*, 31(4), 295–304.

Nair, M., Jayalakshmy, K.V., Balachandran, K. K., Joseph, T., 2006. Bioaccumulation of Toxic Metals by Fish in a Semi-Enclosed Tropical Ecosystem. *Environmental Forensics*, 7, 197– 206.

Nair, R. R., 1976. Unique Mud Banks, Kerala, Southeast India. *American Association on Petroleum Geologists Bulletin*, 66(4), 617 –621.

Nair, R. R., & Murthy, P. S. N., 1968. Clay mineralogy of Mud banks of Cochin. *Current Science*, 87 (20), 589 –590.

Nakatsuka, S., Okamura, K., Norisuye, K., Sohrin, Y., 2007. Simultaneous determination of suspended particulate trace metals (Co, Ni, Cu, Zn, Cd and Pb) in seawater with small volume filtration assisted by microwave digestion and flow injection inductive coupled plasma mass spectrometer. *Analytica Chimica Acta*, 594, 52 – 60.

Nalewajko, C., & Lean, D. R., 1980. Phosphorus, In: *The Physiological, Ecology of Phytoplankton*, Morris (Ed.), Oxford: Blackwell Science Publisher, pp. 235–258.

Naqvi, S. W. A., Jayakumar, D. A., Narvekar, P. V., Naik, H., Sarma, V. V. S., De Souza W., Joseph, S., George, M. D., 2000. Increased marine production of N_2O due to intensifying anoxia on the Indian continental shelf. *Nature*, 408, 346 – 349.

Naqvi, S. W. A., Naik, H., Pratihary, A., D"Souza, W., Narvekar, P.V., Jayakumar, D. A., Devol, A. H., Yoshinari, T., Saino, T., 2006. Coastal versus open – ocean denitrification in the Arabian Sea. *Biogeosciences*, 3, 621– 633.

Naqvi, S. W. A., & Unnikrishnan, A. S., 2010. Hydrography and biogeochemistry of the coastal ocean, In: *Surface Ocean – Lower Atmosphere Processes*, Corinne, L. Q., Eric, S.S. (Eds.), American Geophysical union, Florida,pp. 243– 250.

Nelson, D. W., & Sommers, L. E., 1996. Total carbon, organic carbon, and organic matter, In: *Methods of Soil Analysis, Part 3: Chemical Methods,* Sparks, D. L., Page, A. L., Helmke, P. A., Loeppert, R. H., Soltanpour, P. N., Tabatabai, M. A., Johnston, C. T., Sumner, M. E. (Eds.), American Society of Agronomy, Inc. and Soil Science Society of America, Inc., Madison,Wisconsin, pp. 961-1010.

Nicholas, B. H., Adina, P., Christopher, P. H., Richard, G. L., Alexandria, B. B., 2006. Human development is linked to multiple water body impairments along the California Coast. *Estuaries and Coasts*, 29, 860–870.

Nobi, E., Dilipan, E., Thangaradjou, T., Sivakumar, K., Kannan, L., 2010. Geochemical and geo-statistical assessment of heavy metal concentration in the sediments of different coastal ecosystems of Andaman Islands, India. *Estuarine, Coastal and Shelf Science*, 87(2), 253 – 264.

NRC (National Research Council), (1980). *Committee on Dietary Allowances*. Food and Nutrition Board, USA.

NRCC (National Research Council of Canada), 1973. *Lead in Canadian Environment*. National Research Council of Canada, Ottawa.

Nriagu, J. O., 1980. *Cadmium in the Environment*. John Wiley & Sons, New York.

Nriagu, J. O., 1988. A silent epidemic of environmental metal poisoning. *Environmental Pollution*, 50, 139 – 161.

Nriagu, J. O., & Nieboer, E., 1980. Chromium in the Natural and Human Environments, In: *Advances in Environmental Science and Technology*, John Wiley and Sons, New York, pp.180 –212.

Nriagu, J., & Nieober, E., 1988. *Chromium in the natural and human environments*. Wiley Series, New York.

Nriagu, J.O., 1979. Copper in the atmosphere and precipitation, In: *Copper in the Environment. Ecological Cycling*, Nriagu, J.O. (Ed.), Wiley-Interscience, New York, pp. 43 – 75.

Olson, R. J., 1980. Nitrate and ammonium uptake in Antarctic waters. *Limnology and Oceanography*, 26, 1064 – 1074.

Orren, M. J., Eagle, G. A., Hennig, H. F. K. O., Green, A., 1980. Variations in trace metal content of the mussel *Choromytilus meridionalis* with season and sex. *Marine Pollution Bulletin*, 11, 253– 257.

Ouseph, P. P., 1992. Dissolved and particulate trace metals in the Cochin estuary. *Marine Pollution Bulletin*, 24, 186–192.

Owens, R. E., Balls, P. W., Price, N. B., 1997. Physicochemical processes and their effects on the composition of suspended particilate materials in estuaries: Implication for monitoring and modeling. *Marine Pollution Bulletin*, 34, 51 – 60.

Ozseker, E., & Eruz, C., 2011. Heavy Metal (Ni, Cu, Pb, Zn) Distribution in Sediments from the Coast of Trabzon in the Black Sea. *Indian Journal of Marine Science*, 40(1), 48– 54.

Pacunski, R. E., Livingston, P. A., Miller, B. S., 1998. *Food of the flathead sole Hippoglossoideselassodon in the eastern Bering Sea*.US Department of Commerce, NOAA Technical Memorandum, Boulder.

Paerl, W., 2009. Controlling Eutrophication along the Freshwater–Marine Continuum: Dual Nutrient (N and P) Reductions are Essential. *Estuaries and Coasts*, 32, 593–601.

Pane, E. F., Richards, J. G., Wood, C. M., 2003. Acute waterborne nickel toxicity in the rainbow trout (Oncorhynchus mykiss) occurs by a respiratory rather than iono regulatory mechanism. *Aquatic Toxicology*, 63, 65–82.

Panigrahy, P. K., Das, J., Das, S. N., Sahoo, R. K., 1999. Evaluation of the influence of various physico – chemical parameters on coastal water quality around Orissa by factor analysis. *Indian Journal of Marine Sciences*, 28, 360 – 364.

Panigrahy, P. K., Nayak, B. B., Acharya, B.C., Das, S. N., Basa, S. C., Sahoo, R. K., 1997. Evaluation of heavy metal accumulation in coastal sediments of northern Bay of Bengal, In: *Advances in Environmental Science*, Iyer C. S. P. (Ed.), Educational Book Publishers, New Delhi, pp 139 –146.

Panigrahy, R. C., Sahu, J. P., Mishra, P. M., 1984. Studies on some hydrographic features in the surface waters of Bay of Bengal at Gopalpur, Orissa coast. *Bulletin of Environmental Science,* 1, 10 –14.

Parizanganeh, A., Lakhan, V. C., Jalalian, H., 2007. A geochemical and statistical approach for assessing heavy metal pollution in sediments from the southern Caspian coast. *International Journal of Environment Science and Technology*, 4(3), 351 – 358.

Paropkari, A. L., 1990. Geochemistry of sediments from the Mangalore- Cochin shelf and upper slope off southwest India: Geological and environmental factors controlling dispersal of elements. *Chemical Geology,* 81, 99 – 119.

Paropkari, A. L., Prakash Babu, C., Mascarenhas, A., 1992. A Critical evaluation of depositional parameters controlling the variability of organic carbon in Arabian Sea sediments. *Marine Geology*, 107, 213– 226.

Patel, B., Bangera, V. S., Patel, S., Balani, M. C., 1985. Heavy metals in the Bombay Harbour Area. *Marine Pollution Bulletin*, 16, 22–28.

Patriarca, M., Menditto, A., Rossi, B., Lyon, T. D. B., Fell, G. S., 2000. Environmental exposure to metals of newborns, infants and young children. *Microchemical Journal,* 67, 351–61.

Pattan, J. N., Masuzawab, T., Naidu, P. D., Parthiban, G., Yamamoto, M., 2003. Productivity fluctuations in the southeastern Arabian Sea during the last 140 Ka. *Paleogeography, Palaeoclimatology, Palaeoecology*, 193, 575 –590.

Pekey, H., 2006. Heavy Metals Pollution Assessment in Sediments of the Izmit Bay, Turkey. *Environmental Monitoring and Assessment*, 123, 219-231.

Pentreath, R. J., 1976. The accumulation of inorganic mercury from sea water by the plaice, *Pleuronectesplatessa*. *Journal of Experimental Marine Biology and Ecology*, 25, 103 – 120.

Pettijohn, F.J., 1957. *Sedimentary Rocks (2nd edition)*. Harper and Row, New York.

Phillips, D. J. H., 1976. The use of biological indicator organisms to monitor trace metal pollution in marine and estuarine environments – a review. *Environmental Pollution*, 16,167–229.

Philips, D. J. H., 1977. The common mussel *Mytilus edulis* as an indicator of pollution by zinc, cadmium, lead and copper. Effects of environmental variables on uptake of metals. *Marine Biology*, 38, 59 – 69.

Phillips, D. J. H., 1980. *Quantitative Aquatic Biological Indicators*. Applied Science Publishers Ltd., London.

Philips, D. J. H., Thompson, G. B., Gabuji, K. M., Ho, C. T., 1982. Trace metals of toxicological significance to man in Hong Kong seafood. *Environmental Pollution Series B*, 3, 27– 45.

Phillips, D. J. H., & Rainbow, P. S., 1988. Barnacles and mussels as biomonitors of trace elements: a comparative study. *Marine Ecological Progress Series*, 49, 83–93.

Plaskett, D., & Potter, I. C., 1979. Heavy metal concentrations in the muscle tissue of 12 species of teleost from Cockburn Sound, Western Australia. *Australian Journal of Marine and Fresh water Research*, 30, 607– 616.

Potter, T. L., & Simmons, K. E., 1998. *Composition of petroleum mixtures-Total petroleum hydrocarbon criteria working group series volume 2*. Amherst Scientific Publishers. Amherst, MA.

Prafulla, V., Francis, L., Lakshmanan, P. T., 2001. Concentrations of Trace Metals in the Squids, *Loligo duvauceli* and *Doryteuthis sibogae* Caught from the Southwest Coast of India. *Asian Fisheries Science*, 14, 399 – 410.

Prasannakumar, S., Muralidharan, P. M., Prasad, T. G., Ganus, M., Ramaiah, N., De Souza, S. N., Sardesai, S., Madhupratap, M., 2002. Why is the Bay of Bengal less productive during summer monsoon compared to the Arabian Sea. *Geophysical Research Letters*, 29, pp 88.1– 88.4.

Price, N. M., & Morel, F. M. M., 1991. Co limitation of phytoplankton growth by nickel and nitrogen. *Limnology and Oceanography*, 36, 1071–1077.

Purushothaman, A., & Venugopalan, V. K., 1972. Distribution of dissolved Silicon in the Vellar Estuary. *Indian Journal of Marine Science*, 1, 103– 105.

Qasim, S. Z., & Sen Gupta, R., 1980. Present status of marine pollution in India, In: *Management of Environment*, Patel, B. (Ed.), Wiley Eastern Ltd., New Delhi, pp. 310–329.

Qasim, S. Z., 1977. Biological productivity of the Indian Ocean. *Indian Journal of Marine Science*, 6, 122– 137.

Qasim, S. Z., Bhattathiri, P. M. A., Abidi, S. A. H., 1968. Solar radiation and its penetration in tropical estuary. *Journal of Experimental Marine Biology and Ecology*, 2, 87 – 103.

Qasim, S. Z., & Sen Gupta, R., 1988. Some problems of coastal pollution in India. *Marine Pollution Bulletin*, 19,100 – 106.

Rainbow, P. S., & Philips, D. J. H., 1993. Cosmopolitan biomonitors of trace metals. *Marine Pollution Bulletin*, 26 (11), 593 – 601.

Rainbow, P. S., 1995. Biomonitoring of heavy metal availability in the marine environment. *Marine Pollution Bulletin*, 31 (12), 183 – 192.

Rainbow, P. S., 1997. Ecophysiology of trace metal uptake in Crustaceans. *Estuarine Coastal and Shelf Science*, 44, 169– 175.

Rajagopalan, M. S., Thomas, P. A., Mathew, K. J., Daniel Selvaraj, G. S., 1992. Productivity of the Arabian Sea along the southwest coast of India. *Bulletin of Central Marine Fisheries Research Institute*, 45, 9 – 37.

Rajamohan, R., Rao, T. S., Anup Kumar, B., Sahayam, A. C., Balaram Krishna, M. V., Venugopalan, V. P., Narasimhan, S. V., 2010. Distribution of heavy metals in the vicinity of a nuclear power plant, East coast of India: with emphasis on Copper concentration and primary productivity. *NISCAIR Online Periodicals Repository*, 39(2), 182 –191.

Rajashree, G., & Panigrahy, R. C., 1996. Ecology of phytoplankton in coastal waters off Gopalpur, East coast of India. *Indian Journal of Marine Sciences*, 2, 13–18.

Rajendran, A., Rajgopal, M. D., Reddy, C. V. G., 1980. Distribution of dissolved silicate in the Arabian Sea and Bay of Bengal. *Indian Journal of Marine Sciences*, 9, 172–178.

Rajesegar, M., 2003. Physico chemical characteristics of the Vellar estuary in relation to shrimp farming. *Journal of Environmental Biology*, 24(1), 95 – 101.

Ramaiah, N., & Nair, V. R., 1993. Population abundance and species composition of chaetognaths in the Bombay harbour – Thana and Bassein Creek estuarine complex. *Indian Journal of Marine Sciences*, 22, 89–93.

Ramaiah, N., & Nair, V. R., 1997. Distribution and abundance of copepods in the pollution gradient zones of creek, west coast of India. *Indian Journal of Marine Sciences*, 26, 20– 25.

Ramaiah, N., & Nair, V. R., 1998. Phytoplankton characteristics in a polluted harbour – Thana – Bassein creek estuarine complex. *Indian Journal of Marine Sciences*, 27, 281 – 285.

Ramaiah, N., Abbas, M. S., Nair, V. R., 1992. Distribution of decapod larvae in the Bombay harbour – Thana – Bassein Creek region. *Journal of the Indian Fisheries Association*, 22, 21 – 32.

Ramakrishnan, R., Perumal, P., Santhanam, P., 1999. Spatio- temporal variations of hydrographical features in the Pichavaram mangroves and Mohi aqua farm, Southeast coast of India. *International Seminar on Applied Hydrogeochemistry*, Annamalai University, India, 197 – 203.

Ramamurthy, V. D., 1979. Baseline study of the level of concentration of mercury in the food fishes of Bay of Bengal, Arabian Sea and Indian Ocean. *Bulletin of the Japanese Society of Scientific Fisheries*, 45 (11), 1405–1407.

Rao, C.V., & Satyanarayana Rao, T. S., 1974. Distribution of trace elements, iron, copper, manganese and cobalt in the Bay of Bengal. *Journal of Marine Biological Association of India*, 16, 94–112.

Rao, S. D. V., 1969. Asterionella Japonica bloom and discoloration off Waltair, Bay of Bengal, *Limnology and Oceanography*, 14, 632– 634.

Rao, V. P., Nair, R. R., Hashimi, N. H., 1983. Clay minerals distribution on the Kerala continental slope. *Journal of Geological Society of India*, 24, 540–546.

Reddy, S. M., Mehta, B., Dave, S., Joshi, M., Karthikeyan, L., Sarma, S. K. V., Basha, S., Ramachandraiah, G., Bhatt, P., 2007. Bioaccumulation of heavy metals in some commercial fishes and crabs of the Gulf of Cambay, India. *Current Science*, 92, 1489–1491.

Redfield, A. C., Ketchum, B. H., Richards, F. A., 1963. The influence of organisms on the composition of seawater, In: *The Sea*, Hill, M. N. (Ed.), Wiley Interscience, New York, pp. 26 – 77.

Reinfelder, J. R., Fisher, N. S., Luoma, S. N., Nichols, J. W., Wang, W. X., 1998. Trace element trophic transfer in aquatic organisms: a critique of the kinetic model approach. *Science of the Total Environment*, 219,117–135.

Reish, D. J., 1972. The use of marine invertebrates as indicators of varying degrees of marine pollution, In: *Marine and Sealife*, Ruivo, M. (Ed.), Fishing News Books Ltd., London, pp. 203– 207.

Rejomon, G., 2005. *Biogeochemistry of trace metals in the Indian Exclusive Ecnomic Zone (EEZ) of the Arabian Sea and Bay of Bengal*, Doctoral Thesis, Cochin University of Science and Technology, Cochin, India.

Rejomon, G., Nair, M., Joseph, T., 2010. Trace metal dynamics in fishes from the southwest coast of India. *Environmental Monitoring and Assessment*, 167 (4), 243–255.

Riisgard, H. U., & Hansen, S., 1990. Biomagnification of mercury in a marine grazing food-chain: algal cells *Phaeodactylum tricornutum*, mussels *Mytilus edulis* and flounders *Platichthys flesus* studied by means of a stepwise-reduction-CVAA method. *Marine Ecology Progress Series*, 62, 259– 270.

Riley, J. P., & Chester, R., 1971. *Introduction to Marine Chemistry*. Academic Press, London.

Roesijadi, G., & Robinson, W. E., 1994. Metals regulation in aquatic animals; mechanisms of uptake, accumulation and release, In: *Aquatic Toxicology (Molecular, Biochemical and Cellular Perspectives)*, Malins, D. C., Ostrander, G. K. (Eds.), Lewis, London, pp. 237–539.

Roth, I., & Hornung, H., 1977. Heavy metal concentrations in water, sediments and fish from Mediterranean coastal area, Israel. *Environmental Science and Technology*, 11, 265–269.

Rouse, G. W., & Pleijel, F., 2001. *Polychaetes*. Oxford University Press, New York.

Rubio, B., Nombela, M. A., Vilas, F., 2000. Geochemistry of Major and Trace Elements in Sediments of the Ria de Vigo (NW Spain): an Assessment of Metal Pollution. *Marine Pollution Bulletin*, 40(11), 968–980.

Ryther, J. H., 1969. Photosynthesis and fish production in the sea. *Science*, 166, 72–76.

Sabnis, M. M., 1984. *Studies of some major and minor elements in the polluted Mahim River Estuary*. Ph.D. Thesis, University of Mumbai.

Sadiq, M., 1992. *Toxic metal chemistry in marine environment*. Marcel Dekker Inc., New York.

Saha, J. G., 1972. Significance of mercury in the environment. *Residue Review*, 42, 103–163.

Saha, M., Sarkar, S. K., Bhattacharya, B., 2006. Interspecific variation in heavy metal body concentrations in biota of Sunderban mangrove wetland, northeast India. *Environment International*, 32, 203–207.

Sahu, A., Panigrahi, M. K., Sahu, S. K., Panigrahi, A. K., 2002. Aquatic mercury pollution by a chlor alkali industry and its impact on the ecology of human health in Ganjan Area- A case study, In : *Ecology of Polluted waters*, Kumar, A. (Ed.), New Delhi, pp.465 –496.

Sahu, K. C., & Panda, D. K., 1987. Mercury contamination in Rushikulya estuary near Ganjam,Orissa, In: *Proceedings in Role of Earth Sciences in Environment, Indian institute of Technology*, Sahu, K. C., (Ed.), New Delhi, pp.181 – 912.

Saiz-Salinas, J. I., Ruiz, J. M., Frances-Zubillaga, G., 1996. Heavy metal levels in intertidal sediments and biota from the Bidasoa estuary. *Marine Pollution Bulletin*, 32, 69–71.

Salomons, W., & Forstner, U., 1984. *Metals in the Hydrocycle*. Springer – Verlag, Berlin.

Salonen, J. T., Seppanen, K., Nyyssonen, K., Korpela, H., Kauhanen, J., Kantola, M., Tuomilehto, J., Esterbauer, H., Tatzber, F., Salonen, R., 1995. Intake of mercury from fish, lipid peroxidation, and the risk of myocardial infarction and coronary, cardiovascular and any death in Eastern Finnish men. *Circulation*, 91, 645–655.

Sankar, T. V., Zynudheen, A. A., Anandan, R., Nair, V. P. G., 2006. Distribution of organochlorine pesticides and heavy metal residues in fish and shellfish from Calicut region, Kerala, India. *Chemosphere*, 65(4), 583 – 590.

Sankaranarayanan, V. N., & Reddy, C. V. G., 1968. Nutrients of northwestern Bay of Bengal. *Bulletin of National Institute of Science*, 38, 148 – 163.

Sankaranarayanan, V. N., & Reddy, C.V.G., 1973. Copper content in the inshore and estuarine waters along the central West Coast of India. *Current Science*, 42, 223–224.

Sankaranarayanan, V. N., Udayavarma, P., Balachandran, K. K., Pylee, A., Joseph, T., 1986. Estuarine characteristics of the lower reaches of the River Periyar. *Indian Journal of Marine Sciences*, 15, 166–170.

Santschi, P. H., Nixon, S., Pilson, M., 1984. Accumulation of sediments, trace metals (Pb, Cu) and hydrocarbons in Narragansett Bay, Rhode Island. *Estuarine, Coastal and Shelf Science*, 19, 427 – 450.

Santschi, P., Honener, P., Benoit, G., Brink, M. B., 1990. Chemical process at the sediment- water interface. *Marine Chemistry*, 30, 269– 315.

Sanzgiri, S., & Moraes, C., 1979. Trace metals in Laccadive Sea. *Indian Journal of Marine Sciences*, 8, 254– 257.

Sanzgiri, S., & Braganga, A., 1981. Trace metals in the Andaman Sea. *Indian Journal of Marine Sciences*, 10, 238 – 240.

Sanzgiri, S., Mesquita, A., Kureishy, T. W., Sengupta, R., 1981. Evaluation of trace metals Cd and Pb in Arabian Sea waters, In: *Oceanography of the Indian Ocean*, Desai, B.N. (Ed.), pp. 369 –378.

Sanzgiry, S., Mesquita, A., Kureishy, T. W., 1988.Total Mercury in water, sediments and animals along the Indian Coast. *Marine Pollution Bulletin*, 19 (7), 339– 343.

Sarkar, A., Ramesh, R., Battacharya, S. K., Rajagopalan, G.,1990.Oxygen isotope evidence for a stronger winter monsoon current during the last glaciations. *Nature*, 343, 549 – 551.

Sasmal, S. K., Panigrahy, R. C., Misra, S., 2005. *Asterionella* bloom in the northwestern Bay of Bengal during 2004. *International Journal of Remote Sensing*, 26, 3853 – 3858.

Sastry, J. S., & D"Souza, R. S., 1972. Upwelling and upward mixing in the Arabian Sea. *Indian Journal of Marine Sciences*, 1, 17–27.

Satpathy, K. K., 1996. Seasonal distribution of nutrients in the coastal waters of Kalpakkam, East coast of India. *Indian Journal of Marine Sciences*, 25, 221 – 224.

Satpathy, K. K., Usha Natesan, Sarguru, S., Mohanty, A. K., Prasad, M. V. R., Sarkar, S. K., 2008. Seasonal variations in mercury concentrations in the coastal waters of Kalpakkam, southeast coast of India.*Current Science,* 95(3), 374–381.

Satyanarayana, D., Panigrahy, P. K., Sahu S. D., 1993. Texture, mineralogy, carbon, nitrogen and phosphorus of Visakhapatnam shelf sediments, east coast of India. *Indian Journal of Marine Sciences*, 22, 235– 239.

Satyanarayana, D., Panigrahy, P. K., Sahu, S. D., 1994. Metal Pollution in harbor and coastal sediments of Visakhapatnam coast of India. *Indian Journal of Marine Science*, 23, 52 – 54.

Scanes, P. R., & Roach, A. J., 1999. Determining natural 'background' concentrations of trace metals in oysters from New South Wales, Australia. *Environmental Pollution*, 105, 437– 446.

Schaule, B. K., & Patterson C. C., 1981. Lead concentrations in the northeast Pacific: evidence for global anthropogenic perturbations. *Earth and Planetary Science Letters*, 54, 97– 116.

Scoullos, M. J., 1986. Lead in coastal sediments: the case of the Elefsis Gulf, Greece. *Science of the Total Environment*, 49,199–219.

Selvaraj, K., Ram Mohan, V., Szefer, P., 2004. Evaluation of metal contamination in coastal sediments of the Bay of Bengal, India: geochemical and statistical approaches. *Marine Pollution Bulletin*, 49,174 –185.

Sen Gupta, R., Ali, M., Bhuiyan, A. L., Hussain, M. M., Sivalingam, P. M., Subasinghe, S., Tirmizi, N. M., 1990. UNEP, Regional Seas Report and Studies No. 123, pp 42.

Sen Gupta, R., & Qasim, S.Z., 1985. The Indian Ocean- An Environmental Overview, In: *The Oceans- Realities and Prospects*, Sharma, R. C.(Ed.), Rajesh Publications, New Delhi, pp. 7– 40.

Sen Gupta, R., Sankaranarayanan, V. N., DeSousa, S. N., Fondekar, S. P., 1976. Chemical Oceanography of the Arabian Sea. Part-III, Studies on nutrient fraction and stoichiometric relationships in the northern and eastern basin. *Indian Journal of Marine Sciences,* 5, 58–71.

Sengupta, R., & Qasim, S. Z., 2001. Health of the Indian Ocean, In: *The Indian Ocean– a Perspective volume*, Sengupta, R., Ehrlich, D. (Eds.), pp. 327 – 371.

Sengupta, R., SIngbal, S. Y. S., Sanzgiri, S., 1978. Atomic – absorption analyses of a few trace metals in Arabian Sea waters. *Indian Journal of Marine Sciences*, 8, 295 – 299.

Sericano, J. L., Wadi, T. L., Jackson, T. J., Brooks, J. M., Trip, B. W., Farrington, J. W., Mee, L. D., Readman, J. W., Villeneuve, J. E., Goldberg, E. G., 1995. Trace organic contamination in the Americas: an overview of the US National Status and trends and the International Mussel Watch' programmes. *Marine Pollution Bulletin*, 31, 214– 225.

Sfriso, A., Marcomini, A., Pavoni, B., 1987. Relationships between macroalgal biomass and nutrient concentrations in a hypertrophic area of the Venice Lagoon Italy.*Marine Environmental Research*, 22, 297–312.

Shailaja, M. S., & Nair, M., 1997. Seasonal differences in organochlorine pesticide concentrations of zooplankton and fish in the Arabian Sea. *Marine Environmental Research* , 44(3), 263 –274.

Shaw, B. P., Saha, A., Chaudhari, S. B., Panigrahi, A. K., 1988. Mercury in the Rushikulya river estuary. *Marine Pollution Bulletin*, 19, 233 – 234.

Sheppard, F. P., 1973. *Submarine geology (3rd ed.)*. Harper and Row, New York.

Shetye, S. R., Gouveia, A., Shenoi S. S. C., Sundar, D., Michael, G. S., Almeida, A. M., Santhanam, K., 1991. The coastal current off western India during the northeast monsoon. *Deep Sea Research*, 38, 1517–1529.

Shetye, S.S., Sudhakar, M., Mohan, R., Tyagi, A., 2009. Implications of organic carbon, trace elemental and $CaCO_3$ variations in a sediment core from the Arabian Sea. *Indian Journal of Marine Sciences*, 38 (4), 432–438.

Shilla, D., Qadah, D., Kalibbala, M., 2008. Distribution of heavy metals in dissolved, particulate and biota in the Scheldt estuary, Belgium. *Chemistry and Ecology*, 24(1), 61–74.

Shirodkar, P. V., Mesquita, A., Pradhan, U. K., Verlekar, X. N., Babu, M. T., Vethamony, P., 2009. Factors controlling physico-chemical characteristics in the coastal waters off Mangalore – A multivariate approach. *Environment Research*, 109, 245–257.

Shirodkar, P.V., & Jayakumar, D. A., 1990. Nutrients and dissolved oxygen in upper 1000m in equatorial Western Indian Ocean. *Indian Journal of Marine Sciences*, 19, 47–52.

Shriadah, M. A., & Saif, M., 1999. Environmental characteristics of the United Arab Emirates waters along the Arabian Gulf: Hydrographical survey and nutrient salts. *Indian Journal of Marine Sciences*, 28, 225 – 232.

Shuklin, V. M., & Kavun, V. I. A., 1995. The use of marine bivalves in heavy metal monitoring near Vladivostok. *Marine Pollution Bulletin*, 31 (12), 330 – 333.

Silvany- Neto, A. M., Carvalho, F. M., Chaves, M. E. C., Brando, A. M., Tavares, T.M., 1989. Repeated surveillance of lead poisoning among children. *Science for the Total Environment*, 78, 179 – 186.

Simpson, W. R., 1981. A critical review of cadmium in the marine environment. *Progress in Oceanography*, 10 (1), 70.

Singbal, S. Y. S., George, M. D., Topgi, R. S., Noronha, R., 1982. Levels of certain heavy metals in marine organisms from Aguada Bay, Goa. *Mahasagar- Bulletin of National Institute of Oceanography*, 15, 121-124.

Singbal, S.Y. S., Sanzgiri, S., Sen Gupta, R., 1978. Total mercury concentrations in the Arabian Sea waters off the Indian Coast. *Indian Journal of Marine Sciences,* 7, 124–126.

Singh, K. P., Malik, A., Mohan, D., Sinha, S., 2004. Multivariate statistical techniques for the evaluation of spatial and temporal variations in water quality of Gomtiriver (India) - a case study. *Water Research*, 38, 3980–3992.

Sivadasan, C. R., & Nambisan, P. N. K., 1988. Seasonal variation of mercury, copper and zinc in the prawn *Metapenaeusdobsoni* from Cochin Backwaters. *Marine Pollution Bulletin*, 19, 579–580.

Skirrow, G., 1975. The dissolved gases- Carbon dioxide, In: *Chemical Oceanography*, Riley, J. P., & Skirrow, G. (Eds.), Academic Press, London, pp. 1–192.

Smith, R. L., Paulson, A. C., Rose, J. R., 1978. Food and feeding relationships in the benthic and demersal fishes of the Gulf of Alaska and Bering Sea, In: *Environmental Assessment of the Alaskan Continental Shelf*, Final Reports Biological Studies, NOAA, Boulder, pp. 33–107.

Smith, S. V., Silvia E. I., Victoria, D., Francisco J. A., Jose, D.C., Brian, N. P., Oscar, G. Y., 2008. Sediment Organic Carbon in Todos Santos Bay, Baja California, Mexico. *Estuaries and Coasts*, 31,719 – 727.

Spry, D. J., Wiener, J. G., 1991. Metal bioavailability and toxicity to fish in low-alkalinity lakes: a critical review. *Environment Pollution*, 71, 243–304.

Srinivas, K., 2000. *Seasonal and interannual variability of sea level and associated surface meteorological parameters at Cochin*. Ph.D Thesis, Cochin University of Science and Technology, Cochin.

Stewart, H. B., 1958. Sedimentary reflections of depositional environment in San Miguel lagoon, Baja California, Mexico. *Bulletin American Association of Petroleum Geologist*, 42, 2567–2618.

Subramanian, K. S., & Meranger, J. C., 1979. Ammonium pyrrolidinedithiocarbamate methylisobutyl ketone – graphite furnace atomic absorption system for some trace metals in drinking water. *International Journal of Environmental AnalyticalChemistry*, **7**, 25–40.

Subramanian, V., & Mohanachandran, G., 1990. Heavy metals Distribution and Enrichment in the sediments of Southern East coast of India. *Marine Pollution Bulletin*, 21, 324– 330.

Sujatha, C. H., Aneesh kumar, N., Renjith, K. R., 2008. Chemical assessment of sediment along the coastal belt of Nagapattinam, Tamil Nadu, India, after the 2004 tsunami. *Current Science*, 95(3), 382 –385.

Sukumaran, S., & Sarala Devi, K., 2009. Polychaete diversity and its relevance in the rapid environmental assessment of Mumbai Port. *Current Science*, 97, 1439–1444.

Suzumura, M., Ueda, S., Suni, E., 2000. Control of phosphate concentration through adsorption and desorption process in ground water and seawater mixing at sand beaches in Tokyo Bay. *Japan Journal of Oceanographic Society of Japan*, 56, 667–673.

Swami, B., Suryawanshi, U. G., Karande, A.A., 2000.Water quality status of Mumbai (Bombay) harbour - an update. *Indian Journal of Marine Sciences*, 29, 111– 115.

Szefer, P., 1991. Interphase and trophic relationships of metals in a southern Baltic ecosystem. *Science of the Total Environment*, 101, 201–215.

Szefer, P., 1998. Distribution and behaviour of selected heavy metals and other elements in various components of the southern Baltic ecosystem. *Applied Geochemistry*, 13, 287–292.

Tada, K., Morishita, M., Hamada, K., Montani, S., 2001. Standing stock and production rate of phytoplankton and a red tide outbreak in a heavily eutrophic embayment, Dokai Bay, Japan. *Marine Pollution Bulletin*, 42, 1177–1186.

Takarina, N. D., Browne, D. R., Risk, M. J., 2004. Speciation of heavy metals in coastal sediments of Semarang, Indonesia. *Marine Pollution Bulletin*, 49, 854 – 874.

Tam, N. F. Y., & Wong, Y. S., 2000. Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps. *Environmental Pollution*, 110,195–205.

Tavakoly Sany, B., Salleh, A., Sulaiman, A. H., Mehdinia, A., Monazami, G. H., 2011. Geochemical Assessment of Heavy MetalsConcentration in Surface Sediment of West Port, Malaysia. *World Academy of Science, Engineering and Technology*, 80, 83 – 87.

Taylor, A., 1998. *Zinc, copper and cadmium accumulation, detoxification and storage in the gastropod molluscs* Austrocochlea constricta *and* Bembicium auratum *and an assessment of their potential as biomonitors of trace metal pollution in estuarine environments*. M. Applied Science, University of Canberra.

Tenholder, V. J. H. M., Roozemond, A. S. H., Kolar, Z., 1978. The uptake tissue distribution, and retention of hexavalent chromium by young rainbow trout (*Salmogardineri*), In: *Aquatic Pollutants: Transformation and Biological Effects*, Hutzinger, O., Van Lelyveld, I. H., Zoitmann, B.C.J. (Eds.), Pergamon Press, Elmsford, New York, pp. 475 – 476.

Thain, J. E., 1984. Effects of mercury on the prosobranch mollusk *Crepidula fornicate*: acute lethal toxicity and effects on growth and reproduction of chronic exposure. *Marine Environmental Research*, 12, 285 – 309.

Thamban, M., Rao, V. R., Schneider, R. R., Grootes, R. M., 2001. Glacial to Holocene fluctuations in hydrography and productivity along the southwestern continental margin of India.*Paleogeography, Palaeoclimatology, Palaeoecology*, 165, 113–127.

Thompson, J. A. J., Macdonald, R.W., Wong, C. S., 1980. Mercury geochemistry in sediments of a contaminated fjord of coastal British Columbia. *Geochemical Journal*, 14, 71–82.

Tomas, C. R., 1997. *Identifying Marine Phytoplankton*. Academic Press ,New York.

Tomilson, D. C., Wilson, J. G., Harris, C. R., Jeffrey, D. W., 1980. Problems in assessment of heavy metals in estuaries and the formation of pollution index. *Helgol Meeresunlters*, 33, 566–575.

Trask, P. D., 1939. *Recent Marine Sediments*, American Association of Petroleum Geologists, Tulsa, Okla.

Turekian, K. K., & Wedephol, K. H., 1961. Distribution of the elements in some major units of the Earth's crust. *Geological Society of America Bulletin*, 72, 175 – 192.

Turner, R. E., 2002. Element ratios and aquatic food webs. *Estuaries*, 25, 694–703.

Tuzen, M. M., & Soylak, M., 2007. Determination of trace metals in canned fish marketed in Turkey, *Food Chemistry*, 101, 1378 –1382.

Uma devi., 1997. Heavy metal toxicity to an intertidal gastropod, *Morulo granulata*: tolerance to copper, mercury, zinc and cadmium. *Journal of Environmental Biology,* 18(3), 287 –290.

UNEP, 1996. *The state of the marine and coastal environment in the Mediterranean Region*. UNEP, Athens.

UNEP/FAO/IAEA/IOC, 1984. *Sampling of selected marine organisms and sample preparation for trace metal analysis*. Reference methods for marine pollution studies, Review 2, 19.

Unnithan, R. V., Vijayan, M., Radhakrishnan, E. V., Ramani, K. N., 1977. Incidence of fish mortality from industrial pollution in Cochin backwaters. *Indian Journal of Marine Sciences*, 6, 81–83.

Usero, J., Regalado, E. G., Gracia, I., 1996. Trace metals in bivalve mollusks *Chameleogallina* from the Atlantic Coastof Southern Spain. *Marine Pollution Bulletin*, 32, 305–310.

Usero, J., Regalado, E. G., Gracia, I., 1997. Trace metals in bivalve mollusks *Ruditapesdecussatus*and *Ruditapesphilippinarum*from the Atlantic Coast of southern Spain. *Environment International*, 23, 291–298.

Van der Putte, I., Laurier, M. B. H. M., Van Fijk, G. J. M., 1982. Respiration and osmoregulation in rainbow trout (*Salmogairdneri*) exposed to hexavalent chromium at two different pH values. *Aquatic Toxicology*, 2, 99 – 112.

Varshney, P. K., Nair, V, R., Abidi, S. A. H., 1983. Primary productivity in near shore waters of Thal, Maharastra Coast. *Indian Journal of Marine Science*, 12, 27 – 30.

Venkataraman, K., & Wafar, M., 2005. Coastal and marine biodiversity of India. *Indian Journal of Marine Sciences*, 34, 57– 75.

Venugopal, B., & Luckey, T. P., 1975. Toxicology of non radioactive heavy metals and their salts, In: *Heavy metal toxicity, safety and Hormology*, Luckey, T. D., Venugopal, B., Hutchson, D., (Eds.), Stuttgart, pp. 4 – 73.

Vijayram, K., & Geraldine, P., 1996. Are the heavy metals cadmium and zinc regulated in freshwater prawns. *Ecotoxicology and Environmental Safety*, 34, 180 –183.

Wang, W. X., & Fisher, N. S., 1999. Assimilation efficiencies of chemical contaminants in aquatic invertebrates: a synthesis. *Environmental Toxicology and Chemistry*, 18, 2034 – 2045.

Waring, J. S., Maher, W. A., Frank Krikowa, 2006. Trace metal bioaccumulation in eight common coastal AustralianPolychaeta. *Journal of Environmental Monitoring*, 8, 1149–1157.

Weber, D. N., & Dingel, W. M., 1997. Alterations in neurobehavioral responses in fishes exposed to lead and lead-chelating agents. *American Zoologist*, 37, 354–362.

White, S. L., & Rainbow, P. S., 1984. Zinc flux in *Palaemon elegans* (Crustacea: Decapoda): moulting, individual variation and tissue distribution. *Marine Ecological Progress Sereis*, 19,153– 166.

White, S. L., & Rainbow, P.S., 1982. Regulation and accumulation of copper, zinc and cadmium by the shrimp *Palaemon elegans*. *Marine Ecological Progress Sereis*, 8, 95–101.

WHO (World Health Organization), 1990. *IPCS-Methylmercury*. Environment Health Critic 101, Geneva.

WHO (World Health Organization), 1991. *IPCS-Inorganic mercury*. Environment Health Critic 118, Geneva.

WHO (World Health Organization), 1993. *Evaluation of certain food additives and contaminants*. Technical Report Series No. 837, Thirty third report of the Joint FAO/WHO Expert Committee on Food Additives, Geneva.

WHO-IPCS-Environmental Health Criteria Report- with ILO and UNEP, 1987. *International Program of Chemical Safety*. Geneva, Switzerland .

Wiener, J.G., & Spry, D. J., 1996. Toxicological significance of mercury in freshwater fish, In: *Environmental Contaminants in Wildlife: Interpreting Tissue Concentrations*, Beyer, W. N., Heinz, G. H., Redmon-Norwood, A.W. (Eds.), Lewis Publishers, Boca Raton, FL, USA, pp. 297 – 339.

Williams, T. M., Rees, J. G., Kairu, K. K., Yobe, A. C., 1996. Assessment of contamination by metals and selected organic compounds in coastal sediments and waters of Mombasa, Kenya. *Technical Report W C- 96-37*, 1 – 85.

Windom, H. L., Niencheski, L. F., Smith, R. G., 1999. Biogeochemistry of Nutrients and Trace Metals in the Estuarine Region of the Patos Lagoon (Brazil). *Estuarine, Coastal and Shelf Science*, 48, 113–123.

Wong, P. T. S., Silverberg, B. A., Chau, Y. K., Hodson, P. V., 1978. Lead and aquatic biota, In: *The Biogeochemistry of Lead in the Environment*, Nriagu, J. O., (Ed.), Elsevier, Amsterdam, pp. 270 – 279.

Wong, P. T. S., & Trevorrs, J. T., 1988. Chromium toxicity to algae and bacteria, In: *Chromium in the Natural and Human Environments*. Nriagu, J. O., Nieboer, E. (Eds.), Wiley Series in Advances in Environmental Science and Technology, John Wiley and Sons, New York, pp. 305 – 316.

WQC (Water Quality Criteria), 1972. A *Report of the Committee on Water Quality Criteria*. NAS Washington DC, USA.

Yap, C. K., Rahim Ismail, A., Ismail, A., Tan, S. G., 2003. Species diversity of macrobenthic invertebrates in the Semenyih River, Peninsular Malaysia. *Pertanika Journal of Tropical Agricultural Science*, 26(2), 139– 146.

Yousuf, M. H., Shahawi, M. S., Ghais, S. M., 2000. Trace metals in liver, skin and muscle of *Lethrinus lentjan* fish species in relation to body length and sex. *Science of the Total Environment*, 256, 87 – 94.

Zabel, T. F., 1989. Current standards and their relation to environment behavior and effects: the case of Pb. *Science of the Total Environment*, 78, 187 – 204.

Zauke, G. P., Calson, B., Savinov, V. M., Savinova, T., 2003. Heavy metals of inshore Benthic invertebrates from the Barents Sea. *Science of the Total Environment*, 306, 99–110.

Zepp, R. G., 1997. Interactions of marine biogeochemical cycles and the photo degradation of dissolved organic carbon and dissolved organic nitrogen, In: *Marine Chemistry*, Gianguzza, A., Pelizzetti, E., Sammarkano, S. (Eds.), Kluwer Academic Publication, London, pp. 329 – 352.

Zhou, H.Y., & Wong, M. H., 2000. Mercury accumulation in freshwater fish with emphasis on the dietary influence. *WaterResearch*, 34, 4234–4242.

Zingde, M. D., Singbal, S. Y. S., Reddy, C. V. G., 1979. Some observations on pollutants of Versova Bay (Goa). *Mahasagar*, 12, 69 – 74.

Zingde, M. D., Trivedi, S. K., Desai, B. N., 1979. Physicochemical studies on coastal pollution off Bombay. *Indian Journal of Marine Sciences*, 8, 271– 277.

Zingde, M. D., & Desai, B. N., 1981. Mercury in Thane Creek, Bombay harbor. *Marine Pollution Bulletin*, 12, 237 – 241.

Zingde, M. D., 1985. *Waste water effluents and Coastal marine environment of Bombay*. Proceedings of Sea water quality demands, Naval Chemical and Metallurgical Laboratory, Bombay.

Zingde, M. D., 1989. Environmental status of the coastal marine environment of India, In: *Management of Aquatic Ecosystems*, Agarwal, V. P. (Ed.), Society of Biosciences, MuZaffarnagar, India, pp. 35 – 37.

Zingde, M. D., Bhosle, N. B., Narvekar, P. V., Desai, N. B., 1989. Hydrography and water quality of Bombay harbor, In: *Environmental Strategy and Biosci*ences, Prakash, R. (Ed.), Society of Biosciences, Muzaffarnagar, India, pp.37 – 58.

Zingde, M. D., & Govindan, K., 2000. Health status of the coastal waters of Mumbai and regions around, In: *Environmental problems of coastal areas in India*, Sharma, V. K., (Ed.), Book well, New Delhi, pp. 119 –132.