CHEMICAL EVALUATION OF SELECTED ORGANICS AND TRACE METALS IN THE MANGROVE MACROFLORA OF COCHIN

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By

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Dedicated to my beloved parents

Prof (Mrs) and Mr. E.S. Andrews

Certificate

This is to certify that this thesis entitled ***Chemical Evaluation of Selected Organics and Trace Metals in the Mangrove Macroflora Of Cochin*** *is a bonafide record of the research work carried out by Smt. Geetha Andrews under my supervision and guidance in the Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, in partial fulfillment of the requirements for the degree of Philosophiae Doctor of the Cochin University of Science and Technology and no part thereof has been presented before for any other degree, diploma, associateship, fellowship or any other similar title or recognition.*

Dr. Jacob Chacko

Supervising Guide

Kochi-16
July, 2010

Declaration

I hereby declare that this thesis entitled ***Chemical Evaluation of Selected Organics and Trace Metals in the Mangrove Macroflora Of Cochin*** *is an authentic record of the research work carried out by me under the supervision of Dr. Jacob Chacko, Professor, Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, in partial fulfillment of the requirements for the Ph.D degree of the Cochin University of Science and Technology and no part of it has previously formed the basis for the award of any degree, diploma, associateship, fellowship or any other similar title or recognition in any University.*

July, 2010

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Chapter I

The Legacy Of Mangrove Ecosystems

1.1.1 Introduction

Mangrove ecosystems are near shore marine habitats formed by a very special association of flora and fauna that live in the inter tidal areas of low lying tropical and subtropical regions. They are one of the most threatened ecosystems of the world, with climate change playing a prominent role in their survival (Eric et al, 2008). The earliest known references on mangroves are found in an inscription from the time of the Egyption King Assa between 3580-3536 B.C. The mangrove ecosystem serves as a transient zone between land and ocean (Wattayakorn, 2000). They are highly productive and auto tropic in nature, as all nutrients such as C, N, H_2O and O_2 are cycled in this ecosystem. Nitrogen turnover is found to be very large indicating an active coupling between production and decomposition processes in the ecosystem (Alongi,2004). They also act as a filter for the exchange of suspended particles, nutrients and pollutants between the land and ocean and modify solutes and particulates by physical, chemical and biological processes (Pinsak and Erik, 2002). Tidal exchange and deposition of fine particles are the most determining factors for the existence and distribution of the mangroves (Alongi, 2002). Closely related and complex physical, chemical and biological processes are involved in the formation and maintenance of the mangrove ecosystem. Soil characteristics such as siltiness, electrical conductivity, pH, cation exchange capacity as well as nutrients have a major influence on mangrove growth. Mangroves show salt tolerance, but it varies among different species. Extremely high salinity is always detrimental to mangroves. Similarly, sedimentation rates also play an important role because, as the sediment grain size varies, changes in sediment food quality, faunal movement etc tend to vary with sedimentation, affecting the ecosystem. The mangrove ecosystem is a fragile one and a slight disturbance in any one of the above mentioned

parameters is sufficient to effect a disturbance. Mangrove forests (Alongi, 2002) comprise of trees, shrubs, palms, epiphytes, ground ferns and grasses. The ecosystem is also rich in algae, fungi, bacteria, as well as phytoplankton, of which diatoms such as *coscinodiscus, biddulphia*,etc are the dominant ones. The zoo plankton population varies from protozoa to eggs. They are also breeding grounds for various types of birds, reptiles, mammals and fishes. It is well known that mangrove sediments are under permanent reducing conditions due to water logging, has high concentrations of organic matter and significant presence of sulphate reducing bacteria. Mangrove waters may contain pollutants like pesticides, fertilizers, untreated domestic sewage and industrial waste as well as chemicals like tannic acid and flavanoids. Thus they act as sinks for anthropogenic contaminants (Machado et al, 2002). Mangrove ecosystems have served as the life-blood to societies that depend on them for their livelihood, by providing resources that sustain them and also by promoting various economic activities. Apart from resources such as fishing, they support agriculture, herding of domestic livestock and hunting of wild herbivores migrating in response to flooding pattern. Human activities hundreds of kilometers inland such as digging of canals, diversion of water flows, construction of roads, dredging and filling, etc greatly modify mangrove wet land conditions by changing ground water flow and modifying salinity levels. Over the recent past, the mangrove ecosystems are threatened owing to the pressures of unplanned urbanization and land use pattern for alternative agricultural practices. In order to accommodate the burgeoning populace many of the world's wetlands have paved way to residential layouts, industrial complexes, fish farms etc. Exploitative attitudes of the society for economic benefits has subjected these ecosystems to stresses, in some cases leading to destruction and alteration, hampering their functioning. The results of mangrove ecosystem loss leading to environmental and ecological destruction and depreciation of socio-economic benefits have largely gone unnoticed where communities do not depend on their resources for survival. Mangroves protect coastlines and development from erosion and damage by tidal surges, currents, rising sea level, and storm energy in the form of waves, storm surges and wind. Roots of mangrove trees and plants bind and stabilize the substrate (Krauss et al., 2003). With the tsunami that hit the coastal areas of South

East Asia on the 26th of December 2004, there is a heightened awareness on the importance of mangroves acting as natural barriers, saving the sea facing areas from the devastating effects of nature's fury. Many reports have appeared about the mangrove wall acting as an effective protector against the onslaught of tsunami than man made wall (Roland et al, 2008). Realising their importance, in the costal areas of India as elsewhere in the world efforts are on to propagate and protect the mangroves with the help of local population. Perhaps this increased awareness will go a long way in protecting these wonders of nature in the coming years.

1.1.2 Flora and fauna of mangrove ecosystems

Mangroves are very specialized ecosystems found at the interface between land and sea (Santanu, 2008). Mangroves comprise of halophytic marine tidal forests made up of trees, shrubs, palms epiphytes, ground ferns and grasses. Climatic variations such as physiological impacts of dry winds, variation of soil and water characteristics, length of dry and wet seasons as well as geomorphic processes such as tidal erosions, river channel switching, mud flat accumulation etc tend to affect the distribution and zonation of mangroves, which in turn will affect the mangrove environment itself. Mangrove environment produces permanent, semi resident or migratory mode of life to more than 2000 species of flora and fauna. Mangroves can be classified into three broad categories- 1) True mangroves, which are mainly restricted to inter tidal areas between the high water levels of neap tide and spring tide. They show fidelity to the mangrove environment and form pure strands. They have morphological specializations fitted to suit their habitat. About 80 species of true mangrove trees or shrubs are recognized of which 50-60 species make a significant contribution to the structure of mangrove forests. Some common examples are *Rhizopora, Brugiera, Ceriops, Kandelia, Avicennia, Sonneratia, Nypa, Lumnitzera, and Laguncularia.* (2) Minor species of mangroves which do not form conspicuous vegetation or pure communities. They may occupy the peripheral habitats and very occasionally form pure strand. e.g.: *Exoecaria agallocha, Acanthus* and *Aegiceras corniculatum.* (3)The mangal associates which are found both in the proximity of mangroves as well as in the transitional vegetation landwards and seawards. e.g.: *Hibiscus, ficus, casuarina.*

These can tolerate salinity but lack the characteristics of mangroves (Lacerda, 2002).

Based on their geomorphology they are divided into river based, tide dominated, wave dominated, drowned bedrock valley and carbonate. Competition for space, soil nutrients, oxygen and solar radiation influence the zonation as well temporal and spatial distribution of mangrove trees. Mangroves colonise a number of substrates including silty and clayey mud, calcareous mud, quartz sand, coral reef as well as cracks and hollows of rocky substrates. They prefer sediments that have been deposited by tides. The sediments in mangrove ecosystems are characterised by high organic content and are anoxic due to the presence of compounds such as H_2S, CO_2, ethylene etc. which are produced in the reducing environment of mangroves. Mangrove trees are evergreen, sclerophyllous and broad leaved. They are excellent examples of plants showing adaptations to living conditions. They have specialized root systems such as pnuematophores, prop roots and knee roots, which facilitate exchange of air between the plant and the environment. Since the mangrove environment may be saline, the mangrove plants posses salt excluding or mitigating methods such as concentrating salt in the leaves and shedding them periodically or ultra filtration at the root level itself. Metallic plaques present on the roots prevent the entry of harmful chemicals such as sulphides in to the transport system of mangrove plants (Alongi, 2004). Mangrove ecosystems trap very fine sediments with a high organic content and are therefore home to microbes, fungi as well as bacteria. The sulphate reducing bacteria present in the reducing environment of mangrove environment makes the soil acidic due to H_2S production. Mangrove waters being rich in nutrients are known to harbour pathogenic bacteria such as *Aeromones, Vibrio, and Shingella.* Edible sea weeds such as species of *Gracillaria, Ulva and Caulerpa* are known to be present in the mangrove area. Mangroves provide crucial habitats for many marine species (Beck et al, 2001). The mangrove fauna also comprises of insects, crustaceans, molluscs, reptiles, monkeys, birds as well as a variety of fishes belonging to the species such as *Etroplus, Ilisha, Liza, Lates, Mugil, and Polynemus.*

1.1.3 Ecological role of mangroves

Mangroves are specific inter tidal wetlands covering nearly 200,000 km^2 along the tropical and sub tropical coastlines. They are the most productive terrestrial ecosystems of the world (Bouillon et al, 2008). The mangrove ecosystems play an important role in the management of natural hazards at much lower cost (UNEP, 2006). Mangrove swamps are formed in areas of accretion and in areas where the sedimentation is large; the swamp can advance at enormous rates (Ellis and Nicholls, 2004). They act as sacrificial belt and protect the coastal areas against cyclones, storms, tidal waves or typhoons by reducing current velocity through friction and their complex root system. The dense root system of mangrove forests pay a share to shoreline stabilization and storm protection, by helping to dissipate the wave force and protect the coast by reducing the damage of wind and wave action(Kathiresan and Rajendran,2005). They are more effective than concrete barriers in protecting the coastal environs from soil erosion thereby safe guarding agriculture, human settlement etc present in the inner land. Mangroves play significant roles like filtering land runoff and trapping of sediments, the latter being dependent on tidal influences. Like other wetlands they can be used as a low cost water treatment system, because they have a large capacity to retain heavy metals and nutrients like nitrogen and phosphorus and accumulating them in the sub-soil (Benjamine, 2004) thereby decreasing the potential for eutrophication and excess plant growth in the neighbouring waters. They sequester carbon dioxide thereby mitigating the effects of global warming (Emerton and Kekulanada, 2002).

Mangrove swamps being sites of protein rich detritus serve as nursery habitats for juvenile fishes (Laegdsgaard and Johnson, 2001) which spend their adulthood elsewhere. Detritus exported from the mangrove swamps have many effects on the local estuaries. In addition contributing significantly to the estuarine carbon budget, litter decomposition of mangroves contributes in a big way to the nutrient cycling of the habitats closer to the mangal environment. The dissolved organic carbon that is flushed out stimulates microbial growth in the estuary and so fuels the microbial food chain, essentially providing more food for the detritivorous. Secondly the dissolved nitrogen that is also exported stimulates the growth of

phytoplankton which in turn provides more detritus for the benthos. The exchange of organic carbon may be site specific, depending on the geomorphology and tidal hydrology of the region. The shading by the mangrove canopy and the high turbidity of mangrove waters reduce the predation risk of various fishes like *snappers, grunts* etc (Cocheret et al, 2004). The total mangrove area available as juvenile habitat is known to be a limiting factor for the adult population size for coral reef fish species such as *Gerres Cinereus* (Benjamin, 2004). Mangrove related fisheries are given a higher rating than natural fisheries or agricultural products such as wood. The annual economic values of mangroves, estimated by the cost of the products and services they provide, have been estimated to be USD 200,000 900,000 ha^{-1}(Wells et al., 2006). The monetary value of mangroves is second only to the values of estuaries and sea grass beds and is higher than the economic value of coral reefs, continental shelves and the open seas. It has been suggested that if mangrove ecosystem are deforested beyond the levels of 2 km^{2} yr^{-1} it will lead to a decline in the shrimp harvest and revenue. Periodically inundated wetlands are very effective in storing rainwater, which help in recharging ground water supplies, which in turn depends upon the soil texture and its permeability, vegetation, sediment accumulation, surface area to volume ratio and water table gradient. The mangrove fauna is emerging as a potential source of valuable products like antimicrobial agents, plant based drugs, mosquitosides, gallotannins, and uv screening compounds (Kathiresan and Bingham, 2001). Also, mangroves provide a natural sunscreen for coral reefs, reducing exposure to harmful solar radiation and risk of bleaching: decomposing phytoplankton detritus and decaying litter from mangroves and seagrass beds produce a colored, chromophoric component of dissolved organic matter, which absorbs solar ultraviolet radiation, which can be transported over adjacent coral reefs and reduce coral reef exposure to harmful solar radiation (Anderson et al., 2001; Obriant, 2003). Mangroves are also being converted into recreational and ecotourism sites. The functional properties of mangrove ecosystem demonstrate clearly its role in maintaining the ecological balance. Their vast biodiversity also makes them excellent study sites for the environmentally enlightened scientist.

1.1.4 Traditional and commercial uses of mangroves

Mangroves can be considered as nature's gift to mankind as they sustain the life of local people. For centuries, salt marshes including mangrove ecosystems have been used by local inhabitants for fishing, hunting and cattle grazing. Around 14th century the Portuguese learned the technique of using mangroves to create rice-fish-mangrove farms and taught the technique to the people of African countries such as Angola and Mozambique. Mangroves have a significant role in the economy of coastal regions as the income from fishing activities related to mangroves quite often top the income chart of these areas (Alongi, 2002). Mangroves provide excellent fodder for cattle and it is believed that cattle fed on mangrove leaves produce more milk (Kathiresan and Rajendran, 2003). Mangroves provide timber for construction of buildings as well as marine vessels, be it the country rafts or canoes and boats, for paper industry, smoking of fish, as well as for the production of charcoal. *Rhizopora* billets provide the best charcoal with highest calorific power, exceptional slow burning properties and no smoke. Mangrove bark is being used as a source of tannin and vegetable dye as early as 1790 in South America. The ash of *Avicennia* and *R. mangle* being rich in sodium salts is used as a substitute for soap. Mangrove plants are a rich source of steroids, tri terpenes, saponins, flavanoids and alkaloids, many of which have significant antiviral and analgesic activity. Fresh leaves of Pluchea *indica* are used against gangrenous ulcers (Bandaranayake, 1998). *E. Agallocha* (blinding tree) exudes an acrid milk sap rich in alkaloids and is injurious to human eyes is used for different purposes such as against epilepsy. Ultra violet absorbing phenolic compounds present in the leaf epidermis of tropical mangroves have shown protective effect against UV- B and hence has potential use in cosmetics and sunscreen lotions (Kathiresan, 2003). Mangroves are thus a source of novel agrochemicals and medicinal compounds. Many mangrove species are used in folk medicine (Agooramurthy et al, 2008). Chemicals identified from *Calophyllum inophyllum* are prospective lead compounds for anticancer drugs and novel inhibitors of HIV –1-reverse transcriptase. Mangrove parts are also edible. Dry leaves of mangrove species like *B. cylindrica*, *Ceriops decandra*, *R.apiculata*, *R.lamarki* etc are used as tea substitutes. Fruits of *Sonneratia* are known to yield

a fruit drink, while that of *Rhizopora* is used to make wine. The fruits of *Kandelia Candel* and *B. Gimnoriza* are used to make cake and pastry. Mangroves are also being promoted as centers of eco tourism thereby providing alternate means of income generation. They may also emerge as a new source for many biologically active compounds (Kathiresan et al., 2006). Efforts are now being made to identify toxicants and chemicals with medicinal values from mangroves and their potential economic values. Hence there is a growing importance for mangroves, though the exploration of mangrove plants for pharmacologically important compounds is still in its infancy.

1.2.1 Distribution of Mangroves-a world profile

Mangroves extent over 15.5 million ha world wide dominating nearly ¼ of the world population. Mangroves are found along the tropical and subtropical coasts of Africa, Australia, Asia and Americas. Mangroves develop best in regions experiencing rather regular climates, with abundant rainfall distributed evenly throughout the year. Tall, dense and floristically diverse mangroves are almost exclusively found either in the equatorial zone which includes countries like Malaysia, Indonesia, Columbia etc or in the tropical summer rainfall zone which includes most coastal areas of India, Burma, Thailand, Indonesia, etc. Equatorial mangrove forests often rival the biomass of many tropical rain forests. Sporadic or scattered mangroves prevail in the subtropical dry zones such as Northwest Indian Coast, Pakistan, African Red Sea coast etc and in the warm climate found in countries like Australia and New Zealand. There are 9 orders, 20 families, 27 genera and roughly 70 species of mangroves with the Indo-Pacific, Indonesia, Australia, Brazil, and Nigeria together holding about 43% of the world's mangrove forests (Alongi, 2002).

Among the continents, Asia has the largest mangrove area. The mangroves of South and Southeast Asia are especially noted for their biodiversity. About 50 mangrove species have been identified along the coastal regions of Asia among which some mangroves species like *Aegiceras floridum*, *Heritiera globosa* are endemic to the region. The mangrove area in Asia accounts for about 38% of

global mangrove area. Among Asian countries, Indonesia is the country with the largest mangrove area. Indonesia, together with Myanmar, Malaysia, Bangladesh, and India account for more than 80% of the Asian mangrove area. High rain fall coupled with significant riverrine output favours the development of luxuriant mangroves in the South East Asian countries. The most extensive and luxuriant growth extents along the delta system of major rivers of Indo- Pacific regions (about 6.9 million ha) with the Bangladesh part of Sunderbans with an area of almost 600,000 ha, including waterways, making it the biggest mangrove ecosystem of the world. The Suderbans is a UNESCO world heritage site. The Indian part of the Sunderbans is rich in species but lower in complexity and structure than the Bangladesh part probably due to variation in salinity. Mangroves are usually temperature limited, though there is nothing obvious about their physiology that limits them to higher temperatures. Warm temperatures are of paramount importance to the existence of mangroves. Mangroves are most common where the mean temperature in the coldest month does not dip below 10^0C. One possibility is that they might be able to cope with salt stress easier at higher temperature (Collin Little, 2000). Some species like *A. Marina and A.Germinans* can tolerate light frost up to -4^0C, but they do not survive lengthy frost.

The mangroves propagate through viviparous germinated seedlings. Since mangroves are quite often subjected to water logging, tidal flushing, sedimentation, as well as changes in hydrography, they have a large number of propagules. Factors such as high humidity existing in tropics that reduces evaporation loss and wind flow parallel to the land that helps in the dispersion of propagules are beneficial to mangroves. Mangroves usually possess sharp ecotones with adjacent ecosystems because environmental conditions such as flooding, prolonged hydro period, salinity, anoxic conditions and accumulation of toxic substances such as H_2S makes it extremely difficult for non- halophytic and non wetland plants to grow and reproduce in a mangrove environment. Also each species of mangroves is associated with a particular tidal range and changes in environmental conditions are known to induce destruction or changes in mangrove communities. Hence an advanced knowledge of climatic conditions about a mangrove ecosystem is essential because the mineral constituents and

pedogenetic processes are related to prevailing climatic factors. Therefore each mangrove ecosystem must be characterised by its climatic identity card which would integrate all fundamental climatic factors.

1.2.2 Mangroves of India

India has a very long and diversified coastline which is approximately 7516.5 km^2 with varying ecological features. According to Forest Survey of India (2003), mangroves of India are spread over 4500 square kilometres, along the coastal states of India and accounts for about 5% of the world's mangrove vegetation. West Bengal has the maximum mangrove area, followed by Gujarat and Andaman and Nicobar Islands. Fossil specimens of mangroves point to the existence of luxuriant mangrove vegetation along the Indian coast. The first scientific report on Indian mangroves, *Hertus Bengalensis* was published in 1814 by Roxburgh which described the mangrove flora of Sunder bans. The natural ecosystem mangrove wetlands including the Sundarbans is under threat due to anthropogenic activities. This ecosystem has become vulnerable to pollution such as oil spillage, heavy metals, and agrochemicals – which may have changed the mangrove ecosystem's biogeochemistry (Mohamed et al, 2009). The Indian mangrove ecosystem is distributed with in the inter tidal or deltaic zones with silted up muddy shoreline, along both the east and west coasts. The coastal or deltaic mangrove flora continuously enriches the soil and water for sustainable agriculture, brackish water aqua culture and natural fisheries. The mangroves of the Indian sub continent are of three types. Among these the deltaic mangroves existing along the deltas of east coast cover about 70% of the total Indian mangals. These mangroves are distributed in the 5 major deltas and estuarine mouths of the four maritime states mainly Tamilnadu, Andhra Pradesh, Orissa and West Bengal. These deltaic mangroves found along the Cavery delta in Tamil Nadu, the Krishna delta in Andhra Pradesh, where dense mangrove vegetation are found on the western side of Krishna delta, the Mahanadi delta in Orissa and Sundarbans in the West Bengal on Ganga delta which has the largest area of about 4,200 km^2 among these deltaic mangroves. They are formed mainly by deposition of silt and clay particles carried down by the rivers the Cauvery,

Krishna, Godavari, Mahanadi, Brahmaputra and Ganges and perennial supply of fresh water along the deltaic coast.

The Sunder bans of India and Bangladesh put together form the single largest block of mangroves of the world and has about 35 true mangrove species and more than 35 mangrove associated flora or mangals. The Sunder bans together with Andaman and Nicobar Islands hold approximately 80% of the mangroves of India. The Indian part of Sunder bans situated in the 24 Parganas district of the Indian state of west Bengal, is created by the confluence of three rivers, Ganga, Brahmaputra and Meghna. The Sunder bans delta covers an area of 38,500 sq.kms with a major portion of it falling in Bangladesh. The Indian Sunder bans is the estuarine phase of the River Ganges and comprises 9,630 square km, out of which 4,264 square km. of intertidal area, covered with thick mangroves, is subdivided as forest sub ecosystem and 1,781 km^2 of water areas aquatic sub ecosystem. The rest has been reclaimed for human settlement and agricultural purposes (Biswas et al, 2004). It consists of 54 small islands, and swamps crisscrossed by innumerable waterways and canals, and are named after the Sundari trees growing abundantly here. Spread over 2585 sq.km, the Sunder bans National Park situated in West Bengal, India, is the world's biggest estuarine mangrove forest and was declared a UNESCO World Heritage site in 1987. The park is home to a wide variety of plant life in addition to an amazing variety of wildlife. Endangered species like Olive Ridley turtles, Gangetic Dolphins, the fishing cat, River Terrapin, etc find a home here. The park is known as the habitat of the endangered Royal Bengal tiger too, which number more than 200 and is also a home to birds such as spotted-billed pelicans, white ibis, eagles, ospreys, falcons, Caspian terns and open-billed herons, to name a few.

The coastal mangroves existing in the west coast of India comprises about 12% of the mangrove ecosystems. They are comparatively less spreading and stunted due to less extended and steeper gradient of the west coast line in the western ghat and lacking of major perennial estuaries, deltas or vast flat inter tidal silted up deltaic lands. The west coast is characterised by typical funnel-shaped estuaries of the rivers like Indus, Tapti and Narmada characterised by creeks and backwaters and hence the backwater - estuarine type mangroves occur on the

coasts of Arabian sea (Naskar and Mandal, 1999). The major mangrove zones of the Indian west coast are located along the Gujarat coast, the Maharashtra coast, the Kerala coast and the Goa coast. Gujarat state on the west coast has got the second largest area of mangroves along the Rann of Kutch and Kori creek. In Maharashtra and Goa, mangroves exist in large patches especially along the Mondovi estuary and Kundalika estuary. Mangroves of Karnataka cover an area of 6000 ha and only very sparse stretches of mangroves exist in Kerala state. In addition to this, mangroves are also situated in the Andaman Nicobar Islands and the Lakshadweep islands. Insular type mangroves are present in Andaman and Nicobar islands where the lagoons and islets support a rich mangrove flora spread over an area of about 770 sq. km. with dominant species of Rhizophora *mucronata, Avicennia* spp., *Ceriops tagal* as indicated by Gopal and Krishnamurthy. The mangroves of Andaman and Nicobar Islands and Lakshadweep are frequently mixed with thick adjoining evergreen forests and occasionally they grow under the canopy of tall evergreen trees. The mangroves of India are considered to be very fertile but fragile, with high economic potential. These coastal endangered mangrove ecosystems protect the coastal areas from oceanic cyclones, tidal thrust, strong wind, checks soil erosion and also provides habitat to a number of species of flora and fauna. They are also a source of livelihood for local population.

1.2. 3 Mangroves of Kerala

Kerala lies towards the southwest coast of India, between the latitudes 8° 18' and 12°48' N and longitudes 74°52' and 77°24'with an area of about 38855sq.km. Mangroves are known as *Kandal kadu* in Malayalam, the language of Kerala. Reports of FSI (2003) based on the analysis of remote sensing data showed the presence of 800 ha area of mangrove cover in the State, with 300 ha moderately dense and 500 ha open mangrove vegetation. A recent study by Radhakrishnan et al,. (2006) showed that mangrove vegetation in four northern districts of Kerala -- Kasargod, Kannur, Kozhikode and Malappuram – is approximately 3,500 ha, which represents about 83 per cent of mangrove cover in the state. Out of approximately 1671 hectares (Suma, 2000) of Kerala's mangroves, more than half are located in Payyannur in northern Kerala. They grow in the inner reaches of the

inter tidal margin of estuaries, lagoons, back- waters and creeks along the extensive coastal region. Mangroves are also distributed in Veli, Ashramam, Ashtamudi, Keeryad Island, Chetwai, Vypeen Island, Mallikkad, Kumarakom, Pathiramanal, Edakkad, Pappinissery, Kungimangalam and Chittarai and in several other small patches across the state.

Kerala state boasts of 17 true mangrove species and 23 semi-mangroves (Unni 1998). The dominant mangrove species of Kerala are *Avicennia marina, Avicennia officinalis, Rhizophora mucronata, Excoecaria agallocha, Acrostichum aureum, Acanthus ilicifolius* and *Cerbera odollam, Thespesia populnea and Sonneratia caseolaris*. With regard to fauna in the mangroves, studies by Radhakrishnan et al. (2006) recorded 48 species of fauna comprising of 144 species of invertebrates (*Arachnida* – 24, hymenopterans in the super family *Chalcidoidea* – 11, *Odonata* – 23, *Lepidoptera* – 33, *Mollusca* – 21, *Annelida* –7 and *Crustacea* – 25 species), 122 species of fishes, 14 species of herpetofauna, 196 species of birds and 13 species of mammals. The high population density in Kerala has placed tremendous pressure on the mangroves of Kerala. The forest survey of India (2003) has shown that there was a reduction of 8 km^2 of mangroves of Kerala between the years 2001 and 2003.Vast lands of mangroves have been reclaimed for urbanization, construction of harbours, ports, prawn farming, coconut plantation, and paddy cultivation. Thus the mangroves of Kerala are in a degrading condition. Further, the present peculiar geomorphology of the estuarine area of Kerala, because of heavy sand mining from the rivers, pose problems for the natural regeneration of mangroves (Sunil Kumar, 2002). They are in need of urgent measures to protect them from being extinct vegetation.

1.3 .1 Major threats to mangrove ecosystems

Mangroves are among the most wide spread and productive inter tidal ecosystems in the world, covering up to 75% of the tropical coastline. In spite of the ecological and economical importance, they are being widely destroyed at the rate of 1% of the total mangrove area per year. Over the past fifty years, approximately 1/3 of the world's mangrove forests have been lost (Alongi, 2002). Nature as well as man is responsible for the destruction of mangrove

ecosystem (Valiela et al, 2001). Natural processes such as storms, cyclones, hurricanes, tides, sea level changes, drought, floods etc can be detrimental to the existence of mangroves. Global warming and eutrophication also plays havoc with the mangroves. Bacteria, viruses, fungi, boring insects and crustaceans which feed on mangrove propagules are other natural agents bringing destruction to mangroves. High rates of sedimentation can also prove to be fatal to mangrove habitats by initiating changes in the biogeochemistry of the environment and smothering the pnuematophores (Ellis and Nichols, 2004).

The greatest threat to mangroves is through human activities. Vast tracts of mangroves have been converted to shrimp farms or agricultural fields, in addition to being used for construction and recreational purposes. Building of major dams and roads have lead to collapse of agriculture forcing local inhabitants to resort to increased mangrove felling as an alternative source of income. Clear cutting of mangrove forests for timber contributes to changes in mangrove forests (Oo, 2002). This can lead to major modifications of soil properties of mangrove forests; disturb the watershed level (Dai et al, 2001) and loss of soil nutrients. Solomon et al (2002) have reported up to 70% loss of total soil phosphorous following clear cutting of mangroves. Changes in nutrient ratios leads to variations in phytoplankton population dominance and succession as well as changes in hydrochemistry. Replanted trees require at least 10years before they are able to provide any economic return. If tree cover is not re-established, interstitial water and soil conditions may change considerably (Rubin and Gorden, 1998). Urbanisation often resulted in increased sedimentation in coastal waters, which destroys the flora and fauna of mangrove ecosystem. Since mangroves are usually close to human habitats they are used as dumping grounds for sewage. Land use changes result in increased nutrient and toxic material loading into water bodies which may pose unacceptable ecological risk to coastal ecosystems including mangroves (Steven, 2003). Terrestrial run offs containing fertilizers, pesticides, effluents carried by rivers containing trace metals, organic toxicants such as poly nuclear hydrocarbons, polychlorinated biphenyls, oil spills and petroleum hydrocarbons pose a threat to mangroves. By 2025, due to global warming and green house effect, temperature is expected to increase by 0.5-0.9^{o}C leading to a sea level

rise by 3-12 cm (IPCC, 2001). This may induce changes in soil chemistry and structure as well as variation in communities of flora and fauna. The mangroves may or may not tolerate the sea level rise depending on the tide level (Mc Kee et al, 2007), species composition sediment accretion rate etc. Since ecological ties between mangroves and adjacent environment serves as a key for sustainable development, it is essential that awareness is created to preserve mangrove ecosystems. Despite these listings, it is not possible to assess completely the value of loss of species and food webs present in this ecosystem (Daur et al, 2002). Failure to conserve these habitats would by all possibility lead to severe economic and ecological consequences, lasting for decades.The active participation of local community, NGO's, and citizens' groups with active support from the media at all levels of planning, executing and monitoring is required for implementation and realisation of these goals (Alongi,2002).

1.3.2 Conservation of mangroves

Coastal wetlands have the potential to accumulate carbon at high rates over long time periods because they continuously accrete and bury organic-rich sediments. Chmura et al. (2003), calculated that, globally, mangroves accumulate around 0.038 Gt C per year, which, when taking area of coverage into account, suggests that they sequester carbon faster than terrestrial forests (Suratman 2008). However if current patterns of use, exploitation and impacts persist, coastal wetlands will become carbon sources rather than sinks. Jaenicke et al (2008) estimate that widespread loss of vegetated coastal habitats has reduced carbon burial in the ocean by about 0.03 Gt C per year.

Management, restoration or conservation of mangrove ecosystem requires an integrated, broad-based inter-agency partnership, all working towards a common goal involving mangrove research groups, government machinery, forest department, educational institutions pollution control board and ecologically sensitive people (Alongi, 2002). Mangrove conservation requires a collaborated research involving natural, social and inter-disciplinary study aimed at understanding the various components, such as monitoring of water quality, socio-economic dependency, biodiversity and other activities as an

indispensable tool for formulating long term conservation strategies. The restoration program should be realistic, designed to suit individual regions and specific to the problems of degradation in the region. It must take into account all aspects of the ecosystems, including habitat restoration, elimination of undesirable species and restoration of native species from the ecosystem perspective with holistic approach. This often requires reconstruction of the physical conditions, chemical adjustment of the soil and water, biological manipulation, reintroduction of native flora and fauna, etc. Involving the local educational institutions by conducting educational programs aimed at raising the levels of public awareness and comprehension of mangrove ecosystem restoration goals and methods will ensure active participation from all stake holders that show environmental sensitivity and value the opportunity for hands-on environmental education. Restoration program should be viably planned, so that project designers, executors and evaluators are able to work in a manner complementary to each other. People should be made to understand that by destroying mangroves they are doing away with nature's protective bio-shield and also doing away with an amazing biodiversity. Realizing the social and economic value of mangroves such as nature based tourism spots and propagating the message is the only way to prevent their indiscriminate destruction in the coming years.

1.4.1 Metal pollution in inter- tidal sediments

Heavy metal contamination of the environment due to anthropogenic inputs to inter tidal sediments from riverine, marine and atmospheric sources which began during the last decades of the19th century is ever since on the increase. Enrichment of inter tidal sediments with trace metals is a common phenomenon throughout the world (Gerhard and James, 2003). Sources of estuarine contamination have historically been urban point sources such as industrial effluents, sewage and to a lesser degree, urban runoff and atmospheric deposition (Daniel, 2000). Trace metals such as Ni, Co, Cu, and Zn etc are naturally present in inter tidal sediments. Tidal effect, as well as characteristics of sediments such as grain size, mineralogy, organic carbon content together with digenetic history can be important in influencing the trace metal

concentration and bioavailability. Concentration of heavy metals in fine grain sediments commonly range from background levels of a few μgg^{-1} to several hundred μgg^{-1} in polluted sediments. The level of contamination is of particular interest to the environmental health, as the estuarine environments are often sites of intense human and animal activity (David and Johanna, 2000). The concentration of trace metals in sediments varies with space, time and sediment mixing and in a well-mixed system; the spatial variation of trace metals might be small. A general decrease in sediment trace metal concentration is known to occur in a seaward direction. Inter tidal sediments are particularly prone to variability in sediment characteristics with depth when compared to other sedimentary environments such as lakes primarily due to tidal wave action, which can have profound effects in influencing particle size and sorting. Diagenetic history of inter tidal sediment profiles might also be more complex than in lakes since inter tidal environments may be subject to reworking and more rapidly fluctuating pore water compositions.

Land use changes and increasing urbanization can lead to increases in the out puts of a diverse set of trace elements associated with the operation and maintenance of infrastructure(Gerhart and James, 2003) resulting in increased loadings of toxic elements such as trace metals into the environment. Sediment enrichment of trace elements might pose unacceptable risks to valued ecological resources within the ecosystem. It suppresses primary production, alters species composition and size of phytoplankton community leading to a phytoplankton community with different nutrient and trace metal requirements and sensitivity than the original one affecting the higher trophic levels which graze on the phytoplankton and recycling of nutrients and trace metals. These may also include local extinction of an ecologically important species, reduced population sizes of valued ecological resources such as commercial fishery, increase in populations of less desirable species such as blue green algae. The ecological effects of trace metals may vary with precipitation rates, salinity, sediment type and land use (Riedel et al, 2000). Temporal and spatial loadings of trace elements in estuarine systems are complex. Speciation of trace elements can be controlled by biomass and species composition of phytoplankton, which in turn mediate tropic transfer

rates and control trace element availability to higher tropic levels (Bundy et al, 2003). The concentration of metals in sediments is of a higher magnitude than that in solutions. Trace element fluxes from sediments are affected by oxygen concentration and activity of benthic fauna. Studying the concentration and partitioning of trace metals in inter tidal sediments will enhance our awareness on the bioaccumulation and biological effects of trace metals in inter tidal environments. The sediment bound trace metals can cause bio magnification along the food chain and lead to metal toxicity which in turn depends on geo chemical as well as anthropogenic activities (Mohapatra and Rangarajan, 2000). Also trace metal concentration in inter tidal sediments will provide useful historic records of pollution in the future.

Metal pollution may arise due to natural weathering, human activities and suspended particulate matter. The influence of river transported suspended particles and associated organic matter are known to decrease with the distance from the shore. Studies have shown that tidal mudflats and particularly mangrove substrates contain a much greater load of trace metals than other shoreline sediments. The high organic content and low pH prevailing in mangroves makes them ideal metal accumulators (Akshayya et al, 2007). The physical and chemical conditions of mangroves may effectively trap trace metals in non-bio available forms. Though mangrove sediments are known to act as a sink for metals, the bio-availability of metals is found to be less (Machado and Lacerda, 2002). This is because most of the metals present are bound to organic chelating agents like tannins or other refractory organic compounds. For example mercury which may form dimethyl mercury which is volatile and unstable under normal conditions may accumulate and persist in the reducing environment of mangroves. Yet another reason may be the anoxic conditions prevailing in mangroves giving rise to the presence of sulphides which rapidly precipitate stable metal sulphides. Thus trace metals bound to organic complexes show reduced bio availability in the mangrove environment. Hence mangals may help to control trace metal pollution in tropical coastal areas. Low bio availability of trace metals in mangrove sediments in turn reduces the concentration of heavy metals in mangroves. Organism growth, reproduction and behavior are potentially affected by elevated

environmental metal concentrations present in the mangrove sediments. Sediment bound metals can be made available to an organism by solubilization which in turn depends on a number of environmental factors like pH, salinity, DO, temperature etc. Salinity variation is also known to cause variation in metal toxicity. High salinity is known to have a detoxifying effect on organisms.

Chemical or cellular variation that can be measured in tissue or body fluid samples of an organism provides evidence of exposure to and effects of one or more chemical pollutants such heavy metals. Biochemical alterations are usually the first detectable quantitative responses to metal exposure and demonstrate that the metal has reached sites of toxic action and is exerting a biological effect. For e.g.: peroxidase enzyme is produced in response to a number of environmental stressors, including heavy metals (Dietz et al., 1999). Another example is Phytochelatin, a low molecular weight peptide which can be used as an indicator of metal pollution as it is known to be biosynthesized in response to bioaccumulation of metals. Reduction in the levels of photosynthetic pigments in leaves including chlorophylls a and b and accessory pigments such as carotenoids, on exposure to heavy metal has been observed in many plants for metals such as Cu, Pb, Zn. Reduced growth, survival, reproduction, carbon assimilation, and production of carbon – based products along the estuarine food chain via detrital export, change of electrical conductance of plants etc can be used as an indicators of metal accumulation. Disruptions in the mangrove soil conditions may change the metal binding capacity of the sediment leading to mobilization of the metals which in turn will shift the mangals from a heavy metal sink to a heavy metal source *(*Kathiresan and Bingham, 2001*)*.

1.4.2 Uptake of metals by mangrove flora and fauna

Aquatic plants are known to possess unique sorption potentials and consequent stress responses. Various plant and algal species are known to accumulate metals in their biomass. Hence they have been tried for scavenging as well as monitoring the heavy metal pollution (Savitha and Suchi, 2007).

Macro algae which are generally fixed in one location and hence accumulate metals over time have been widely used as bio monitors for metal pollution (John and Martin, 2004). Even thin species of macro algae such as *M. hariotti* are reported to have notably high metal concentrations of Cu, Zn, Mn Al and Pb (Farias et al, 2002). Water hyacinth is another plant that has shown sorption potential for a huge array of metals without itself getting much affected. Similarly duckweed species can de effectively utilized for the removal of Cd, Hg, and Cu. Although small in size, these plants appear to have a remarkable in- built resistance capacity against metals. Other examples are Hydrilla, Vallisnera, and Potamogeton. Not only can many of these plants be used for detoxification of metals from water, but also many of the metals can be recovered subsequently by proper acid treatment of the slurry after biogas collection from the huge biomass (Lekov and Kristic, 2002).

Mangroves, due to their inherent physicochemical properties have an extra ordinary capacity to accumulate metals in their sediments (Marchand et al, 2005). The metal accumulated in sediments is many folds higher than that in the overlying water. Plants can also accumulate metal ions in an order much higher than the surrounding media (Kim et al, 2003).Various biochemical reactions and dissolution processes will convert the metals in sediments and water to bio available forms which helps in the uptake of metals by mangrove plants. The mobility and availability of heavy metals are generally low especially when the soil pH, organic matter and clay fraction content is high (Rosselli et al, 2003). Uptake of metals by plants could be due to adsorption, absorption, and also through some physiological adaptiveness and homeostasis. Metal binding with cell wall is rather common in lower group of plants such as fungi and bacteria. Another method is by compartmentalization i.e. transport of metals to apparently vacant spaces. Yet another method is by synthesis and binding with cellular proteins, peptides or by formation of buffering molecules such as phytochelatin, a tripeptide. The latter is considered to be a carrier for metal transport into the vacuole. Factors such as oxygen exclusion by underground roots leading to formations of iron plaques on them help in the exclusion of metals at the root level itself and physiological adaptations present in mangroves that prevent metal accumulation inside the

plant body are responsible for the low concentration of trace metals in mangroves (Machado et al, 2005). This is evident from the fact that the concentration of heavy metals in *Rhizopora apiculata* seedlings decrease from root to stem to leaves. Heavy metals accumulated in soils can cause severe phyto toxicity and cause evolution of metal tolerant plant population. Metal tolerant species which are active bio accumulators tend to trans locate metals to their above ground biomass. Heavy metal tolerant species can be used to minimize the migration of contaminants in the soil (Susarla et al., 2002). Though mangroves generally tend to accumulate metals mainly in the roots, there still looms the possibility of metal contamination of the food chain by the decaying roots (Weis and Weis, 2004). Mangrove trees and plants export the leaves as detritus (Machado & Lacerda, 2002). Though mangrove leaves tend to accumulate only low concentration of metals, it is still detrimental to the environment, due to the large amount of litter production by mangroves which counter balances the low concentration of metals in the leaves of mangrove plants. Hence there is the possibility of metal contamination from mangrove vegetation by the leaching out of metals from decaying vegetation to nearby water bodies, thus spreading metal contamination and possible deleterious effects of metal toxicity. Mangroves are known to be the nursery ground for a number of fishes including prawns. Crustaceans which feed on mangrove matter are known bio accumulate metals. The metals present in the mangrove sediments and biota (George and Tresa, 1997) may enter the food chain and cause toxicity in organisms due to inactivation of cellular enzymes responsible for normal organism survival and function. Birds which feed on the mangrove plants and fruits may also face the possibility of bioaccumulation of metals. Investigations of metals exported within detritus have proved that Cu, Zn, Cd, Pb, Mg, and Mn are all exported from the mangrove forests via detritus used as food source, and are subsequently detectable in the tissues of mangrove oysters and various fishes. Heavy metals are a serious ecological concern as they have long half life period in the soil thus having far reaching consequences on the biological system including soil microorganism and biota (Ram et al, 2000). The level of uptake, accumulation and distribution of trace metals in mangrove plants differ seasonally, spatially and with the saline environment (Sarangi et al., 2002). Thus due to their impact on the survival

of many organisms including man it is important to get information on the bio accumulation of metals in mangrove flora and fauna as in is an indication of natural and anthropogenic impact on the environment.

1.5 Significance of the study

Mangroves are considered to play a significant role in global carbon cycling. Themangrove forests would fix CO_2 by photosynthesis into mangrove lumber and thus decrease the possibility of a catastrophic series of events - global warming by atmospheric CO_2, melting of the polar ice caps, and inundation of the great coastal cities of the world. The leaf litter and roots are the main contributors to mangrove sediments, though algal production and allochthonous detritus can also be trapped (Kristensen et al, 2008) by mangroves due to their high organic matter content and reducing nature are excellent metal retainers. Environmental pollution due to metals is of major concern. This is due to the basic fact that metals are not biodegradable or perishable the way most organic pollutants are. While most organic toxicants can be destroyed by combustion and converted into compounds such as CO, CO_2, SO_x, NO_x, metals can't be destroyed. At the most the valance and physical form of metals may change. Concentration of metals present naturally in air, water and soil is very low. Metals released into the environment through anthropogenic activities such as burning of fossils fuels, discharge of industrial effluents, mining, dumping of sewage etc leads to the development of higher than tolerable or toxic levels of metals in the environment leading to metal pollution. Of course, a large number of heavy metals such as Fe, Mn, Cu, Ni, Zn, Co, Cr, Mo, and V are essential to plants and animals and deficiency of these metals may lead to diseases, but at higher levels, it would lead to metal toxicity. Almost all industrial processes and urban activities involve release of at least trace quantities of half a dozen metals in different forms. Heavy metal pollution in the environment can remain dormant for a long time and surface with a vengeance. Once an area gets toxified with metals, it is almost impossible to detoxify it. The symptoms of metal toxicity are often quite similar to the symptoms of other common diseases such as respiratory problems, digestive disorders, skin diseases, hypertension, diabetes, jaundice etc making it all the more difficult to diagnose metal poisoning. For example the Minamata disease caused by mercury pollution in addition to affecting the nervous system can

disturb liver function and cause diabetes and hypertension. The damage caused by heavy metals does not end up with the affected person. The harmful effects can be transferred to the person's progenies. Ironically heavy metal pollution is a direct offshoot of our increasing ability to mass produce metals and use them in all spheres of existence. Along with conventional physico- chemical methods, bio-system approachment is also being constantly used for combating metal pollution.

Cochin is a highly industrialised city located on the southwest coast of Kerala. There are several patches of mangroves distributed around the Cochin estuary, especially on the Vypeen Island located on the southern side of the Cochin estuary. The mangroves of Cochin are connected by a number of channels and inlets to the Cochin estuary. The Cochin estuary receives drainage from the river Periyar and its tributaries which in turn receives effluents from a number of major and minor industries located on its bank. Besides this, land run off and dumping of sewage increases the pollution load reaching the Cochin estuary. The pollution index of Cochin will definitely show an increasing pattern with industrialization around the Cochin estuary posed to show an upward mobility, with the realization of the international container terminal at Vallarpadom in Cochin, the proposed gas cracking unit to be set up by GAIL at Puthuvypu island on the western side of Cochin estuary, as well as the proposed marina at Mulavukad island near Cochin estuary. Industrialization of Cochin will definitely leave its mark on the mangroves of Cochin and there is the possibility of these mangrove areas eventually turning into a sink for metals and other toxic wastes. Fishing is done extensively in and around Cochin using country boats mechanized boats as well as with Chinese dip nets. The islands around Cochin estuarine system are well known for prawn farming and paddy cultivation. Paddy cultivation and prawn farming are done in an alternate manner in many areas. Prawn culture is mainly based on trapping the juvenile prawns that flow in along with the tides from the river discharge and harvesting then periodically. Of late this method is found to be less viable and the cultivators have shifted to growing procured spawns. Substantial amounts mangrove detritus is exported from mangrove forests to the surrounding communities(Machado et al, 2002).The loss of natural prawns and fishes in the rivers is considered as an impact of increasing degradation of mangroves and pollution load in the Cochin area as elsewhere in

the world(Nyunja et al, 2009). The Vypeen island which is a narrow strip of land running from Cochin bar mouth to Munambam about 40 km north, has a sizeable area of mangroves. The nursery role of mangroves to juvenile fishes is well established (Cocheret and Nagelkerken, 2004). The potential role of mangrove ecosystems as sinks for metal contaminants in tropical and subtropical areas is widely accepted (Akshayya et al., 2007). The trend of metal export from mangrove sediments to mangrove plants are also reported (Machado et al, 2002). Since the juveniles feed on these detritus, bio magnification of these toxic wastes along the food chain producing far reaching consequences looms very heavily on Cochin. Increase in salinity with rise of temperature as a consequence of climatic changes may also affect the trace metal biogeochemistry of the mangroves of Cochin. Though studies have been done to assess the metal contamination of mangrove sediments of Cochin not many studies have been done regarding the accumulation of toxic metals in the flora of Cochin mangroves. Therein lays the significance of this work.

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Chapter II

Study Sites, Materials and Methods

2.1 The Cochin Estuary

Cochin is the largest city in Kerala on the southwest coast of India, located at 9^0 58 'Nand 76^0 17'E. Cochin has a tropical climate with no extremities. It receives abundant rainfall during June to September from southwest monsoon and to a lesser extent during October to December from north-west monsoon. It has a population of above five lakhs, which keeps on increasing due to rapid industrialization. An all weather harbour, Cochin is an important centre of trade and commerce. It has a maritime history dating almost two thousand years back. The Portuguese, Dutch and the English have established themselves in Cochin one time or the other. Cochin consists of mainland Ernakulam, Willington Island, Fort Cochin and Mattancherry peninsula, Vypeen, Bolgatty Island, Gundu Island, as well as a number of small islands dotting its backwaters. Cochin has a number of industries both big and small engaged in the manufacture of chemicals, pesticide, insecticide, tyres, rayon, and machinery. The rapid industrialisation is making Cochin more and more polluted and leaving it with shrinking green spaces.

Cochin estuary is a typical tropical estuary. It is the largest of the estuaries on the Kerala Coast, connected to a chain of islands where prawn and fish farms are found abundantly. The hydrography of the estuary is controlled mainly by discharges from Periyar river on the north and Muvattupuzha river on the South and also by tidal action through the Cochin bar mouth. Saline water intrusion to the southern parts of the estuary is regulated through the Thannermukkom bund, a salt water barrier commissioned in 1975. The bulk of the sedimentary material is being supplied to the Cochin

estuary by the rivers Periyar and Muvattupuzha. Four more rivers namely, Achankovil, Meenachil, Manimala and Pamba discharge water into the estuary on opening of the Thannermukkom bund during the rainy season. The mangroves of Cochin are mainly located in the northern part of Cochin Port, Puthuvypu, Kannamali, and Mangalavanam. The mangroves around Cochin estuary are visited by more than 8 species of prawns, 12 species of estuarine fishes, which spent their adult life elsewhere. Increasing human population as well as escalating industrialisation is threatening the existence of the mangroves of Cochin. Adding to the woe is the ever-increasing load of effluents containing harmful chemicals given out by the numerous industries located on the banks of the river Periyar as well as by sewage dumping from the city. The on going Vallarpadom container terminal project and the completion of the Goshree Island bridges has added further fuel to the pollution load of Cochin and the Vypeen island. This may be detrimental to the existence of the ever-shrinking mangroves of Cochin. The Valanthakadu island in Cochin which is well known for it mangrove vegetation is under the threat of extinction due to the proposed high-tech city project. Awareness about the ecological importance of mangroves is on the rise in Cochin by nature loving NGO's and eco-conscious society members. Mangrove propagation and rehabilitation is being carried out with the help of the local population. Mangroves are also becoming an important tourist attraction of Cochin where the so called eco-tourism is being aggressively promoted. One can only hope that these wonders of nature will be protected and cherished for their ecological and economical importance, and not become a folk tale for the future generations.

2. 2 Sampling Sites

2.2.1 Station 1: Fisheries Station, Puthuvypu

The Vypeen Island is the most densely populated area of the world

situated Southwest, across the backwaters of Cochin. The Vypeen Island is located close to the Cochin estuary at 10° 10' N and 76° 18'E. It has an area of about 87.17 km^2 and has the Cochin backwaters in the east and the Arabian sea on the west. It has an extensive network of canals connected to the backwaters and the sea. Vypeen island boasts of the oldest fort built by the Europeans in India.-the Palllipuram fort built around 1503. Puthuvypu is a sea accreted area situated on the Vypeen Island. This accretion is known to have taken place after the opening of the Cochin harbour in the year 1929. Puthuvypu has a sizeable area of mangroves growing on sea accreted land. *Avicennia officianalis, Rhizopora apiculata, Rhizopora mucronata, Acanthus ilicifolius* and *Bruguiera cylindrica* are some of the mangrove species commonly found in the Vypeen area. It is an area of intense fishing related activities. The fisheries station at Puthuvypu is about 3 km north of Vypeen, on the western side of Vypeen- Munambam road. It is located close to the sea and is almost undisturbed except by the research activities carried out at the station and is also free from sewage dumping. *Avicennia Officianalis* is the major mangrove vegetation present in this area. *Rhizopora mucronata* and Rhizopora *apiculata* are also seen, with the latter being more abundant. *Acanthus illicifolius* occur as scattered patches.

2.2.2 Station 2: Murukumpadom

This station on the western side of Vypeen, Munambam road, about 1km away from it. Murukumpadam is a densely populated area, with intense fishing related activities. There are a number of fishery related units and berths for mechanized fishing boats in and around Murukumpadam. A significant portion of the mangrove covered areas have been cleared for human settlement. *Avicennia marina* shows a luxuriant growth in this area followed by Rhizopora *apiculata*. *Bruguiera cylindrica* is also seen interspersed with *Avicennia marina* plants. *Acanthus ilicifolius* is present as dense patches, especially during monsoon. This area is found to be water logged except during the pre- monsoon period. The environment is disturbed by human activities. It is also close to the road transport

pathway. Water scarcity is acute in this region and people have to depend on potable water brought in by tanker lorries during premonsoon. The marshiness of the place makes it a notorious area for mosquito breeding.

2.2.3 Station 3: Mangalavanam

Mangalavanam is on the eastern side of Cochin estuary, in the heart of the city of Cochin. It is considered as the green lung of the city. Mangalavanam is a protected bird sanctuary and is famous for its mangroves as well as for the numerous birds inhabiting its greenery. The native and migratory birds use the canopy in Mangalavanam for roosting. Forty one species of birds belonging to twenty five families have been located in Mangalavanam. The Black crowned *Night Heron* and the *Little Coromant* species were found here in large numbers. It is connected to the Cochin estuary through a narrow canal. This canal carries effluents from the nearby locales. *Avicennia officinalis* is found abundantly in areas close to the canal inundated by tidal flow. Patches of *Rhizopora apiculata* and *Rhizopora mucronata* are also found in Mangalavanam at places located slightly away from the canal. *Acanthus illicifolius* is found as scattered patches in areas which are not frequently wetted by tides. This bird sanctuary is now threatened by the high rise buildings being built in its proximity as well as by the heavy vehicular traffic following the opening of the Goshree bridges and the on going construction of the Vallarpadam container terminal.

2.2.4 Station 4: Munambam

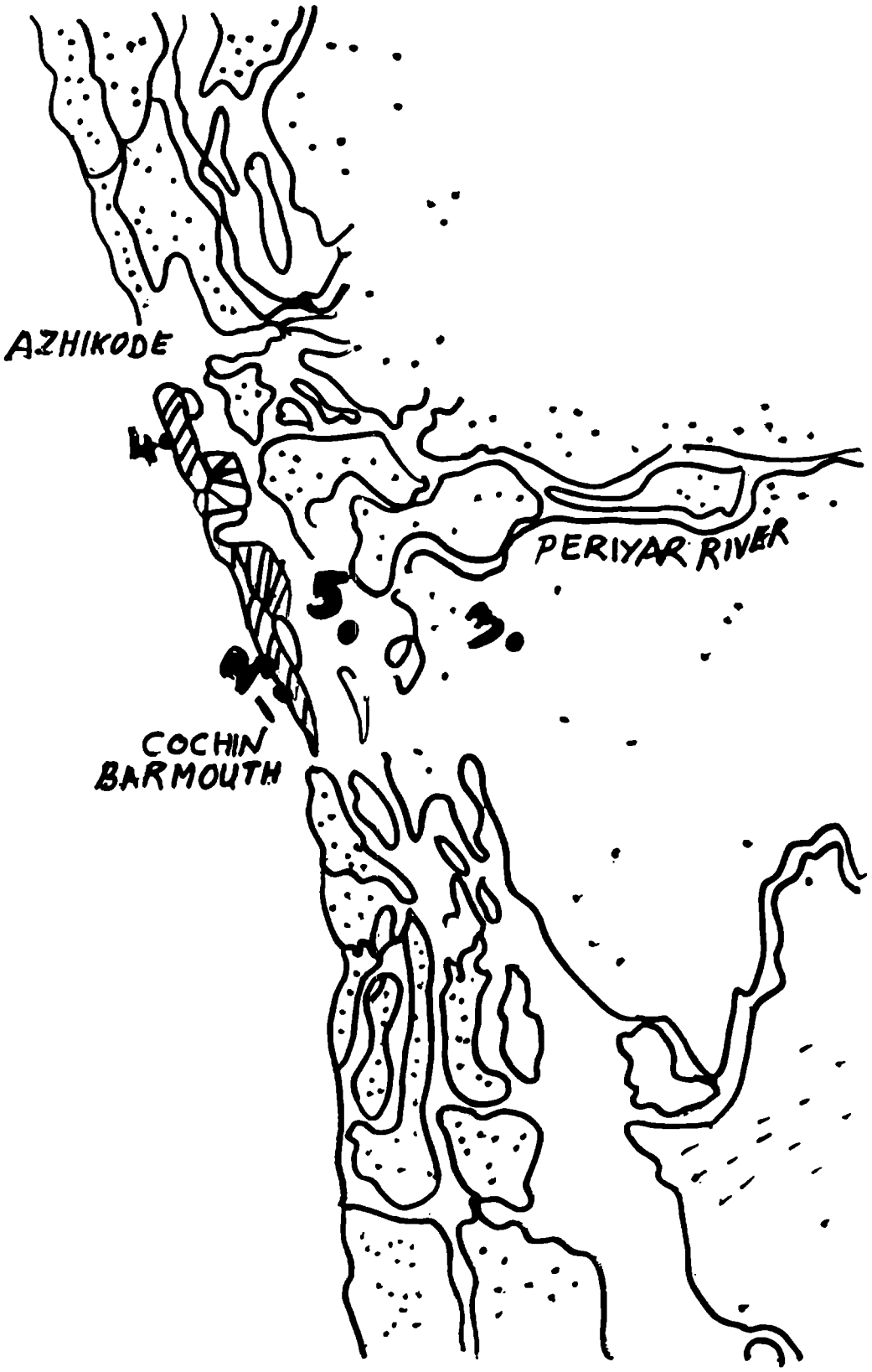
This is on the northernmost end of Vypeen Island, very close to the Munambam harbour. Munambam is an area of robust fishing and tourism related activities. Here the main mangrove species are *Avicennia marina* and *Rhizopora mucronata* interspersed with small patches of *Acanthus illicifolius*. Scanty vegetation of *Rhizopora apiculata* is also seen. This site

is connected to prawn farms in the locality and is in the close proximity of human habitation. Hence this station is under considerable anthropogenic influence. Among all the study sites, the density of mangrove vegetation is least here. The Arabian Sea is closest at this site when compared to all the others sites.

2.2.5 Station 5: Gundu Island

Gundu island is a non- mangrove station, selected for reference purpose. It is the smallest of all islands that constitute the city of Cochin. It is located between the mainland of Cochin City and the Vypeen Island. The area of this island is only 5 acres. It is accessed by boat, usually from the Vypeen Island. It has only sparse greenery, with coconut trees forming the major vegetation. The only building on it is a coir factory, which produces ropes and carpets. This island is now being used for short recreational purposes. It is under the influence of effluents brought downstream by the rivers emptying into the Cochin estuary. Gundu Island is also under constant and direct tidal influence.

Map showing the location of the stations chosen as study sites:



2.3 MATERIALS AND METHODS

2.3.1 Sampling Procedures

Samples were collected on bi monthly basis from 2001 February to 2002 January. All glassware and plastic bottles were cleaned as per the analytical requirement. Surface water samples were collected in clean plastic containers after rinsing it with the sample water a number of times. pH and salinity were determined immediately on returning to the laboratory. The water sample for dissolved oxygen analysis was fixed with the prescribed reagents immediately after collecting it in a DO sampling bottle as per the method used. Similarly, the samples for determining dissolved ammonium was treated with phenol reagent and stored in an icebox until reaching the laboratory.

Sediment cores were collected using an acid washed, clean polymer corer. Each core was packed in clean polythene bag, tightly closed and kept in an icebox. On reaching the lab was the core samples were kept frozen until used for analysis. The air-dried sediment samples required for analysis were powdered using an agate mortar and pestle. The plant parts were washed thoroughly with distilled water, followed by milli-Q water and stored in polythene bags in a freezer until used for analysis. The plant parts required for determination of moisture was kept immediately in the oven on reaching the laboratory.

2.3.2 Analytical Techniques

The glassware used were soaked in the prescribed solutions for the required period, washed with distilled water, followed by milli-Q water and dried.

2.3.2.1 Hydrography

i) pH

Measured with a calibrated pH meter.

ii) Salinity

Modified Mohr's method developed by Knudsen was used (Grasshoff et al, 1983a).5 ml of the water sample was pipetted out into a conical flask and diluted to about 20ml with milli-Q. Titrated with standardized AgNO3 solution using K_2CrO_4 solution as indicator. From the titer value, chlorinity was determined. Salinity was then calculated using the generally accepted and universally used (IAPSO), salinity chlorinity relation.

iii) Dissolved Oxygen

The Winkler's Method was used to determine dissolved oxygen in water samples (Grasshoff, 1983 ,b).The DO bottle was filled to the brim without generating turbulence to avoid atmospheric oxygen. The DO was fixed by adding 1 ml of Winkler A followed by 1 ml of Winkler B. The bottle was stoppered and shaken well for 5 minutes. Added 1 ml of H_2SO_4 to dissolve the precipitated $Mn(OH)_2$ and shaken well. Pipetted out 20ml of the above solution into a conical flask and titrated against standardized thiosulphate, using starch as indicator. From the titer value the DO was calculated.

iv) Alkalinity

A known volume of water sample is taken and to this a known volume of 0.01N HCl is added. Titrated the solution against 0.01N NaOH using bromothymol blue as indicator. From the titer value, the alkalinity was calculated (Grasshoff,1983,a).

v) Dissolved Nutrients

The concentration of dissolved nutrients was carried out using Spectronics Genesis -10 spectrophotometer, as per the standard procedure (Grasshoff,1983 c).

a) Dissolved Nitrite

Nitrite concentration was found out spectrophotometrically by measuring the concentration of the azo dye formed by the reaction between nitrite in the sample, the aromatic amine suphanilamide and N- (1-Naphthyl) – ethylenediamine. The dye is allowed to develop for 15 minutes and the concentration of nitrite was determined at 540nm.

b) Dissolved Ammonium

Determined by the indophenols blue method, using nitroprusside catalyst, as suggested by Karloff. In this process, phenol reacts with hypochlorite in the presence of NH_3 to give blue coloured indophenol. Concentration of dissolved ammonium was determined spectrophotometrically at 630 nm.

c) Dissolved inorganic phosphate

To a known volume of the sample, added ascorbic acid and mixed reagent (prepared by mixing ammonium hepta molybdate tetrahydrate solution and K antimony tartarate solution), following the procedure given in the ascorbic acid method. The phosphate concentration was measured within 10-30 minutes spectrophotometrically at 880 nm.

vi) Hydrogen Sulphide

The DO bottle was filled with the water sample without turbulence and the H_2S fixed with ZnO solution, stoppered and shaken well. The precipitated ZnS is allowed to settle down. Added H_2SO_4 and a known volume of KIO3. Stoppered and shaken well until the precipitate dissolved. A definite volume was pipetted out and titrated against standard thiosulphate using starch as indicator. The volume of thiosulphate required to react with a known volume of std KIO_3 was found out. From this, the volume of thiosulphte required to react with the excess KIO_3 in the water sample was calculated and the concentration of H_2S was found out (Grasshoff, 1983a).

2.4 Sediment Analysis

2.4.1 Total Organic Carbon

The wet oxidation method of El Wakeel and Riley was employed. Homogenized, air dried sediment sample was treated with 1 N $K_2Cr_2O_7$ and con. H_2SO_4 with cooling. After 30 minutes, it was diluted and mixed with 85 % H_3PO_4, NaF and ferroin indicator. Back titrated this solution with standardized ferrous ammonium sulphate and the percentage of organic carbon was calculated (Gaudette et al, 1975).

2.4.2 Sedimentary Protein

A weighed amount of dry sample was homogenized with 1N NaOH. The samples were maintained at 80 ^{0}C for 30 minutes to dissolve the proteins. Cooled, centrifuged and a known aliquot of the extract was mixed with Cu reagent, followed by Folin -Phenol reagent after 10 minutes. Appropriate blank and standards were treated similarly. After 40 minutes the samples

were analysed spectrophotometrically at 750 nm (Lowrey et al, 1951). Bovine albumin was used as the standard.

2.4.3 Exchangeable ammonium

The method of Keeney and Nelson (1982) was used. A known weight of the dry sediment was shaken with 2N KCl on a mechanical shaker for 1 hr. Filtered the solution and using the extract, the concentration of ammonium was determined colorimetrically by the indophenol blue method described above.

2.4.4 Tannin and Lignin

It is based on the formation of a blue colour on reduction of Folin – Ciocalteau- Phenol reagent by the aromatic OH groups present in tannin and lignins. The effect of Mg and Ca hydroxides and bicarbonates were suppressed by the addition of Tri Sodium Citrate (Nair et al, 1989).

Accurately weighed dry sediment was leached with 0.05 M NaOH for 72 hrs and sub sampled at 5, 15, 45, and 120 minutes and thereafter at random up to 72 hrs. To a known aliquot of the extract was added in rapid succession, 1.6 M Tri Sodium Citrate solution followed by Folin Ciocalteau reagent and Carbonate-Tartrate reagent and allowed to stand for 30 minutes. The absorbance was measured spectro photometrically at 760nm against a reagent blank of 0.05 NaOH treated similarly. Tannic acid standards were used to prepare the calibration curve (APHA, 1985).

2.4.5 Texture

Sedimentary texture was determined by Pipette analysis. A known weight of the sediment, freed from carbonates and organic matter was dispersed overnight in 5% Sodium Hexametaphosphate (calgon) and left overnight to deflocculate the particles. Wet sieving was carried out using a 63μ ASTM sieve. The remaining portion was subjected to pipette analysis for calculating the silt and clay fraction (Krumbein and Pettitjohnson, 1938; Lewis, 1984).

2.4.6 Trace Metals

Dried and powdered sediment was digested in a mixture of acids (Con HCl+ Con HNO_3 + $HClO_4$) taken in the ratio 1: 1: 2 at 70^0C. The residue was extracted with milliQ water. Centrifuged and made up in a standard flask and analysed for trace metal concentration with atomic absorption spectrophotometer (Perkin Elmer Model 3110), using air- acetylene flame (George and Tresa, 1997).

2.5 Mangrove Plant Part analysis

2.5.1 Moisture

A known mass of fresh plant part was heated at 105^0C in an oven until constant weight was obtained. From this the % of moisture per gram weight was found out.

2.5.2 Organic Carbon

About 1 g of dried, powdered plant material was heated at 550^0C for hrs.

From the difference in mass the amount of organic carbon was found out (Ong Che, 1999).

2.5.3 Kjeldhal Nitrogen

Accurately dried and powdered plant part was digested with con. H_2SO_4 in the presence of a pinch of $CuSO_4$ as catalyst in a Kjeldhal flask. An aliquot of the made up solution is pipetted into a Kjeldhal's distillation apparatus followed by 40% NaOH solution. The apparatus is connected to a steam generator and the ammonia liberated is absorbed into boric acid containing 1or 2 drops of mixed indicator taken in a conical flask. The contents of the conical flask are titrated against 0.02 N HCl. A duplicate was also done. Knowing the weight of the sample taken and the titre value, the Kjeldhal nitrogen can be calculated (Jones, 1991, Jones 2001).

2.5.4 Protein

Plant protein is assumed to contain 16% N. Based on this assumption, from the estimated N content in the plant sample (mg/g), the protein content (mg/g) is calculated by multiplying with 6.25.

2.5.5. Tannin and Lignin

The process of Nair et al (1989) and APHA (1995) was used.

2.5.6. Chloride content of leaves

The dry plant leaf was taken in a crucible and moistened with 5% Na_2CO_3 solution. Evaporated to dryness and charred on a hot plate until smoking stops. Combusted at 500 ^{0}C for 24 hrs.

Dissolved the residue in 5N HNO_3. Diluted to known a volume and titrated with standard 0.1N $AgNO_3$ solution until precipitation is complete, then

added a slight excess. Stirred well and filtered through filter paper (What man no.41) and the precipitated Ag Cl was washed thoroughly. The combined titrate and washings were mixed with a saturated solution of Fe $(NH4)_2$ $SO_4.12.H_2O$ followed by 12 N HNO_3. Titrated the excess $AgNO_3$ with 0.1N Potassium Thiocyanate. The titre value was used to calculate the amount of chloride in the leaf (AOAC, 1990).

2.5.7 Trace Metals

Dried plant part was digested in a mixture of acids (con. HCl+ con.HNO_3+ $HClO_4$) taken in the ratio 1: 1: 2 at 70 ^{0}C. The residue was extracted with dilute acid and made up to 25 ml. This was then analysed by AAS using air- acetylene flame to determine the concentration of trace metals (George and Terse, 1997).

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Chapter III

Hydrography of Mangroves

3.1 Introduction

Mangrove forests comprise a dominant and productive ecosystem along most of the world's tropical and subtropical coastlines.They have a peculiar hydrochemistry which is generally controlled by tides, mangrove vegetation and creek geometry. The residence time of water in mangrove forests is highly dependant on forest topography,size and type. Mangroves grow along the depositional environments in protected coastal areas, in estuaries and lagoons. Once established, they accelerate sediment accretion, by trapping suspended matter and decreasing erosion. Mangroves are exposed to tidal fluctuations and corresponding variability in salinity and water sources. Water quality of mangroves is known to affect the ecology of mangroves. The complex hydrochemistry chemistry of mangroves is a result of a large number of interacting physical and biological factors controlling various environmental processes as well as properties of the shore face sediment on which mangroves develop, the physiographical characteristics of the area, the influences of climate and the modification by vegetation. Therefore, the dynamics of water and inorganic and organic compounds depend on interactions controlled by tides, runoff, seasonal fluctuations, and meteorological events. Coastal ecosystems are constantly subjected to multiple stressors resulting from both human and natural environmental variations. Land use pattern, anthropological activity etc will influence the quality of water. Salinity, redox potential, pH and sulphide concentration are parameters that play key roles in the development of mangroves and their spatial distributions. To cope with the variation of these properties, mangroves have developed many adaptations that give them wide ranges of tolerance. These adaptations result in geochemical modifications in the sediment. Additionally, climate, tidal flooding, vegetation evolution, bio turbation

and organic matter content are parameters that also contribute to the complexity of the geochemistry of mangrove inhabited deposits. Change in water quality may lead to local extinction of an ecologically important species, reduced population sizes of commercially important fishery or reduced species diversity. It may also promote the growth of undesirable species such as blue green algae ctenophores (Steven M. Bartell, 2003). Atmospheric pollutants which are deposited on water surface can regulate water quality. The deposition from atmosphere occurs through two dominant forms- wet deposition associated with atmospheric precipitation and dry deposition caused by gravitational settling of particles and turbulent deposition of small, particles and trace gases.

Mangrove ecosystems are known to be potentially significant sources of organic matter to adjacent estuaries and coastal waters on a global scale. The biogeochemical functioning of mangrove environments has been well described for a number of sites around the world, but our ability to elucidate carbon and nutrient budgets of these ecosystems and their impact on the coastal zone is still limited. The transport of material between the intertidal zone and the water column (estuary, lagoon, or tidal creeks) is a crucial aspect in understanding the functioning of these systems (Flindt et al., 2007). Particulate organic matter can be exported from mangrove systems, but additionally, suspended matter from the water column can be an important source of organic matter to the inter tidal zone. Nutrient species are known to play an important role in maintaining water quality. Increased nutrient loadings have been of concern in many coastal systems as it will change phytoplankton species composition, dominance and succession, because phytoplankton species vary in their nutrient requirements. Low levels of eutrophication may be beneficial to benthos, but higher levels will lead to reduction in diversity and functioning. Reduction of nutrients alone will not improve the water quality of coastal ecosystems (Riedel, 2003). Water quality factors such as DO, pH, salinity, and temperature can determine the solubulisation of metals, which in turn may lead to bio accumulation in mangrove vertebrates by passive uptake across permeable surfaces such as gills and digestive tract. Also when water reaches the mangrove environment, its trace metal load will be incorporated into sediments through chemical precipitation of dissolved phases and deposition of metal rich fine particulates. The

hydrochemistry of mangroves may affect the SPM quality and quantity. Pore water drainage to tidal channels during low tides has an influence on the water fluxing out of mangrove sediments which in turn will influence the trace metal geochemistry of mangrove sediments. When photosynthetic oxygen production ceases during night, H_2S from sediments diffuses upwards through the mud and escapes to the shallow water covering the sediments. Metal present in the water then get deposited as sulphides. Photosynthesis by diatoms and green algae also contributes to the precipitation of metal carbonates and hydroxides from the water column to sediments. Removal of carbon dioxide from water during day time increases the pH facilitating carbonate precipitation. Metal solubility and uptake are directly affected by pH. Low pH could enhance the solubility and uptake by plants. This in turn could lead to metal accumulation in food chain causing acute and chronic ailments in man (Susana, 2003) The discharge of heavy metals in the environment has several obvious impacts on aquatic ecosystems. Increasing awareness of ecological hazard of toxic metals from urban and industrial sources has involved considerable interest in the study of levels and fate of heavy metals in the aquatic environment (Ahmed et al., 2003). Mineralization in intertidal sediments and exchange of inorganic carbon through pore-water movement and/or diffusion during high affects the heterotrophic characteristics of the water column in mangrove ecosystems.

3.2 pH

pH in natural waters is determined largely by the CO_2 equilibrium. Large changes in the dissociation constants of carbonic acid accompanying salinity changes is likely to be the main cause of pH changes(Luke and Shamus, 2004). The pH values of mangrove waters is known to be neutral, acidic (Macfarlane, 2002) or basic (Mohammed, 2000). pH plays a significant role in the bio geochemical processes of the environment. As pH of water decreases, bacterial activity and nitrogen fixation is inhibited and the importance of fungi increases. The reduced rate of decomposition allows organic material to accumulate leading to low rates of decomposition resulting in reduced mineralisation and nutrient availability. pH also affects heterotrophic de nitrification which is common at pH 7-8. At high H^+ ion concentration metals such as Al, Cu, Cd and Zn will exert a toxic effect. Low

pH values have an impact on the dissolution or sedimentation of heavy metals and contribute to mobilization of metals as exchangeable species in mangrove sediments (Macfarlane, 2002). The effect of pH on the sorption of metals varies with the metal involved and the surfaces on which adsorption occur. In the case of plants, the uptake of cations from solution increases with pH. This is due to the change in electrical potential on the surface with change in pH or due to competition between the metal ions and the H^+ ions for sites on the surfaces (Barrow and Whelan, 1998). pH varies not only in response to seasonal or long term phenomena, but also due to short time scale phenomena such as diurnal variations in photosynthesis and respirations(Kenneth,2002), tidal induced or storm induced variations and oxygen concentrations. pH is known to increase rapidly at lower salinities and the rate of increase became smaller at higher salinities (Luke and Shamus, 2004). The mangrove waters of Cochin are known to show neutral to basic pH (Imelda and Chandrika, 2000), (Suma and Joy, 2003).

Results and discussion

Mangrove trees are known to tolerate pH from 6 to 9. Among the stations considered for research purpose, station 4 showed basic pH during all the three seasons. The highest pH of 9.14 in the present study was observed at station 4 during monsoon season. This is accompanied by a lowering of salinity (16.69ppt) and maximum value of dissolved ammonium (15.08 µmol/L) and low value of dissolved nitrite (1.61µmol/L). The pre-monsoon values of pH are found to be higher than post monsoon values. During pre-monsoon when temperatures are high, the increased value of temperature is also accompanied by an increased value for other hydrographic parameters such as salinity and pH. The high value of pH may also be due to the consumption of CO_2 by photosynthesis.

The lowest pH of 6.73 was observed at station 1 during post monsoon. During pre-monsoon, station 1, 2 and 4 located in Vypeen area, showed a pH range of 7.02-8.44. Previously reported pH from the mangrove sites of Vypeen varied between 7.5 to 8.2 for pre -monsoon (Suma and Joy, 2003). Stations 3, 4& 5 showed basic pH of above 8.2 in the month of February. Eutrophic waters are prone to massive phytoplankton blooms, particularly when temperature and light

intensity increases and the water body become stratified. The death of algal mass, followed by decomposition reduces the oxygen content of water severely. Another factor is the decrease in oxygen soloubility at high temperature which results in an increase in the rate of denitrification (Holm Kristensen and Jepsen, 1991).

Station 3 displayed a higher tendency for slightly basic to acidic pH. This is an anoxic site, with high organic matter content. In environments where the production of oxygen is less, the production rate of CO_2 may be sufficiently high to depress the pH. The low pH values may also be due to the decomposition of organic matter such as mangrove detritus, dead organisms or oil compounds leading to the production of hydrogen sulphide (Mohammed, 2000). At Station R pH showed a basic value during all seasons. This station is also in continuous contact with tidal flow from the riverine sources reaching the estuary. This site is devoid of trees. Hence it experiences good sunlight and consequently higher temperature than all other sites. As temperature increases dissolved ammonium NH_4^+ increases making the system more alkaline (Michael et al, 2002). Another noticeable factor is that during monsoon all the stations showed basic pH. This might be due to decrease in denitrification which reduces with decreases in temperature. This is because the majority of heterotrophs which dominate the denitrification have slower metabolic rates at lower temperature (Michael et al, 2002).

Statistical analysis showed that during pre monsoon pH correlated positively with NO_2^- and negatively with PO_4^{3-} During monsoon there is positive correlation of pH with salinity and alkalinity and negative correlation of pH with dissolved NH_4^+ During pre-monsoon there is a tendency for pH to decrease due to anoxic conditions which produces H_2S. At temperatures higher than 12^o ammonium release would increase (Michael et al, 2002). In post monsoon positive correlation exists between pH and salinity and negative correlation between pH with dissolved NH_4^+ and alkalinity. In post monsoon there is an increase in salinity accompanied by a decrease in oxygen solubility (Best et al., 2007) accompanied by a lowering of pH with increase in salinity. Considering the station wise correlation at station 1 negative correlation is observed between pH and dissolved oxygen while at station 2, positive correlation of pH and dissolved oxygen is

observed. At station 3, pH correlated negatively with dissolved NH_4^+ and positively with H_2S. At station 4, pH showed positive correlation with dissolved phosphate and alkalinity negative correlation with H_2S. At station 5 pH showed positive correlation with salinity, dissolved NO_2^- and PO_4^{3-} The mean value of pH during pre-monsoon was 7.85, for monsoon it was 7.98 and for post monsoon it was 7.46. The mean value of pH at stations 1 to 5 was 7.50, 7.88, 7.46, 8.36 and 7.72 respectively. Two way anova did not show any significant variations.

3.3 Salinity

Mangroves are known to occur in a wide range of salinities and some species of mangroves are known to grow in practically fresh water. Salinity is important to mangroves because it reduces competition from other plant species. Mangrove species such as *Rhizopora*, *Avicennia* and *Laguncularia can* tolerate salinity due to salt exclusion at root level accomplished by negative pressure generated by transpiration in the leaves. *Avicennia* can also extrude salt through salt glands on leaf surfaces, explaining its successful existence in moderately hyper saline areas above the normal tidal level. Though temperature changes in tropics may not be as great as in higher latitudes, it can introduce changes in soil water content and salinity. Salinity becomes a problem for mangrove species only under hyper saline conditions which occur due to poor tidal circulation, combined with low rainfall, high temperature and high evaporation rates. Hyper salinity is known to cause mortality rates as high as 70% among mangroves. Salinity is known to have a profound influence on phytoplankton distribution and influence. It also played a dominant role in determining the photosynthetic rate of algal plankters and thereby the production as in for e.g. –Ice algae, held at salinities of 60-100 psu which showed negligible photosynthesis. Salinity stress causes inefficient photon transfer between pigment molecules leading to a reduction in quantum yield of photosynthesis. Higher salinity is related to inhibition of electron flow in the redox systems involved in photosynthesis (Peter et al, 2005). Fluctuations in salinity may subject organisms to osmotic stress and cause toxicity. The state of heavy metals and their bio availabilities are strongly dependent on the salinity (Miramand, 2001). Metals which are present in a complexed form are known to be released into a solution at high salinities. Similarly, organic contaminants which

are present in aquatic systems may undergo a salting out effect as the salinity increases. Extreme salinities are reported from *salitrals*, which are open areas in the center of large mangrove strands, furthest away from channels and feeder streams. Salinity above 80 ppt has been reported from such areas of Trinidad. Hyper saline conditions can alsc arise if water circulation to mangrove areas is cut off due to manmade activities. For example, in the mangrove areas of Indus delta of Karachi, salinity as high as 47 ppt was observed during summer season. The hyper saline conditions in the Indus delta is due to the decrease in the Indus river discharge due to up damming for increased demand of agriculture in the country (Saifullah, Khan and Ismail, 2002).

Results and discussion

Salinities varying between 2.78ppt during post monsoon season to 37ppt during pre monsoon season has been previously reported from the mangrove sites of Cochin (Imelda and Chandrika, 2000), (Suma and Joy 2003). Seasonal fluctuations of salinity are inversely related to water level changes caused due to both rainfall and tidal influence. The present study showed a marked variation in the salinity on moving from pre monsoon to monsoon and then to post monsoon. Salinity was high during pre monsoon and it decreased during monsoon and again increased during post monsoon for all stations. The salinity in the wet season is significantly lower than the dry season due to variations in precipitation (Pinsak & Eric, 2002). At lower salinities, pH is known to increase rapidly (Luke and Shamus, 2004), which is clearly evident in the month of June, for all stations. The highest salinity was observed at station 4 during February. This station being close to the sea shows higher salinity than all other stations during almost all months. High salinity levels are observed in poorly inundated sites where capillary water may evaporate at soil surface and also in depressions without adequate connections to water bodies. Mangroves typically are established on a raised and sloped platform above mean sea level, and inundated approximately30% or less of the time by tidal waters (Lewis, 2005). Disruptions in fresh water flow in arid areas will lead to the death of mangroves (Medina et al, 2001). The lowest salinity was observed at station 3 during monsoon. The mean salinity in general depends on the seasonal cycle but it is also closely linked to the

occurance of rainfall during the preceding days, especially during the past one week (Pinsak and Eric, 2002). Station 3 receives effluents from the land which will be large during monsoon making the salinity reach almost nil. In fact station 3 showed comparatively low salinity than other stations during all seasons. This station also had a tendency to show almost neutral to acidic pH with the exception during the month of February when it showed basic pH.

Statistical analysis indicated that salinity had positive correlation with pH during monsoon as well as post monsoon. With alkalinity positive correlation is observed in pre monsoon and negative correlation in post monsoon. pH correlated positively with dissolved PO_4^{3-} during pre monsoon. Dissolved oxygen correlated negatively with pH during post monsoon. The means of salinity during pre monsoon,, monsoon and post monsoon were as follows: 25.28, 5.48 and 10.26. The station wise means of salinity for stations 1 to 5 was 13.57, 14.40, 8.09, 20.17 and 12.15 respectively. Two way anova showed significant variation of salinity seasonally with $P<0.001$.

3.4 Dissolved Oxygen

The fate and fluctuations of dissolved oxygen has been identified by the water directive frame work as one of the five general physico-chemical parameters supporting the biological elements (WFD, 2000). The Ospar insists that temperature and salinity are the main physical parameters affecting DO (OSPAR, 2005). Other factors are photosynthesis which produces oxygen and resipiration and nitrification which consumes oxygen. Anthropogenic activities such as loading of organic matter via sewage, riverine discharge and agriculture will also bring about changes in dissolved oxygen (Best and Wither, 2007). Mangroves are known to occur in regions of turbid, silt- laden water and frequently grow on fine anaerobic soils. Oxygen levels are often rather low in mangrove waters. The dissolved oxygen in mangrove waters are known to vary seasonally. The mangrove roots which become submerged during tidal inundation depend on dissolved oxygen during respiration. Oxygen supply is important in determining the rate of decomposition of dissolved organic matter. As decomposition proceeds, oxygen is consumed through respiration by the decomposer

organisms. If the water becomes anaerobic, a variety of bacteria such as denitrifies, sulphate reducers, and methane producers carry out the breakdown of organic matter, which is found to be less efficient. Thus organic matter accumulation may be greater where oxygen supply may be limited. Most tropical coastal waters are well oxygenated, and therefore oxygen supply probably does not limit decomposition. The increased microbial activity rapidly deoxygenates water (Wenchuan et al, 2005). The extent of deoxygenation depends on a number of factors including the dilution of the effluent on entering the river and the amount of biologically oxidisable material present in the effluent. With progressive increase in nutrient content, a decrease in oxygen content of water has been reported (Deegan et al, 2002). In eutrophic waters, blooms followed by death of algal mass and decomposition reduces the oxygen content of water and regulates the entire benthic metabolism(Viaroli and Christian, 2003) severely frequently causing substantial fish kill. Fish eggs and larvae which require higher oxygen levels are particularly vulnerable to low oxygen levels. Hypoxic conditions may force adults to abandon nests exposing the habitat of juvenile fishes to predation. Low DO suppresses the immune system of fishes, making them prone to diseases such as lymphocystis and epidermal hyperplasis (Denise Breitburg, 2002). Low dissolved oxygen also severely degraded benthic (Dauer et al, 2000).The influence of oxygen availability is substantial with some species automatically shutting down denitrification if oxygen is present. Temperature affects oxygen solubility with oxygen solubility decreasing with temperature, which results in an increase in the rate of denitrification and P burial in the sediments (Boesch et al, 2001 a). As salinity increases a reduced solubility of oxygen results (Best & Wither, 2007).

Results and discussion

Dynamic patterns of DO emerge in estuaries from complex interaction among physical, chemical and biological processes(Diaz,2001).In the mangrove environment, dissolved oxygen values during pre monsoon period it is reported to vary between 3.3 to 4.4 ml/L. During monsoon increase due to fresh water influx and dissolved oxygen content is reported to vary between 3.3 to 5.5ml/L. During post monsoon period the amplitude of variation was slightly narrower compared to

monsoon months. In the current observations the maximum DO value of 7.16 ml/L was recorded at station 1 during post monsoon and the minimum at station 5 during monsoon. Among the various seasons, the pre monsoon DO values varied between 5.46 to 1.71ml/L. During monsoon the variation was between 7.09 & 0.111ml/L, while in post monsoon it varied between 7.16 and 0.73 ml/L. In station 1, the dissolved oxygen values did not show many variations from April to August. In October, station 1 recorded a very high value of 7.16ml/L. In station 2, where the tidal influence is low, there is a marked lowering of DO during pre monsoon season corresponding to increased salinity and temperature. In stations 3 and 4, the DO value is high during pre monsoon month of February. As temperature increases, % saturation of oxygen increases. High water temperatures in mangroves support a massive proliferation of algae and microalgae in these waters enriching it with dissolved oxygen. But the elevated temperature will contribute an added stress to the biota which is critical for the larvae of fishes (Turnpenny et al, 2004). Since station 3 is connected to the Cochin estuary through a creek and station 4 to Munambam estuary, the fresh water discharge at the estuary will influence the hydrology of these stations. Stations 1, 3 and 4 showed a decrease in DO towards the end of post monsoon, possibly due to the consumption of oxygen during the decomposition of organic matter(Abdel Aziz,2001) and increased levels of nutrients and comparatively lesser amount of rainfall during monsoon and post monsoon seasons favouring eutrophication.

Statistical analysis showed that during there is no correlation between dissolved oxygen and any of the hydrographic parameters in total correlation. Alkalinity and H_2S correlated positively with dissolved oxygen during monsoon. This is in agreement of observations reported elsewhere. In many estuaries degradation of organic matter within the water column accounts for a substantial fraction of total oxygen consumption (Hopkinson et al, 1999). Dissolved oxygen is known to have significant positive correlation with carbonate alkalinity. The saturation of oxygen in water is also found to be a function of both temperature and salinity. There exists a negative correlation between dissolved oxygen and salinity and a positive correlation between dissolved oxygen and H_2S during post monsoon. In water logged anaerobic areas, organic matter is oxidised bisulphate reducing bacteria,

leading to the production of H_2S.Biological oxidation of the sulphides carried out by sulphide oxidizing bacteria requires O2 as an oxidant (Lymio et al., 2005). In the station wise correlation dissolved oxygen correlated positively with H_2S at all stations. Dissolved oxygen showed positive correlation with dissolved ammonium at stations 1 and 5. Similarly pH correlated positively with dissolved oxygen at stations 2 and 3 and negatively at station 1. Alkalinity also correlated with dissolved oxygen at stations 2, 3 and 4. The mean value of dissolved oxygen is 2.71, 2.04 and 2.71 for pre monsoon, monsoon and post monsoon respectively. The station wise means are 2.81, 3.13, 2.20, 1.61 and 2.66 for stations1 to 5. In cluster analysis dissolved oxygen forms a cluster with H_2S, supporting the correlation between the two at all stations.

3.5 Nutrients

Owing to increased anthropogenic activity, mangrove ecosystems are being increasingly affected by stressors, such as nutrients. The effects of stressors such as nutrients and trace elements on upper trophic levels in coastal systems are modulated by physical and biological attributes of the system (Cloern, 2001). In warm, wet oxic environments, microbial decomposition and nutrient release occurs rapidly. Increase in nutrient content can trigger the growth of harmful algal blooms. Die offs of algal blooms depletes dissolved oxygen, thus affecting the entire water column. Decomposition of biomass is aided by the absence of complex polymers such as cellulose and lignin which are not easily broken down and high proportion of biomass initially present in a liquid state. Nutrient stratification occurs due to heating of water surface and difference in salinity. The nutrient status of water bodies can also increase as biomass, detritus and sediment accumulate (Peter, 2002). The seasonal patterns of nutrient concentrations or nutrient rating can affect biomass, abundance and species composition of phytoplankton. It can also modify interactive effects of trace elements and can influence the bio availability of contaminants. The effects of nutrients are transmitted by food web interactions (M.H. Bundy, 2003). The ecological effects of nutrients and trace elements may vary with precipitation rates, salinity, sedimentation type and land use pattern (Riedel et al., 2000). High nutrient loading potentially affect consumer population, by altering the abundance

and taxonomic composition of prey by degrading habitat arising out of low dissolved oxygen, reduced water clarity, and altered benthic community diversity (Dauer, 2000). Nutrient induced increases in phytoplankton biomass were consistently reflected in increases in growth or abundance of higher trophic levels. The impacts of nutrient stress might include the local extinction of an ecologically important species, reduced population sizes of valued ecological resources such as fishes or reduced species diversity, as well as increase in populations of less desirable species such as blue green algae ctenophores etc. This may be accompanied by undesirable changes in ecosystem structure and function (Stephen, 2003). Fishes ordinarily escape than tolerate lowered water quality. Mangroves can tolerate and use high levels of nitrogen from sources such as sewage and aqua culture effluent (Trott and Alongi, 2000) because of their high rates of primary production. Mangroves can use the high nitrogen and phosphorous inputs to fuel tree production as well as production of other primary producers (Bouillon, 2002). However the impact of nutrients on mangroves depends on various factors such as tidal flushing, forest productivity, area and age of mangroves, intensity and duration of nutrient inputs and utilization, as well as nutrient links between mangrove trees and microbes.

3.5.1 Dissolved Ammonium

Ammonium is nearly always the dominant form of dissolved inorganic nitrogen in mangrove waters. Ammonification results in the production of ammonia from the breakdown of organic nitrogen performed by heterotrophs ranging in size from bacteria, fungi to fish, which is then released into water by zoo plankton. Nearly all organic nitrogen compounds are broken down via this pathway. It can also be formed by the conversion of atmospheric N_2 to NH_3 -N. Ammonia is the central compound of nitrogen cycle (Ilmar et al., 2005). It is usually present in low concentrations in unpolluted estuarine waters (Michael Neil, 2005). In anaerobic conditions ammonium is formed by the degradation of proteins (Ilmar et al, 2005). The main sinks for ammonium are for the production of organic compounds during the decomposition of organic matter and oxidation to nitrite during nitrification. In surface waters ammonium oxidation is photo inhibited. Highest nitrification rates always occurred at the lowest light intensities, but the lowest rates occurred at all

light intensities (Ward, 2005). Ammonium oxidation may be more important with increasing depth and distance offshore. In several oxygen minimum zones heterotrophic bacteria accounted for a significant portion of ammonium uptake. Higher levels of NH_4^+ would lead to faster rates of NH_4^+oxidation. Similarly greater the turbidity of water, greater is the rate of ammonium oxidation due to the presence of greater number of particles which may act as a substratum for NH_4^+ oxidizing bacteria. Temperature variations as much a by 0.9 °C may bring about marginal increases in photosynthesis, litter fall, growth and reproduction, changes in community composition, microbial decomposition etc (ICCP 2001). Ammonium is more readily available than nitrate for plant growth (Kocum et al., 2002). Ammonium assimilation rates are higher than nitrite assimilation rates. Ammonia N does not accumulate in plant and animal tissues. Hence higher concentration of ammonia implies effective decomposition of particulate organic matter. Water column nitrification rates in the marine environments are highly variable, but most of the productive and coastal areas have higher rates than oceanic waters. Also it is the rates of ammonium production rather than its insitu concentration that regulates nitrification. The relationship between nitrification rates and the regeneration rates ammonium obeyed Michelais – Menton kinetics. Nitrification rates are also known to be dependant on temperature, concentration of oxygen and suspended load. Similarly inhibition of denitrification results due to elevated oxygen levels in the presence of light (Wenchuan Qu, 2005). Turbidity can enhance nitrification rates. Night time assimilation of NH_4^+ is half that of day time. Denirtification contributes to the relative scarcity of nitrogen by consuming nitrogen from over lying water and nitrate production by sediment nitrification. The retention and removal of dissolved nitrogen by sediments breaks down when there are large fluxes of ammonium to the water column indicating a pre dominance of ammonification due to bacteria mediated decay of organic matter in sediments. Such a condition may arise when there is an algal bloom or when high flow rates occur (Angus et al., 2004). Increased organic matter deposition associated with nutrient loading could inhibit coupled nitrification – denitrification (Vivek et al, 2002).

Results and discussion

Highest value of 68.69 μ mol/L for dissolved ammonium was observed at station 2 during pre monsoon. Mixing up of water due to disturbance may lead to high ammonium concentration. It may also arise out of decreased oxidation of NH_4^+ to nitrite. In stations 1 and 2 dissolved ammonium decreased from pre monsoon to monsoon and then increased during post monsoon and then again decreased. An inhibition of nitrate uptake can increase the concentration of ammonium which is observed in post monsoon. The ammonium concentration decreased during pre monsoon due to increased photosynthesis and metabolic activity which produces more oxygen bringing about the nitrification of ammonium (Marie Noele, 2002), shown by a corresponding increase in nitrite concentration. The lowering of ammonium concentration in monsoon is due to the dilution of nutrient concentration with abundant rain fall. Sedimentary Fe was low during monsoon. Fe is known to play an important role in the nitrification process (Krishnan and Lokbharathi, 2009). In station 3 there was an increase in dissolved ammonium during April. Station 3 is a migratory bird sanctuary. The increased value of ammonium in April may be due to the mixing of the droppings of the migratory birds with the mangrove water. In tropical mangroves, decomposers will rarely be limited by low temperatures, but in subtropical mangrove forests, decomposition may be faster during summer. The high value of dissolved ammonium may also be due to the release of sedimentary nitrogen as ammonium under high respiration rates (Wei- Jun Cai et al., 2000). Mixing up of waters due to disturbance may lead to high ammonium concentration. Yet another reason may be due to the fact that in anoxic environments, anaerobic bacteria proliferate with nitrogenous oxide reducers absorbing oxygen by reducing nitrate to nitrite and forming ammonia or nitrogen gas. Oxygen uptake, phosphate release and ammonium release is shown to increase exponentially with temperature.

Stations 4 and 5 had comparatively low values of dissolved ammonium. Low NH_4^+ con may be due to the preference of micro organisms for ammonia as the source of nitrogen (Sofia and Alice, 2005). Another reason may be the trapping of ammonia by phytoplankton. The lowest value of dissolved ammonium was

observed at station 4 during post monsoon. When temperatures are low, the majority of heterotrophs that dominate the denitrification have slower metabolic rates and denitrification rates decreases with temperature. Greater the turbidity of water, greater is the rate of ammonium oxidation due to the presence of greater number of particles which may act as a substratum for ammonium oxidizing bacteria. NH^{+}_{4}, which seemed to have disappeared, was either reduced by other processes such as volatization and absorption by the plants, or by the combined nitrification–denitrification process, which eventually transforms the NO^{-}_{2} and NO^{-}_{3} into gaseous N_2 in anoxic regions (Flite et al., 2001).

Statistical analysis showed that dissolved NH_4^+ correlated negatively with pH during monsoon and post monsoon. Alkalinity correlated positively with dissolved NH_4^+ during post monsoon. This shows that ammonium production is a dominant factor which controls the hydrographic parameters in post-monsoon. Dissolved PO_4^{3-} correlated negatively with dissolved NH_4^+ at stations 1, 2 and 5. At station 1 dissolved NH_4^+ correlated positively with H_2S and dissolved oxygen, while it correlated negatively at station 5. At station 4, positive correlation is observed between dissolved NH_4^+ and the three hydrography parameters namely NO^{2-} alkalinity and salinity. The mean value of dissolved NH_4^+ for pre monsoon, monsoon and post monsoon were 27.70, 18.74 and 25.56 µ mol/L respectively. For the five stations the mean value of dissolved NH_4^+ was 21.85, 31.33, 39.24, 15.77 and 13.48. Anova did not show any significant values.

3.5.2 Dissolved Nitrite

The majority of global nitrogen exists as N_2 in the atmosphere and is not readily available to the biota. The supply and environmental cycling of N is largely dependent on the biological decomposition of N containing compounds in the biota, by the activity of blue green algae and symbiotic bacteria, which in turn is frequently limited by available nitrogen. Fe can act as a limiting factor for nitrogen utilization (Pierluigi et al, 2005). Nitrogen enriched feeds used for the enhancement of shrimp growth enhances nitrogen concentration in waterways. Primary production by phytoplankton is the major removal pathway of dissolved

inorganic nitrogen from the water column under algal bloom conditions. Competition between autotrophs and heterotrophs for available dissolved inorganic nitrogen substrates may also result in dissolved inorganic nitrogen uptake from water column (Sundback and Miles, 2000). In some instances, pelagic phytoplankton blooms is reported to assimilate the entire dissolved inorganic nitrogen loading to the water column, thereby removing the dissolved inorganic nitrogen as particulate organic nitrogen. Pelagic bacteria can regenerate dissolved inorganic nitrogen from dissolved organic nitrogen. The total particulate nitrogen may settle down as phyto detritus and high rates of organic matter delivery to the sediments result in a predominance of ammonification, followed by the returning of ammonia to the water column thereby fuelling further algal bloom (Angus et al, 2004). Both blue green algae and symbiotic bacteria reduce N_2 to NH_4^+ But NH_4^+ is only utilized to a limited extend by plants. The mobilization of N from sediments depends on the efficiency with which the blue green algae are able to exploit the available N and the re suspension of algal detritus and sediments by wind or bioturbation.

Nitrite often functions as a short life intermediate produced by the bacterial decomposition of ammonia to nitrate during nitrification (Ilmar et al, 2005). The $NH_4^+$is oxidized by free living bacteria(Nitrosomonas and Nitrococcus,) to NO_2^- which may be further oxidized to NO_3^- by Nitrobacter. Nitrate is readily reduced to NO_2^- by the enzyme nitrate reductase, which is widely distributed in both plants and microorganisms. Under anoxic conditions, NO_3^- and NO_2^- are utilized by bacteria as e^- acceptors. Due to active incorporation into the biota the concentration profiles of N shows a pronounced surface depletion and a progressive increase as biological debris is oxidized. The close coupling of ammonium and nitrite oxidation is known to limit the amount of nitrite present at any one time. When dissolved oxygen concentration is low, nitrate may be reduced to nitrite via denitrification and can be detected in significant quantities in water. Unlike nitrate, nitrite is quite toxic and may cause mortality at concentrations of approximately 0.05 mg/l in sensitive species. Exposure to high concentrations of NO_2^- is known to cause gill damage. Agricultural and urban run off represent a major threat to surface water quality.

Results and discussion:

Nitrite concentration can vary greatly among mangrove water ways. Rapid changes in nitrite concentrations result from changes in nitrification rates which are coupled to mineralization rates. Similarly photo inhibition of NO_2^- production when high levels of ammonia are present has been reported. Also in put of ammonium from sewage discharge results in an increase in nitrite levels before conversion to nitrate. Low dissolved oxygen concentration is known to enhance nitrification (Ilmar et al, 2005). The nitrite concentration is known to vary between 5.99 µM and 1.07 µM in Pichavaram mangroves of Tamil Nadu, South India (Ashok et al,2008). Nitrite average of 0.48 ug/l is reported from the mangrove waters of UAE (Mohammed, 2000). Similarly in the mangroves of Godavari basin the nitrite concentration varied between 0.50-1.72 µ M (Tripathy et al, 2005). Among the study sites, the highest nitrite con of 18.98 µmol/L was observed in station 4 during the pre monsoon season. This may be due to sinking labile organic nitrogen, resulting in a transient build up and decay of nitrite arising out of decaying organic matter. High nitrite levels in station 4 during pre monsoon may be due to a reduction in bacterial population at high salinity during this period. Also the shallowness of water column during pre monsoon allows occasional injection of sedimentary bacteria into the water column during mixing events which may increase the population of NH_4^+ oxidizers in the water column. Nitrite concentrations are reported to be higher in winter than in summer. This is true in the case of station 2 and station 3. The low levels of NO_2^- at stations 1and 2 during all the three seasons may be due to decreased oxidation of NH_4^+ to nitrite, which may arise out of strong competition for available NH_4^+among decomposers, plant roots and nitrifiers. Luther and Popp (2002) showed that nitrification of NO_2^- to NO_3^- by Mn oxides was possible. Soil and water column processes are reported to control NO_2^- flux. In mangrove ecosystems the vegetation influence is also noticed. These may include uptake of nutrients by trees, transformation of the nutrients by the epibiont communities on the submerged prop roots as well as microbial processes carried out by them (Krista Kamar, 2001).

Statistical analysis showed that dissolved NO_2^- correlated positively with pH during pre monsoon. A rapid increase in salinity would also steadily increase nitrification rates (Vivek et al, 2002). Nitrate and ammonium are taken up more or less equally by phytoplankton. Nitrite generated from NO_3^- by denitrification or by the nitrification of ammonium (Robert Mortimer et al, 2004) is subjected to nitrification or used up for the release of ammonium via denitrification, which takes place in anoxic regions via a number of pathways including conventional microbial denitrification using labile organic matter. Hence a lowering of nitrite concentration can be expected in pre monsoon. This explains the positive correlation between pH and dissolved nitrite.In the station wise correlation, negative correlation is observed between dissolved NO_2^- and dissolved PO_4^{3-} H_2S correlated negatively with dissolved NO_2^- at stations 1 and 2. At station 3 positive correlations exists between dissolved NO_2^- and salinity. Salinity is known to correlate directly to NO_2^-. Significant correlation between salinity and nitrite may be attributable to the quality and quantity of the discharged waters. The correlation indicated that salinity is one of the major factors influencing several biotic and abiotic components of the ecosystem (Abdel Aziz, 2001). At station 4 positive correlations exists between dissolved nitrite and dissolved NH_4^+ as well as between dissolved nitrite and alkalinity. The mean of nitrite concentration during pre monsoon was 2.87 µmol/L, during monsoon 0.92 µmol/L and during post monsoon 1.19 µmol/L. The station wise mean of nitrite concentration was 0.39, 0.50, 2.90, 3.97 and 0.55 µmol/L respectively.

3. 5. 3 Dissolved Inorganic Phosphate:

Phosphorous is a primary nutrient that limits the growth of photosynthetic organisms. It is present in many chemical forms in aquatic environments.

But it is the dissolved inorganic P that is readily available for assimilation by algae. Fertilizers, agricultural activities, fossil fuel combustion, animal feeding operations, sewage etc and known to increase the level of phosphorous in the soil. Sediments serve as a source or sink for P P release from sediments may be controlled by factors such as sediment and water temperature, bottom current, macro faunal density, microorganism activity and reduced states of sediments.

Suspended particles and sediment will release phosphorous when dissolved oxygen levels are low (Best et al., 2007). A rapid increase in temperature will facilitate the release of P from sediments. This P is mobilized into waterways through surface and subsurface runoffs (Donald et al., 2002). Benthic release of P will also be significant and is reported to be the greatest source of dissolved inorganic phosphate (Huasheng et al., 1999). Rain fall will exacerbate this problem because of increased influx of P from the land and atmosphere. P limitation of algal blooms has also been observed. P enrichment stimulates the noxious blooms of toxic and harmful blue green algae in waterways. These algal blooms can deplete water quality and produce bioactive compounds including neurotoxins and hepatotoxins, which can even be fatal to humans. The re-flooding of anaerobic sediments released greater amounts of P This was considered due to the decomposition of dead bacteria. Factors such as decomposition of organic matter during drying so that PO_4^{3-} was in a releasable form after flooding and changes in crystalline structure leading to inactivation of binding sites of PO_4^{3-} are reasons for the higher release of P Reduction in organic matter deposition leads to reduction in phosphate loadings. Phospate concentrations in estuaries are found to be highest during summer corresponding to a temperature dependency for phosphate. This is due to the release of P associated with changes in the Fe cycling with sulphate reduction. In winter P is stored in sediments mainly as Fe associated PO_4^{3-} when SO_4^{2-} reduction are low. When temperature dependent SO_4^{2-} reduction rates increases, Fe bound SO_4^{2}- and Fe associated SO_4^{2-} are released. Reduction in P loadings has the potential to improve summer oxygen conditions. The mineralization of N and P in mangrove systems is especially important when considering that one or both is/are usually limiting production (Daniel J Conley, 2000).

Results and discussion:

The highest value of phosphate was recorded at station 3, during April. It corresponded to almost neutral pH and low alkalinity while the lowest value of phosphate was observed at station 4 also in April and corresponded to basic pH

and rather high value of alkalinity. An interesting phenomena noticed is that H_2S at station 3 during April showed the maximum value which also corresponded to the highest phosphate value for that station. But in the case of station 4 the lowest phosphate concentration corresponded to the highest H_2S concentration.

Stations 1, 2 and 3 showed highest values of dissolved phosphate during April while Station 4 had the maximum dissolved phosphate in June. The highest phosphate concentration in station 4 coincided with the highest value of pH also. The increased phosphate concentration may be due to litter fall. Leaves are known to have higher concentration s of P even in rainy season. Leaching of leaves during rainy season may remove P from leaves. Leaves with high tannin content and low N content will decompose slower than those with low tannin and higher N. The presence of organic matter may determine the mineralization rates of vital elements. Phosphorus-containing organic compounds are ingested by heterotrophs and phosphate is excreted to the environment. P that was charge bound to the sediments was the weakest form of binding (Bourges et al, 2000) will also be released during monsoon. Another reason may be, as oxygen levels decrease due to algal degradation, sediment bound P will be released as soluble P into water (Richard & Claus, 2006). Fine clays with high organic content had the potential to release large amounts of P into the water column. Even a 1% release of P would increase dissolved P from 10 to 70 ug/L (Chambers et al, 1997). Considerable increase in phosphate has also been observed due to a large built up of phytoplankton cells representing increased productivity. Stations 1, 2& 4 had lowest values of phosphate in February. Bacteria normally satisfy their rather large requirements of phosphate from organic detritus on which they live. However when this food source is insufficiently rich in phosphate, they are able to assimilate dissolved inorganic phosphate from the water. Topography, geomorphology and hydrology play a significant role in the availability of P.

Statistical analysis showed that dissolved PO_4^{3-} correlated negatively with pH and salinity. Significant correlation between salinity and dissolved inorganic phosphate showed that salinity is one of the major factors influencing many of the biotic and

abiotic factors of the ecosystem. (Abdel Aziz, 2001). At stations 1, 2 and 5 negative correlation exists between dissolved PO4 $^{3-}$ and dissolved NH_4^+.At station 1 negative correlation exists between dissolved PO_4^{3-} and dissolved nitrite. Positive correlation exists between dissolved PO_4^{3-} and H_2S at station 3, while the correlation is negative at station 4. At station 5, dissolved PO_4^{3-} correlated positively with the parameters pH, salinity, and alkalinity and dissolved oxygen. This shows that dissolved PO_4^{3-} has a dominant role in controlling the hydro graphy at station 5. The mean of dissolved PO_4^{3-} during pre monsoon was 14.70, for monsoon it was 16.92 and for post monsoon it was 12.72(µmol/L). The mean value of phosphate at different stations 1 to 5 was 16.56, 13.18, 24.74, 16.75 and 2.68 (µmol/L) respectively. Station 3 which received urban runoff had the maximum mean value for dissolved PO_4^{3-} and station 5 which was under constant tidal action had the least. Estuarine sediments immobilize lesser phosphate than freshwater sediments. In estuaries with high fluvial particle load, desorption of phosphate from particles could provide a phosphate source. Reduced levels of DO in water column can result in the release of phosphate from suspended particles and sediments (Best et al., 2007). Nitrogen limitation of primary production may also lead to increased of phosphorous in estuarine sediments. Anova did not show any significant variations station wise and seasonally.

3.6 Hydrogen Sulphide

H_2S is a metabolic poison present in anaerobic reducing environments. It is a broad spectrum poison affecting mainly the central nervous system. H_2S has a deleterious effect as it blocks aerobic respiration by inhibiting metalloenzymes including cytochrome C oxidase present in mitochondria. As temperature increases organisms may be exposed to greater amounts of toxicants because of increased diffusion or more active uptake of toxic substances. The increase in toxicity can be 2-3 folds per 10 ^{0}C rise in temperature. H_2S is a broad spectrum poison affecting mainly the central nervous system. H_2S has a deleterious effect as it blocks aerobic respiration by inhibiting metalloenzymes including cytochrome C oxidase present in mitochondria. As temperature increases organisms may be

exposed to greater amounts of toxicants because of increased diffusion or more active uptake of toxic substances. The increase in toxicity can be 2-3 folds per 10 ^{0}C rise in temperature. It is the central participant in the S cycle of the biogeochemical process. Free sulphide production and persistence is typical of many estuaries with high organic loading. Higher temperature and increased solar radiation will cause sediment warming leading to increased soil respiration, organic matter decomposition and H_2S release (Bauza and Morrel, 2002). Aeration of sediments with aerial roots and crab holes will reduce the sulphide concentration (Holguin et al., 2001). Lymio et al., (2002 a) reported that clear cutting of trees will lead to the absence of crabs and presence of large amount of undigested litter will make the soil highly sulphidic, which in turn will affect the dissolved H_2S concentration. Mangrove ecosystems are litter rich areas. The major sources of detritus to the mangrove sediments are autochthonous. The major contributors to the benthic detritus pool are leaves, branches, and wood from mangrove trees. Benthic micro algae on the sediment surface, epiphytes on branches and prop roots as well as deposited phytoplankton are additional contributors to the detritus pool. Decomposition of mangrove litter involves enzymatic biochemical reactions controlled by temperature as well as salinity. The amount of dissolved oxygen in mangrove areas is usually lower than that in open sea. Mangrove waters are usually nutrient rich. Eutrophic waters are prone to massive phytoplankton blooms, particularly when temperature and light intensity increases and the water body become stratified. The death of algal mass, followed by decomposition reduces the oxygen content of water severely creating anaerobic conditions. Litter decomposition coupled with organic pollution may further reduce the oxygen content, creating an anoxic zone in the water column (Peter &Siva sothi, 2001).

Some bacteria liberate H_2S from the S- containing amino acids. Several bacteria can use H_2S as a fuel oxidizing it to elemental S or SO_4^{2-} using dissolved oxygen and metal oxides such as iron oxy hydroxides and manganese oxides. Sulphate reducing bacteria such as thiobacillus denitrificans can use NO_3 as an oxidant under anoxic conditions. The purple S use H_2S as e^- donor during photosynthesis, thereby producing elemental sulphur (Jorgensen and Nelson,

2004). H_2S can oxidize spontaneously in the presence of dissolved oxygen to less toxic species such as thiosulphate, sulphite, and sulphur, thereby depleting oxygen (Boaz et al, 2002). The H_2S formed can also react with different species of iron to produce iron sulphides (Chambers et al., 2000). Sulphide oxidation may be an important pathway for the cycling of inorganic sulphur in mangrove ecosystems. Sulphide oxidation may be catalysed by mitochondria, bacteria associated with the root surface, sulphide oxidase enzymes or metals.

In water logged soils, rate of oxygen diffusion decreases and limits the amount of oxygen available for plant root and microbial respiration. The anaerobic micro organisms in soil will use inorganic ions as terminal e- acceptors to break down organic matter. Sulphide oxidation can be coupled to oxidative phosphorylation of adenosine -5'phosphate in mitochondria. Hence this phytotoxin can also serve as a source of usable cellular energy. Under anoxic conditions pyratisation will occur due to the reaction between H_2S and FeS in the aqueous or solid state. Oxidation of Fe (II) in the presence of oxygen and dissolved organic ligands will produce soluble organic Fe (III) (Tallefert et al, 2000). The presence of dissolved sulphide will control the amount of reactive soluble Fe (III). The significance of Fe (III) lies in the fact that it can diffuse into pore waters and supply e^- acceptors at locations such as over lying waters, where hydrous Fe oxides are not present. Increase in pH promotes abiotic reduction of soluble organic Fe (III) sulphide as well as precipitation of FeS and prevents FeS from forming FeS_2. When H_2S is below detection limits, it indicates that sulphide precipitates rapidly as FeS and the rate of sulphate reduction is smaller than the rate of pyratisation (Tallefert et al., 2002). Increased levels of ferrous iron and sulphate may lead to acidification and a subsequent decrease in alkalinity or in other words, the potential for sulphide oxidation will lead to acidification. Sulphide concentrations can also indicate the effects of flooding and abiotic stress on mangrove development.

Results and discussion

H_2S accumulation in water logged areas is due to the deduction of SO_4^{2-} to S^{2-} by sulphate reducing bacteria, which derives energy from this process. (Boaz et

al, 2002). Sulphide concentration below 0.46mM has been reported from mangrove sites (Chen & Twilly, 1999). H_2S concentration did not show any specific pattern at the different stations. The concentration of H_2S was high at stations 1, 2 and 5 during post monsoon, while it was high during pre- monsoon at station 3 and 4. Station 2 stood out during monsoon with very high H_2S concentration during monsoon. This may be due to a large amount of dissolved organic carbon which was brought in by the monsoon runoff (Lymio and Douglas, 2005). Organic carbon present in the medium is oxidized to carbon dioxide by sulphate reducing bacteria, generating H_2S. The low molecular weight fraction of DOC is usually considered as the most suitable substrate for sulphate reducing bacteria. The low sulphide concentrations at stations 1and 2 during pre -monsoon may be due to the aerations of sediments by roots which leads to less liberation of H_2S by sediments (Marchand et al., 2004). Increase in temperature during pre-monsoon will cause dissolved H_2S to escape to the atmosphere, thereby causing a lowering of dissolved oxygen. Lowering of alkalinity with H_2S concentration showing an upward trend was observed at stations 1 and 2 and 5 during post monsoon.

Statistical analysis data showed that in total correlation H_2S correlated positively with dissolved oxygen. In seasonal correlation, during monsoon and post monsoon there exists positive correlation between H_2S and dissolved oxygen. Microbial respiration can also deplete water column of dissolved oxygen in the presence of organic matter (Best et al., 2007). When nitrification increases with light regime during post monsoon, it can deplete dissolved oxygen. But nitrification appears to be limited in estuaries. Nitrate and ammonium are taken up almost equally by phytoplankton. Oxygen depletion is also observed as a consequence of sinking and decay of phytoplankton blooms. In post monsoon there will be an increased degradation of organic matter brought down by the monsoon. This explains the correlation between DO and H_2S. In station wise correlation dissolved oxygen correlated positively with H_2S at stations 1, 2, 3 and 5. Ammonium correlated positively with H_2S at station 1 and negatively at station 5. pH showed positively correlation at station 3 and negative correlation at station 4. Similarly positive correlation is shown by H_2S and dissolved PO_4^{3-} at station 3

while the reverse is shown at station 4. The mean of H_2S during pre monsoon is 4.01, in monsoon 3.43 and in post monsoon 5.03(µmol/L). The station wise means are 3.13, 5.04, 3.10, 4.29 and 5.24(µmol/L) for stations 1 to 5. Anova did not show any significant variations.

3.7 Alkalinity

Alkalinity refers to the capability of water to neutralize acid. This is really an expression of buffering capacity. It essentially absorbs the excess H^+ ions and protects the water body from fluctuations in pH. Respiratory activities taking place in the in the sediment and water column plays an important role in determining the alkalinity of the water column (Bouillon et al., 2007). Alkalinity is an important factor affecting phytoplankton and zoo plankton as it changes the group and species distribution. Zoo plankton grazing impact with increasing alkalinity is also reported. Alkalinity is important for fish and aquatic life because it protects or buffers against rapid pH changes. Living organisms, especially aquatic life, function best in a pH range of 6.0 to 9.0. Higher alkalinity levels in surface waters will buffer acid rain and other acid wastes and prevent pH changes that are harmful to aquatic life. Alkalinity and sulfate are the water quality parameters most often producing internal eutrophication. Increased microbial sulfate reduction also generates excess alkalinity, further enhancing phosphate and ammonium remobilization (Smolders et al., 2006).

Mangrove pore waters are typically rich in total alkalinity and DIC (Bouillon et al., 2007) indicating that build-up of inorganic carbon resulting from mineralization occurs. pH shows a dependence on alkalinity. Increase in alkalinity would normally be accompanied by an increase in pH. Variations in pH resulting from alkalinity changes are greater than those caused by changes in carbon di oxide. The presence of carbon dioxide along with carbonic acid, HCO_3^- and CO_3^{2-} brings about an increase in alkalinity. Waters with low alkalinity will be low in dissolved organic carbon (Michael Neil, 2005). Increased external sulfate loading to wetland soils has been demonstrated to lead to enhanced mobilization of N and P from soils. The uptake and release of nutrients especially N nutrients and metabolic

processes affects alkalinity. Uptake of ammonium decreases alkalinity and lowers pH, whereas uptake of nitrate increases pH. Alkaline pH is required for ammonium oxidizing bacteria. Low alkalinity level has been identified as one of the stress factors affecting the diversity, abundance, production and growth of aquatic organisms. Low alkalinity favours the development of small algal species. In highly alkaline waters, low dissolved CO_2 can limit the rate of diffusion of CO_2 across algal membranes. Large algal species have a greater capacity to remove dissolved inorganic carbon under alkaline CO_2 depleted condition (Stephane and Bernadette, 2000).

In most natural water bodies the buffering system is carbonate-bicarbonate. The presence of calcium carbonate or other compounds such as magnesium carbonate contribute carbonate ions to the buffering system. Alkalinity is often related to hardness because the main source of alkalinity is usually from carbonate rocks (limestone) which are mostly CaCO3. Since hard water contains metal carbonates (mostly CaCO3) it is high in alkalinity. Soft water usually has low alkalinity and little buffering capacity. So, generally, soft water is much more susceptible to fluctuations in pH from acid rains or acid contamination. The relatively oxidized conditions caused by oxygen translocation to subsurface layers via roots and infaunal (crab) provide ideal conditions for the formation of pyrite. The close contact between oxygen and sulfide, on the other hand, also leads to extensive sulfide oxidation and subsequent acidification. The acids generated will consume alkalinity and lower pH. The high metabolic activity in mangrove sediments creates elevated concentrations of total alkalinity, dissolved inorganic and organic carbon, and other metabolites in pore waters. During ebb, pore water can migrate into the water column and increase the concentrations of these solutes. Crab burrows have been found to dramatically enhance the hydraulic conductivity and these could be important mediators for subsurface flow of pore water to tidal creeks (Mazda and Ikeda, 2006). All these processes can profoundly influence the alkalinity of mangrove water.

Results and discussion

The alkalinity was high at all stations during pre monsoon. Alkalinity may be produced through ammonium release, net nitrification, net sulphate reduction and net carbonate dissolution. It decreased considerably as monsoon advanced. During the rainy season it is reported that, dilution led to significant decreases of salinity, alkalinity and dissolved organic carbon in both mangrove creeks and adjacent main channels. For stations 1 and 3 the alkalinity increased with the outset of post monsoon, while it continued to decrease for stations 2, 4 and 6 monsoons. In post monsoon there is a decrease in alkalinity and dissolved ammonium. If algal bloom is supported by NH_4^+ than NO_3^-, alkalinity will decrease (Kenneth, 2002). Station 1 had the highest alkalinity during all the bimonthly observations except in August when it had the least alkalinity. The alkalinity was low at all stations during December. The highest value of alkalinity 4.724 eqts/L was recorded at station 1 during February and the least of 0.036 eqts/L at station 4 during October. Anthropogenic discharges of domestic wastes stimulate methanogenesis by inducing severe oxygen stress and supplying labile organic carbon Active organic matter and nutrient processing can take place when the transported organic matter undergoes significant biogeochemical modifications (Cole et al., 2007) influencing the alkalinity.

Statistical analysis indicated positive correlation of salinity with alkalinity during pre monsoon and negative correlation during post monsoon. Alkalinity is known to be highly correlated to salinity. But here, since a negative correlation was observe between salinity and alkalinity, is must be assumed that the concentration of other dissolved components, especially ammonium is the dominant factor controlling the alkalinity. Similarly positive correlation between alkalinity and pH is observed in pre monsoon while negative correlation is seen in post monsoon. The salinity in the wet season is significantly lower than the dry season due to variations in precipitation (Pinsak and Eric, 2002) and pH is known to increase rapidly (Luke and Shamus, 2004. Substantial reduction in DO can lead to sulphide production in the absence of oxygen (Colclough et al., 2002). A pulse input of phosphate may increase in the ecosystem due to atmospheric and terrestrial deposition during

rain fall. These factors will make the system less alkaline (Huasheng et al., 1999). Alkalinity correlates positively with DO in monsoon and with dissolved ammonium in post monsoon. In station wise correlation, alkalinity and salinity correlates positively in stations 1 and 4, with pH at stations 2 and 4 and with DO at stations 2 and 3. This suggests that heterotrophic processes in the water column and sediments controlled these variables and were related to some extent to the influx of pore waters as well as anaerobic processes (Koné and Borges, 2008). Positive correlation exists between NO_2^- and alkalinity at station 4, while the correlation is negative at station 2.The correlation of alkalinity with dissolved ammonium positively at station 4, and with phosphate at station 5 and H_2S correlates negatively with alkalinity at station 5.

3.8 Conclusion

The hydrography of mangroves has a significant impact on its geochemistry, development and propagation as well as its degradation. The various hydrographic parameters showed interdependency. During pre- monsoon pH showed a positive correlation with dissolved nitrite and a negative correlation with dissolved inorganic phosphate. Salinity correlated positively with dissolved inorganic phosphate and alkalinity. No correlation was observed between dissolved ammonium, H_2S and dissolved oxygen and other hydrographic parameters. Oxygen uptake, phosphate release and ammonium release is shown to increase exponentially with temperature. During pre-monsoon there is a tendency for pH to decrease due to anoxic conditions which produces H_2S. At temperatures higher than 12^o ammonium release would increase(Michael et al., 2002).) A rapid increase in salinity would also steadily increase nitrification rates (Vivek et al., 2002). Nitrate and ammonium are taken up more or less equally by phytoplankton. Nitrite generated from NO_3^- by denitrification or by the nitrification of ammonium (Robert Mortimer et al., 2004) is subjected to nitrification or used up for the release of ammonium via denitrification, which takes place in anoxic regions via a number of pathways including conventional microbial denitrification using labile organic matter. Hence a lowering of nitrite concentration can be expected in pre monsoon. This explains the positive correlation between pH and

dissolved nitrite. Significant correlation between salinity and dissolved inorganic phosphate showed that salinity is one of the major factor influencing many of the biotic and abiotic factors of the ecosystem (Abdel Aziz, 2001).Nitrogen limitation of primary production may lead to increased of phosphrous in estuarine sediments. Estuarine sediments immobilize lesser phosphate than freshwater sediments in estuaries with high fluvial particle load, desorption of phosphate from particles could provide a phosphate source. Reduced levels of DO in water column can result in the release of phosphate from suspended particles and sediments (Best et al., 2007).

Significant positive correlation was observed in monsoon between pH and salinity and between alkalinity and pH. The salinity in the wet season is significantly lower than the dry season due to variations in precipitation (Pinsak and Eric, 2002) and pH is known to increase rapidly (Luke and Shamus, 2004). In monsoon, there exists a positive correlation of dissolved oxygen with H_2S and alkalinity. Dissolved oxygen is known to have significant positive correlation with carbonate alkalinity. The saturation of oxygen in water is also found to be a function of both temperature and salinity. Dynamic patterns of DO emerge in estuaries from complex interaction among physical, chemical and biological processes (Diaz, 2001). In many estuaries degradation of organic matter within the water column accounts for a substantial fraction of total oxygen consumption.(Hopkinson et al,1999). Substantial reduction in DO can lead to sulphide production in the absence of oxygen (Colclough et al., 2002). A pulse input of phosphate may increase in the ecosystem due to atmospheric and terrestrial deposition during rain fall. These factors will make the system less alkaline (Huasheng et al., 1999). Dissolved nitrite and dissolved inorganic phosphate did not show correlation with any hydrographic parameters during monsoon. During post monsoon pH correlated positively with salinity. In post monsoon there is an increase in salinity accompanied by a decrease in oxygen solubility (Best et al., 2007). There is a lowering of pH with increase in salinity. Dissolved ammonium correlated positively with alkalinity and negatively with pH indicating that ammonium production is a

dominant factor which controls the hydrographic parameters in post-monsoon. Dissolved nitrite and dissolved phosphate showed no correlation with any parameters.

H_2S showed positive correlation with DO. In post monsoon there is a decrease in dissolved oxygen. Nitrification increases with light regime and can deplete dissolved oxygen. But nitrification appears to be limited in estuaries. Nitrate and ammonium are taken up almost equally by phytoplankton. An inhibition of nitrate uptake can increase the concentration of ammonium which is observed in post monsoon. Alkalinity is known to be highly correlated to salinity (Bates et al, 1996). But here, since a negative correlation was observe between salinity and alkalinity, is must be assumed that the concentration of other dissolved components, especially ammonium is the dominant factor controlling alkalinity. Oxygen depletion is also observed as a consequence of sinking and decay of phytoplankton blooms. In post monsoon there will be an increased degradation of organic matter brought down by the monsoon.. This explains the correlation between DO and H_2S. Microbial respiration can also deplete water column of dissolved oxygen in the presence of organic matter (Best et al, 2007).

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Data Of Hydrography
(Bimonthly)

pH

		Station 1	Station 2	Station 3	Station 4	Station 5
Pre-Mon	Feb	7.92	7.99	8.13	8.44	8.27
	April	7.02	7.61	7.56	8.21	7.32
Monsoon	June	8.33	8.96	7.65	9.17	7.42
	Aug	7.41	7.6	7.56	8.13	7.53
Post-Mon	Oct	6.73	7.23	7.03	8.09	7.54
	Dec	7.56	7.29	6.85	8.09	8.22

Salinity (ppt)

		Station 1	Station 2	Station 3	Station 4	Station 5
Pre-Mon	Feb	29.53	30.35	19.01	32.35	25.42
	April	27.25	22.55	15.4	34.03	16.94
Monsoon	June	8.49	6.92	1.18	16.96	5.28
	Aug	4.28	2.43	0.55	7.52	1.21
Post-Mon	Oct	3.17	4.215	0.66	11.33	3.32
	Dec	8.69	19.91	11.71	18.82	20.73

Dissolved Oxygen (ml/L)

		Station 1	Station 2	Station 3	Station 4	Station 5
Pre-Mon	Feb	1.711	3.01	3.78	1.15	5.46
	April	2.98	2.01	3.08	1.99	1.78
Monsoon	June	2.16	7.09	1.38	1.28	1.34
	Aug	2.18	2.23	2.07	0.54	0.111
Post-Mon	Oct	7.16	3.68	2.13	3.39	5.98
	Dec	0.728	0.73	0.74	1.28	1.26

Dissolved NH_4^+ (µmol/L)

		Station 1	Station 2	Station 3	Station 4	Station 5
Pre-Mon	Feb	32.76	68.69	23.38	45.51	6.64
	April	13.83	12.04	51.93	10.93	11.31
Monsoon	June	13.78	10.22	23.62	15.08	21.09
	Aug	20.07	38.97	18.91	2.114	23.53
Post-Mon	Oct	41.29	38.62	59.71	1.51	4.721
	Dec	9.365	19.45	57.91	19.47	13.6

Dissolved NO_2^- (µmol/L)

		Station 1	Station 2	Station 3	Station 4	Station 5
Pre-Mon	Feb	0.931	0.047	5.317	18.98	0.931
	April	0.219	0.309	1.511	0.162	0.321
Monsoon	June	0.139	0.461	2.18	1.61	0.092
	Aug	0.691	0.428	1.362	1.063	1.132
Post-Mon	Oct	0.132	0.612	0.321	0.271	0.125
	Dec	0.216	1.12	6.687	1.732	0.698

Dissolved PO_4^{3-} (µmol/L)

		Station 1	Station 2	Station 3	Station 4	Station 5
Pre-Mon	Feb	1.019	2.13	23.74	2.117	5.462
	April	29.33	30.11	49.32	0.974	2.841
Monsoon	June	30.25	9.589	42.15	46.97	1.532
	Aug	15.32	12.72	7.53	2.19	0.984
Post-Mon	Oct	13.28	12.14	12.42	26.15	3.21
	Dec	10.18	12.41	13.29	22.11	2.035

H_2S (µmol/L)

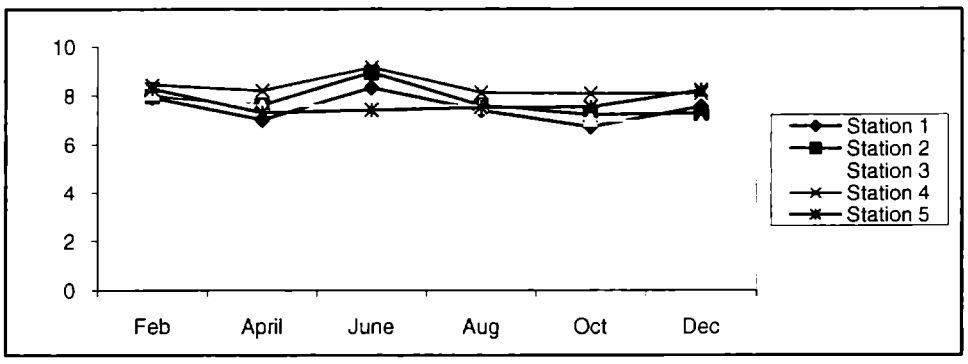
		Station 1	Station 2	Station 3	Station 4	Station 5
Pre-Mon	Feb	2.187	3.657	4.004	4.567	3.429
	April	2.857	2.287	4.567	7.428	5.139
Monsoon	June	3.434	9.141	2.86	1.715	2.861
	Aug	0.569	2.004	3.137	4.568	4.004
Post-Mon	Oct	8.002	9.711	2.862	2.297	10.29
	Dec	1.715	3.434	1.147	5.137	5.714

Alkalinity eqts /L

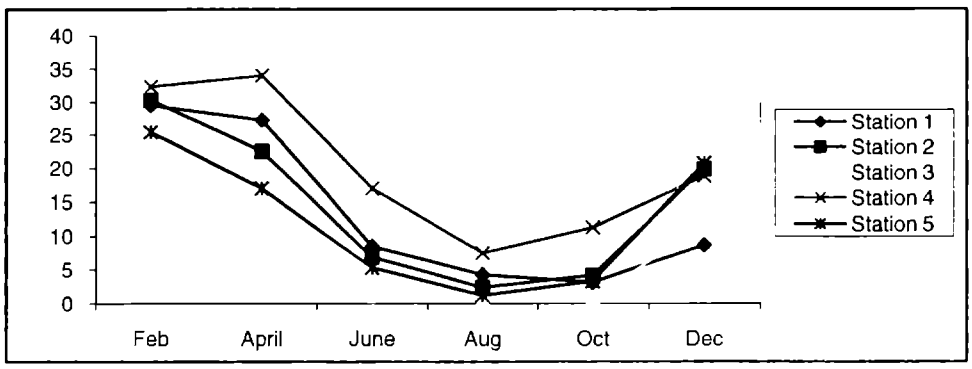
		Station 1	Station 2	Station 3	Station 4	Station 5
Pre-Mon	Feb	4.724	2.412	4.231	4.44	4.11
	April	4.147	3.768	1.524	3.767	1.472
Monsoon	June	4.244	4.192	2.372	3.516	2.063
	Aug	0.381	2.721	2.211	0.94	1.712
Post-Mon	Oct	3.66	0.848	4.281	0.036	0.868
	Dec	0.925	0.842	0.682	0.342	0.719

GRAPHS OF HYDROGRAPHY

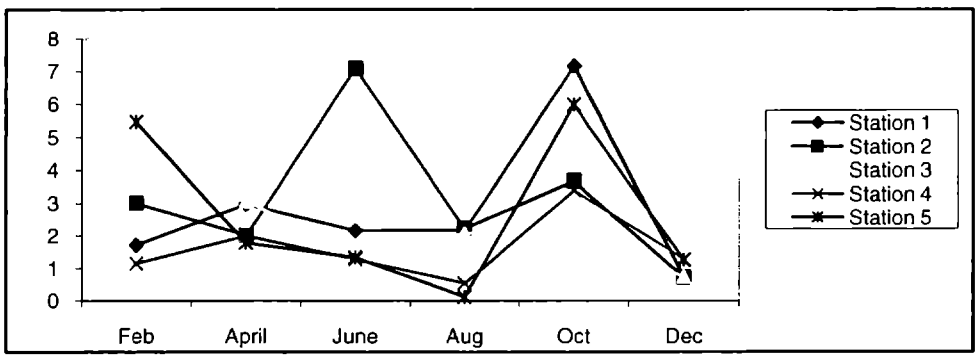
pH



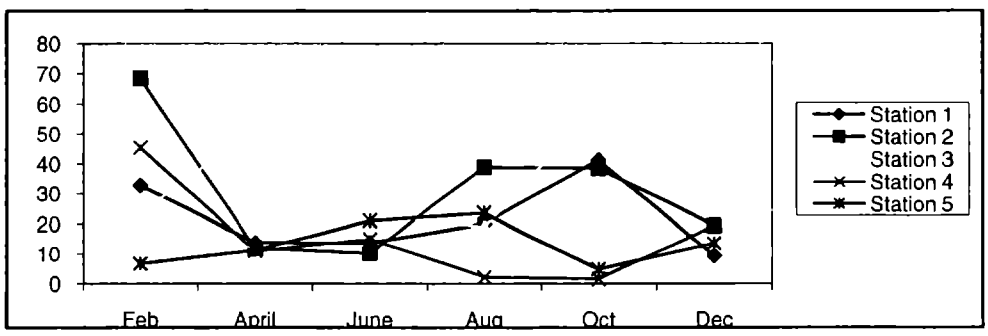
Salinity



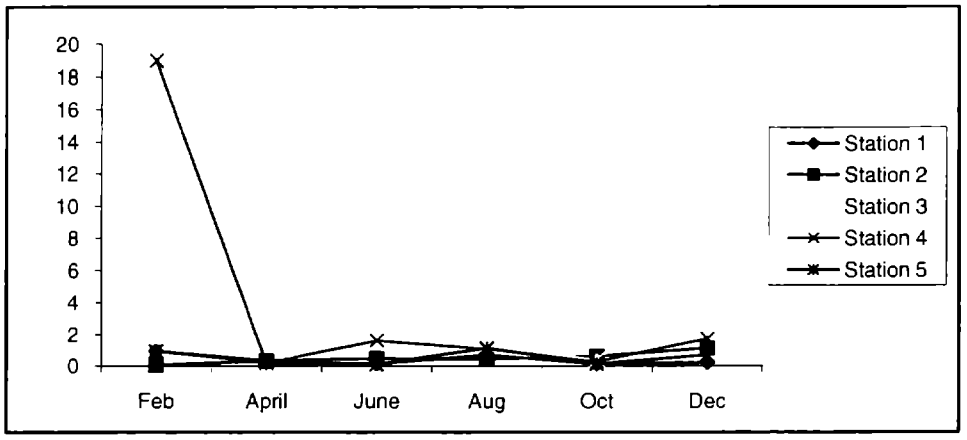
Dissolved Oxygen



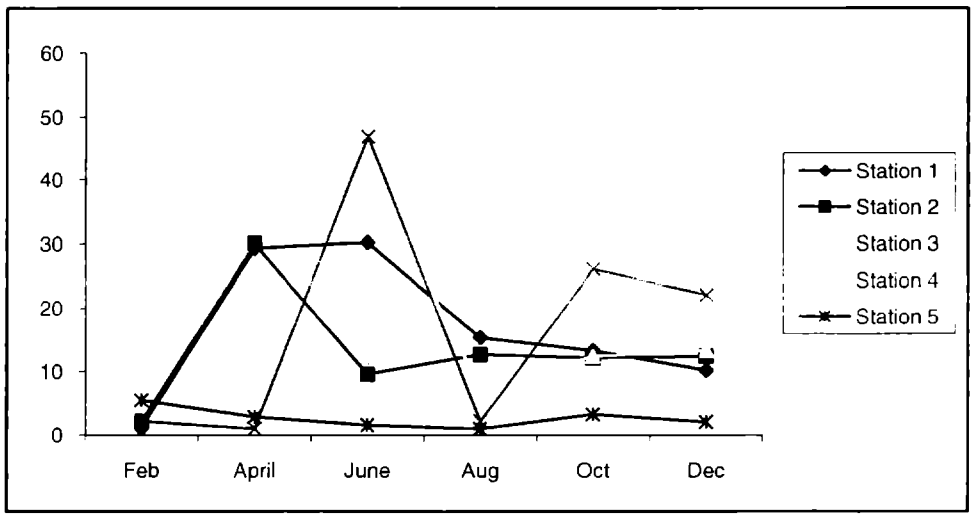
Dissolved NH_4^+



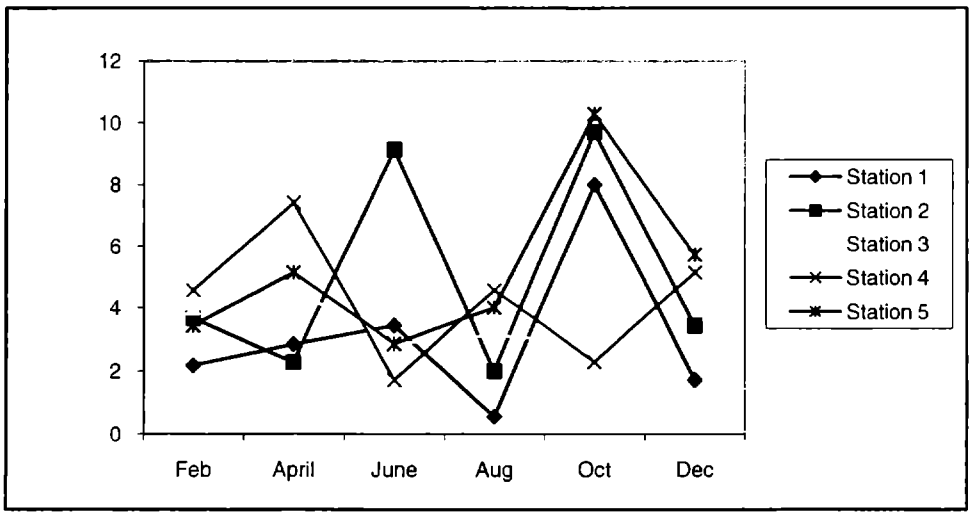
Dissolved NO_2^-



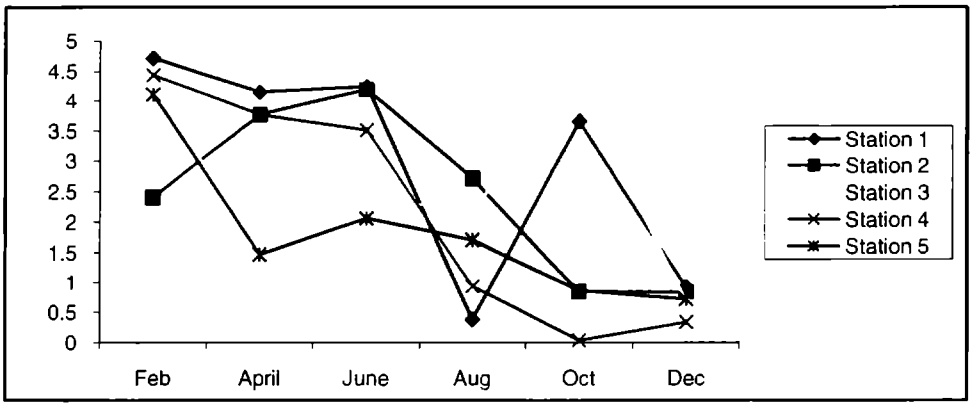
Dissolved PO_4^{3-}



H_2S

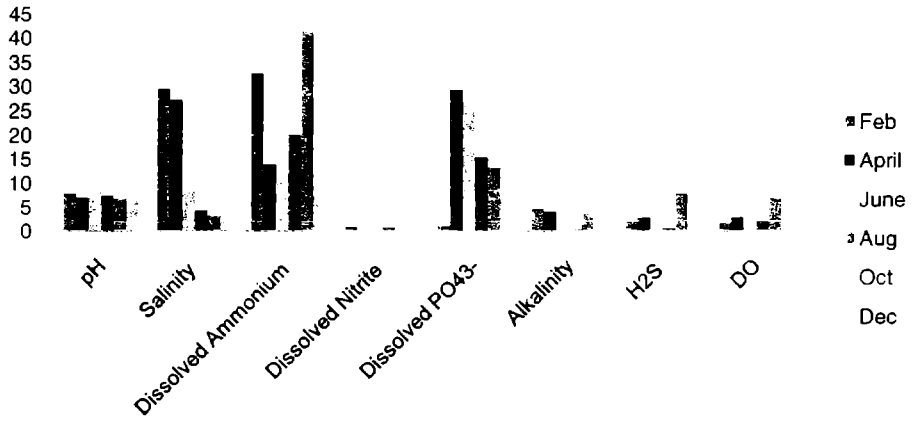


Alkalinity



Variations of Hydrography at different stations (Bimonthly)

Stn 1



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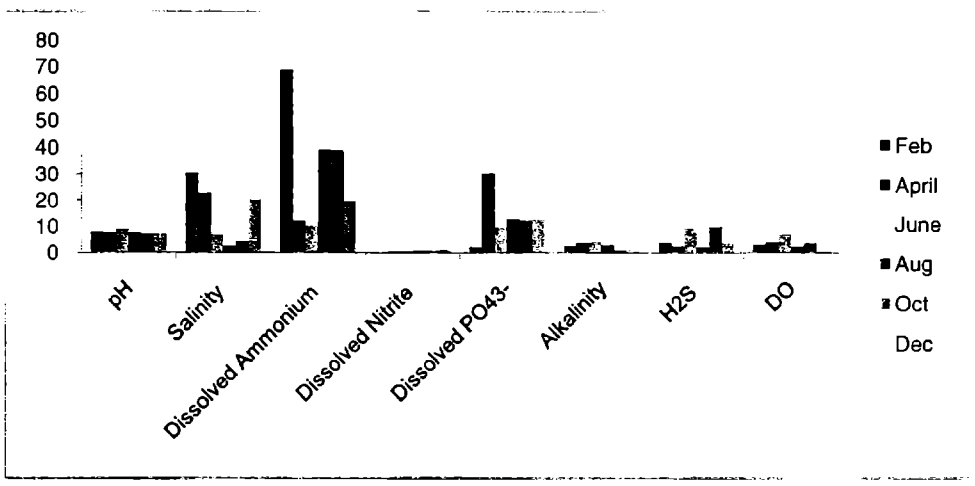

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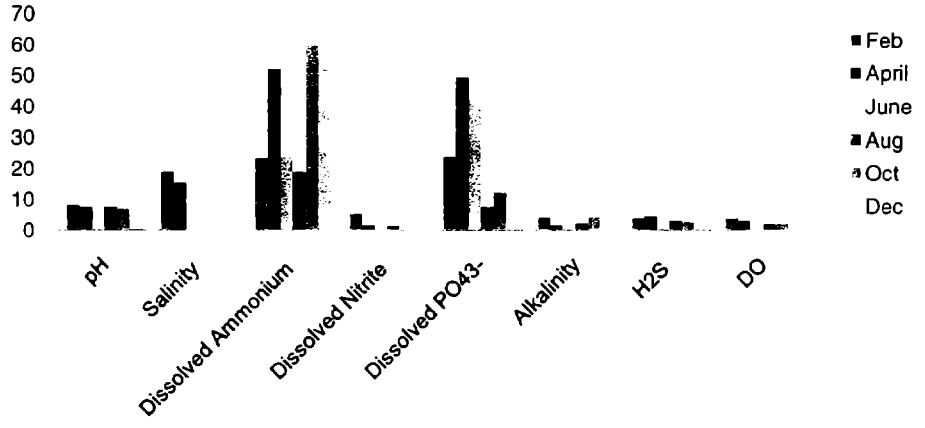

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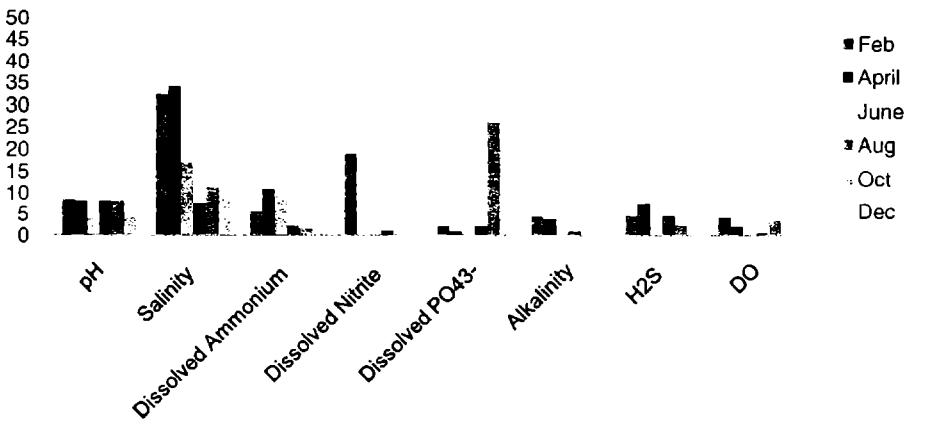

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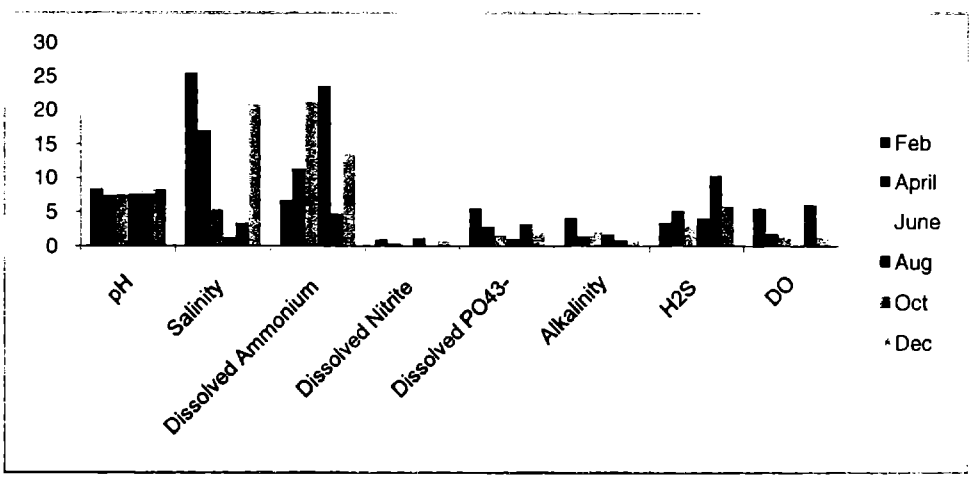

Correlations (Total)									
		pH	Salinity	Diss. NH_4^+	Diss. NO_2^-	Diss. PO_4^{3-}	Alkalinity	H_2S	Diss. O_2
pH	Pearson Correl	1	0.343	-0.357	0.177	0.103	0.274	0.072	0.036
	Sig. (2-tailed)	.	0.063	0.053	0.349	0.588	0.144	0.707	0.85
	N	30	30	30	30	30	30	30	30
Salinity	Pearson Correl	0.343	1	0.026	0.308	-0.078	0.341	-0.066	-0.107
	Sig. (2-tailed)	0.063	.	0.89	0.098	0.683	0.065	0.729	0.575
	N	30	30	30	30	30	30	30	30
Diss. NH_4^+	Pearson Correl	-0.357	0.026	1	0.308	0.007	0.134	-0.108	-0.045
	Sig. (2-tailed)	0.053	0.89	.	0.098	0.972	0.479	0.571	0.813
	N	30	30	30	30	30	30	30	30
Diss. NO_2^-	Pearson Correl	0.177	0.308	0.308	1	-0.069	0.193	-0.073	-0.202
	Sig. (2-tailed)	0.349	0.098	0.098	.	0.718	0.306	0.7	0.285
	N	30	30	30	30	30	30	30	30
Diss. PO_4^{3-}	Pearson Correl	0.103	-0.078	0.007	-0.069	1	0.071	-0.28	0.001
	Sig. (2-tailed)	0.588	0.683	0.972	0.718	.	0.708	0.134	0.997
	N	30	30	30	30	30	30	30	30
Alkalinity	Pearson Correl	0.274	0.341	0.134	0.193	0.071	1	-0.011	0.281
	Sig. (2-tailed)	0.144	0.065	0.479	0.306	0.708	.	0.954	0.133
	N	30	30	30	30	30	30	30	30
H_2S	Pearson Correl	0.072	-0.066	-0.108	-0.073	-0.28	-0.011	1	.595(**)
	Sig. (2-tailed)	0.707	0.729	0.571	0.7	0.134	0.954	.	0.001
	N	30	30	30	30	30	30	30	30
Diss.O_2	Pearson Correl	0.036	-0.107	-0.045	-0.202	0.001	0.281	.595(**)	1
	Sig. (2-tailed)	0.85	0.575	0.813	0.285	0.997	0.133	0.001	.
	N	30	30	30	30	30	30	30	30

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

Correlations (Premonsoon)									
		pH	Salinity	NH_4^+	NO_2^-	PO_4^{3-}	Alkalinity	H_2S	Diss. O_2
pH	Pearson Correlation	1	0.48	0.2	**0.516**	**-0.512**	0.424	0.275	0.111
	Sig. (2-tailed)	.	0.16	0.579	0.127	0.13	0.223	0.443	0.759
	N	10	10	10	10	10	10	10	10
Salinity	Pearson Correlation	0.48	1	0.116	0.255	-.636(*)	0.579	0.128	-0.266
	Sig. (2-tailed)	0.16	.	0.75	0.477	0.048	0.08	0.724	0.457
	N	10	10	10	10	10	10	10	10
Dissolved NH_4^+	Pearson Correlation	0.2	0.116	1	0.288	0.051	-0.304	-0.07	-0.164
	Sig. (2-tailed)	0.579	0.75	.	0.42	0.89	0.393	0.847	0.65
	N	10	10	10	10	10	10	10	10
Dissolved NO_2^-	Pearson Correlation	0.516	0.255	0.288	1	-0.175	0.333	0.112	-0.328
	Sig. (2-tailed)	0.127	0.477	0.42	.	0.629	0.347	0.758	0.355
	N	10	10	10	10	10	10	10	10
Dissolved PO_4^{3-}	Pearson Correlation	-0.512	-.636(*)	0.051	-0.175	1	-0.26	-0.237	0.209
	Sig. (2-tailed)	0.13	0.048	0.89	0.629	.	0.468	0.51	0.562
	N	10	10	10	10	10	10	10	10
Alkalinity	Pearson Correlation	0.424	0.579	-0.304	0.333	-0.26	1	-0.319	0.028
	Sig. (2-tailed)	0.223	0.08	0.393	0.347	0.468	.	0.368	0.938
	N	10	10	10	10	10	10	10	10
H_2S	Pearson Correlation	0.275	0.128	-0.07	0.112	-0.237	-0.319	1	-0.18
	Sig. (2-tailed)	0.443	0.724	0.847	0.758	0.51	0.368	.	0.619
	N	10	10	10	10	10	10	10	10
Dissolved Oxygen	Pearson Correlation	0.111	-0.266	-0.164	-0.328	0.209	0.028	-0.18	1
	Sig. (2-tailed)	0.759	0.457	0.65	0.355	0.562	0.938	0.619	.
	N	10	10	10	10	10	10	10	10

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

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Correlations (Monsoon)									
		pH	Salinity	Dissolved NH_4^+	Dissolved NO_2^-	Dissolved PO_4^{3-}	Alkalinity	H_2S	Diss. O_2
pH	Pearson Correlation	1	.826(**)	-0.538	0.051	0.454	.685(*)	0.464	0.462
	Sig. (2-tailed)	.	0.003	0.109	0.888	0.188	0.029	0.176	0.179
	N	10	10	10	10	10	10	10	10
Salinity	Pearson Correlation	.826(**)	1	-0.485	-0.045	0.489	0.413	0.002	0.073
	Sig. (2-tailed)	0.003	.	0.156	0.901	0.151	0.236	0.996	0.842
	N	10	10	10	10	10	10	10	10
Dissolved NH_4^+	Pearson Correlation	-0.538	-0.485	1	-0.035	0.036	-0.042	-0.472	-0.155
	Sig. (2-tailed)	0.109	0.156	.	0.923	0.922	0.909	0.169	0.669
	N	10	10	10	10	10	10	10	10
Dissolved NO_2^-	Pearson Correlation	0.051	-0.045	-0.035	1	0.494	-0.177	-0.18	-0.336
	Sig. (2-tailed)	0.888	0.901	0.923	.	0.147	0.625	0.618	0.342
	N	10	10	10	10	10	10	10	10
Dissolved PO_4^{3-}	Pearson Correlation	0.454	0.489	0.036	0.494	1	0.438	-0.316	-0.043
	Sig. (2-tailed)	0.188	0.151	0.922	0.147	.	0.206	0.373	0.906
	N	10	10	10	10	10	10	10	10
Alkalinity	Pearson Correlation	.685(*)	0.413	-0.042	-0.177	0.438	1	0.444	0.542
	Sig. (2-tailed)	0.029	0.236	0.909	0.625	0.206	.	0.198	0.106
	N	10	10	10	10	10	10	10	10
H_2S	Pearson Correlation	0.464	0.002	-0.472	-0.18	-0.316	0.444	1	.688(*)
	Sig. (2-tailed)	0.176	0.996	0.169	0.618	0.373	0.198	.	0.028
	N	10	10	10	10	10	10	10	10
Dissolved Oxygen	Pearson Correlation	0.462	0.073	-0.155	-0.336	-0.043	0.542	.688(*)	1
	Sig. (2-tailed)	0.179	0.842	0.669	0.342	0.906	0.106	0.028	.
	N	10	10	10	10	10	10	10	10

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

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

Correlations (Post Monsoon)									
		pH	Salinity	Dissolved NH_4^+	Dissolved NO_2^-	Dissolved PO_4^{3-}	Alkalinity	H_2S	Diss. O_2
pH	Pearson Correlation	1	0.595	-.773(**)	-0.298	0.137	-.635(*)	-0.045	-0.288
	Sig. (2-tailed)	.	0.069	0.009	0.403	0.706	0.049	0.902	0.42
	N	10	10	10	10	10	10	10	10
Salinity	Pearson Correlation	0.595	1	-0.389	0.252	0.107	-0.619	-0.336	-.640(*)
	Sig. (2-tailed)	0.069	.	0.266	0.482	0.768	0.056	0.342	0.046
	N	10	10	10	10	10	10	10	10
Dissolved NH_4^+	Pearson Correlation	-.773(**)	-0.389	1	0.487	-0.001	0.632	-0.127	-0.034
	Sig. (2-tailed)	0.009	0.266	.	0.154	0.997	0.05	0.727	0.926
	N	10	10	10	10	10	10	10	10
Dissolved NO_2^-	Pearson Correlation	-0.298	0.252	0.487	1	0.105	-0.25	-0.424	-0.426
	Sig. (2-tailed)	0.403	0.482	0.154	.	0.773	0.485	0.222	0.22
	N	10	10	10	10	10	10	10	10
Dissolved PO_4^{3-}	Pearson Correlation	0.137	0.107	-0.001	0.105	1	-0.151	-0.396	-0.087
	Sig. (2-tailed)	0.706	0.768	0.997	0.773	.	0.677	0.257	0.811
	N	10	10	10	10	10	10	10	10
Alkalinity	Pearson Correlation	-.635(*)	-0.619	0.632	-0.25	-0.151	1	0.081	0.374
	Sig. (2-tailed)	0.049	0.056	0.05	0.485	0.677	.	0.823	0.287
	N	10	10	10	10	10	10	10	10
H_2S	Pearson Correlation	-0.045	-0.336	-0.127	-0.424	-0.396	0.081	1	.731(*)
	Sig. (2-tailed)	0.902	0.342	0.727	0.222	0.257	0.823	.	0.016
	N	10	10	10	10	10	10	10	10
Dissolved Oxygen	Pearson Correlation	-0.288	-.640(*)	-0.034	-0.426	-0.087	0.374	.731(*)	1
	Sig. (2-tailed)	0.42	0.046	0.926	0.22	0.811	0.287	0.016	
	N	10	10	10	10	10	10	10	10

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

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

Correlations (Station 1)									
		pH	Salinity	NH_4^+	NO_2^-	PO_4^{3-}	Alkalinity	H_2S	Dis. O_2
pH	Pearson Correlation	1	0.131	-0.378	0.266	0.029	0.149	-0.481	-0.686
	Sig. (2-tailed)	.	0.805	0.46	0.611	0.957	0.779	0.335	0.132
	N	6	6	6	6	6	6	6	6
Salinity	Pearson Correlation	0.131	1	-0.026	0.419	-0.099	0.59	-0.266	-0.312
	Sig. (2-tailed)	0.805	.	0.961	0.408	0.851	0.218	0.61	0.547
	N	6	6	6	6	6	6	6	6
Dissolved NH_4^+	Pearson Correlation	-0.378	-0.026	1	0.279	-0.512	0.367	0.657	0.735
	Sig. (2-tailed)	0.46	0.961	.	0.592	0.299	0.474	0.156	0.096
	N	6	6	6	6	6	6	6	6
NO_2^-	Pearson Correlation	0.266	0.419	0.279	1	-0.648	-0.055	-0.531	-0.37
	Sig. (2-tailed)	0.611	0.408	0.592	.	0.164	0.918	0.278	0.47
	N	6	6	6	6	6	6	6	6
PO_4^{3-}	Pearson Correlation	0.029	-0.099	-0.512	-0.648	1	0.181	0.079	0.079
	Sig. (2-tailed)	0.957	0.851	0.299	0.164	.	0.731	0.882	0.881
	N	6	6	6	6	6	6	6	6
Alkalinity	Pearson Correlation	0.149	0.59	0.367	-0.055	0.181	1	0.469	0.301
	Sig. (2-tailed)	0.779	0.218	0.474	0.918	0.731	.	0.349	0.562
	N	6	6	6	6	6	6	6	6
H_2S	Pearson Correlation	-0.481	-0.266	0.657	-0.531	0.079	0.469	1	.914(*)
	Sig. (2-tailed)	0.335	0.61	0.156	0.278	0.882	0.349	.	0.011
	N	6	6	6	6	6	6	6	6
Dissolved Oxygen	Pearson Correlation	-0.686	-0.312	0.735	-0.37	0.079	0.301	.914(*)	1
	Sig. (2-tailed)	0.132	0.547	0.096	0.47	0.881	0.562	0.011	.
	N	6	6	6	6	6	6	6	6

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

Correlations (Station 2)									
		pH	Salinity	NH_4^+	NO_2^-	PO_4^{3-}	Alkalinity	H_2S	Dis. O_2
pH	Pearson Correlation	1	-0.049	-0.188	-0.402	-0.286	0.762	0.342	.842(*)
	Sig. (2-tailed)	.	0.926	0.721	0.43	0.583	0.078	0.507	0.035
	N	6	6	6	6	6	6	6	6
Salinity	Pearson Correlation	-0.049	1	0.288	-0.261	0.001	0.016	-0.481	-0.39
	Sig. (2-tailed)	0.926	.	0.58	0.618	0.999	0.976	0.334	0.444
	N	6	6	6	6	6	6	6	6
Dissolved NH_4^+	Pearson Correlation	-0.188	0.288	1	-0.489	-0.651	-0.345	-0.144	-0.168
	Sig. (2-tailed)	0.721	0.58	.	0.325	0.161	0.503	0.786	0.75
	N	6	6	6	6	6	6	6	6
Dissolved NO_2^-	Pearson Correlation	-0.402	-0.261	-0.489	1	0.082	-0.59	0.119	-0.318
	Sig. (2-tailed)	0.43	0.618	0.325	.	0.878	0.218	0.823	0.539
	N	6	6	6	6	6	6	6	6
Dissolved PO_4^{3-}	Pearson Correlation	-0.286	0.001	-0.651	0.082	1	0.296	-0.303	-0.3
	Sig. (2-tailed)	0.583	0.999	0.161	0.878	.	0.569	0.559	0.563
	N	6	6	6	6	6	6	6	6
Alkalinity	Pearson Correlation	0.762	0.016	-0.345	-0.59	0.296	1	-0.088	0.529
	Sig. (2-tailed)	0.078	0.976	0.503	0.218	0.569	.	0.868	0.281
	N	6	6	6	6	6	6	6	6
H_2S	Pearson Correlation	0.342	-0.481	-0.144	0.119	-0.303	-0.088	1	0.758
	Sig. (2-tailed)	0.507	0.334	0.786	0.823	0.559	0.868	.	0.081
	N	6	6	6	6	6	6	6	6
Dissolved Oxygen	Pearson Correlation	.842(*)	-0.39	-0.168	-0.318	-0.3	0.529	0.758	1
	Sig. (2-tailed)	0.035	0.444	0.75	0.539	0.563	0.281	0.081	.
	N	6	6	6	6	6	6	6	6

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

Correlations(Station 3)									
		pH	Salinity	NH_4^+	NO_2^-	PO_4^{3-}	Alkalinity	H_2S	Diss. O_2
pH	Pearson Correlation	1	0.364	-0.782	-0.002	0.394	0.404	0.74	0.746
	Sig. (2-tailed)	.	0.479	0.066	0.997	0.44	0.426	0.092	0.088
	N	6	6	6	6	6	6	6	6
Salinity	Pearson Correlation	0.364	1	0.121	0.628	0.318	-0.083	0.341	0.557
	Sig. (2-tailed)	0.479	.	0.82	0.182	0.538	0.876	0.508	0.251
	N	6	6	6	6	6	6	6	6
Dissolved NH_4^+	Pearson Correlation	-0.782	0.121	1	0.019	-0.036	-0.212	-0.303	-0.256
	Sig. (2-tailed)	0.066	0.82	.	0.972	0.945	0.687	0.56	0.624
	N	6	6	6	6	6	6	6	6
Dissolved NO_2^-	Pearson Correlation	-0.002	0.628	0.019	1	-0.158	-0.296	-0.441	-0.141
	Sig. (2-tailed)	0.997	0.182	0.972	.	0.765	0.569	0.381	0.79
	N	6	6	6	6	6	6	6	6
Dissolved PO_4^{3-}	Pearson Correlation	0.394	0.318	-0.036	-0.158	1	-0.193	0.549	0.269
	Sig. (2-tailed)	0.44	0.538	0.945	0.765	.	0.714	0.259	0.607
	N	6	6	6	6	6	6	6	6
Alkalinity	Pearson Correlation	0.404	-0.083	-0.212	-0.296	-0.193	1	0.385	0.568
	Sig. (2-tailed)	0.426	0.876	0.687	0.569	0.714	.	0.451	0.239
	N	6	6	6	6	6	6	6	6
H_2S	Pearson Correlation	0.74	0.341	-0.303	-0.441	0.549	0.385	1	.891(*)
	Sig. (2-tailed)	0.092	0.508	0.56	0.381	0.259	0.451	.	0.017
	N	6	6	6	6	6	6	6	6
Dissolved Oxygen	Pearson Correlation	0.746	0.557	-0.256	-0.141	0.269	0.568	.891(*)	1
	Sig. (2-tailed)	0.088	0.251	0.624	0.79	0.607	0.239	0.017	.
	N	6	6	6	6	6	6	6	6

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

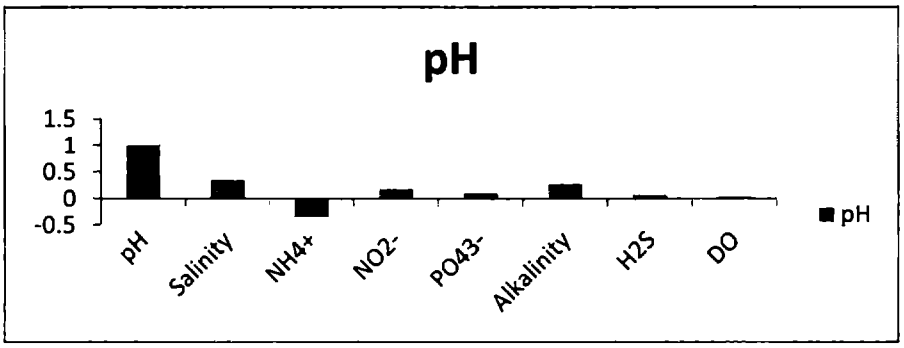
Correlations (Station 4)									
		pH	Salinity	NH_4^+	NO_2^-	PO_4^{3-}	Alkalinity	H_2S	Diss. O_2
pH	Pearson Correlation	1	0.086	0.251	0.137	0.645	0.583	-0.527	-0.244
	Sig. (2-tailed)	.	0.872	0.632	0.795	0.167	0.224	0.282	0.642
	N	6	6	6	6	6	6	6	6
Salinity	Pearson Correlation	0.086	1	0.672	0.524	-0.399	0.779	0.607	-0.019
	Sig. (2-tailed)	0.872	.	0.144	0.286	0.434	0.068	0.202	0.971
	N	6	6	6	6	6	6	6	6
Dissolved NH_4^+	Pearson Correlation	0.251	0.672	1	.921(**)	-0.197	0.63	0.135	-0.341
	Sig. (2-tailed)	0.632	0.144	.	0.009	0.708	0.18	0.799	0.509
	N	6	6	6	6	6	6	6	6
Dissolved NO_2^-	Pearson Correlation	0.137	0.524	.921(**)	1	-0.345	0.562	0.039	-0.282
	Sig. (2-tailed)	0.795	0.286	0.009	.	0.503	0.246	0.942	0.588
	N	6	6	6	6	6	6	6	6
Dissolved PO_4^{3-}	Pearson Correlation	0.645	-0.399	-0.197	-0.345	1	-0.165	-0.785	0.233
	Sig. (2-tailed)	0.167	0.434	0.708	0.503	.	0.754	0.065	0.656
	N	6	6	6	6	6	6	6	6
Alkalinity	Pearson Correlation	0.583	0.779	0.63	0.562	-0.165	1	0.226	-0.287
	Sig. (2-tailed)	0.224	0.068	0.18	0.246	0.754	.	0.667	0.581
	N	6	6	6	6	6	6	6	6
H_2S	Pearson Correlation	-0.527	0.607	0.135	0.039	-0.785	0.226	1	-0.216
	Sig. (2-tailed)	0.282	0.202	0.799	0.942	0.065	0.667	.	0.68
	N	6	6	6	6	6	6	6	6
Dissolved Oxygen	Pearson Correlation	-0.244	-0.019	-0.341	-0.282	0.233	-0.287	-0.216	1
	Sig. (2-tailed)	0.642	0.971	0.509	0.588	0.656	0.581	0.68	.
	N	6	6	6	6	6	6	6	6

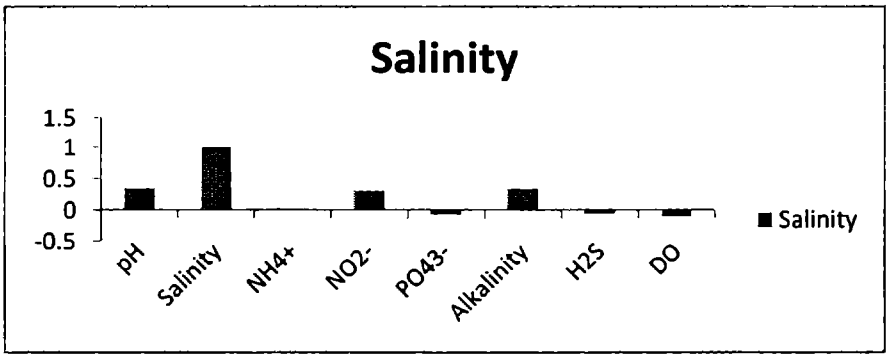
** Correlation is significant at the 0.01 level (2-tailed).

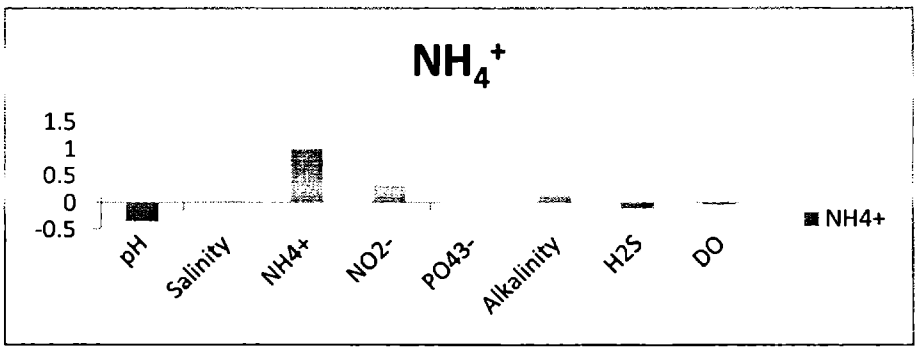
Correlations (Station 5)									
		pH	Salinity	NH_4^+	NO_2^-	PO_4^{3-}	Alkalinity	H_2S	Diss. O_2
pH	Pearson Correlation	1	0.725	-0.345	0.526	0.516	0.377	-0.121	0.289
	Sig. (2-tailed)	.	0.103	0.504	0.283	0.294	0.461	0.819	0.578
	N	6	6	6	6	6	6	6	6
Salinity	Pearson Correlation	0.725	1	-0.48	0.26	0.666	0.435	-0.257	0.23
	Sig. (2-tailed)	0.103	.	0.335	0.619	0.149	0.389	0.623	0.661
	N	6	6	6	6	6	6	6	6
Dissolved NH_4^+	Pearson Correlation	-0.345	-0.48	1	0.242	-.827(*)	-0.127	-0.609	-.888(*)
	Sig. (2-tailed)	0.504	0.335	.	0.644	0.042	0.81	0.199	0.018
	N	6	6	6	6	6	6	6	6
Dissolved NO_2^-	Pearson Correlation	0.526	0.26	0.242	1	0.07	0.381	-0.405	-0.231
	Sig. (2-tailed)	0.283	0.619	0.644	.	0.896	0.456	0.426	0.66
	N	6	6	6	6	6	6	6	6
Dissolved PO_4^{3-}	Pearson Correlation	0.516	0.666	-.827(*)	0.07	1	0.657	0.1	.831(*)
	Sig. (2-tailed)	0.294	0.149	0.042	0.896	.	0.156	0.85	0.04
	N	6	6	6	6	6	6	6	6
Alkalinity	Pearson Correlation	0.377	0.435	-0.127	0.381	0.657	1	-0.598	0.337
	Sig. (2-tailed)	0.461	0.389	0.81	0.456	0.156	.	0.21	0.514
	N	6	6	6	6	6	6	6	6
H_2S	Pearson Correlation	-0.121	-0.257	-0.609	-0.405	0.1	-0.598	1	0.53
	Sig. (2-tailed)	0.819	0.623	0.199	0.426	0.85	0.21	.	0.28
	N	6	6	6	6	6	6	6	6
Dissolved Oxygen	Pearson Correlation	0.289	0.23	-.888(*)	-0.231	.831(*)	0.337	0.53	1
	Sig. (2-tailed)	0.578	0.661	0.018	0.66	0.04	0.514	0.28	.
	N	6	6	6	6	6	6	6	6
* Correlation is significant at the 0.05 level (2-tailed).									

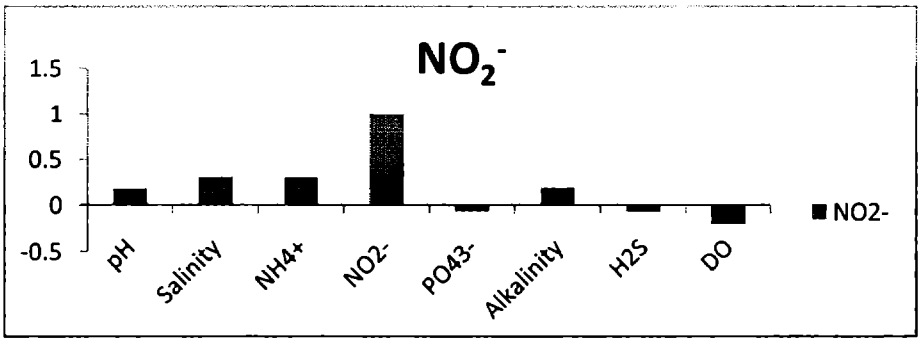
Graphs of Correlation

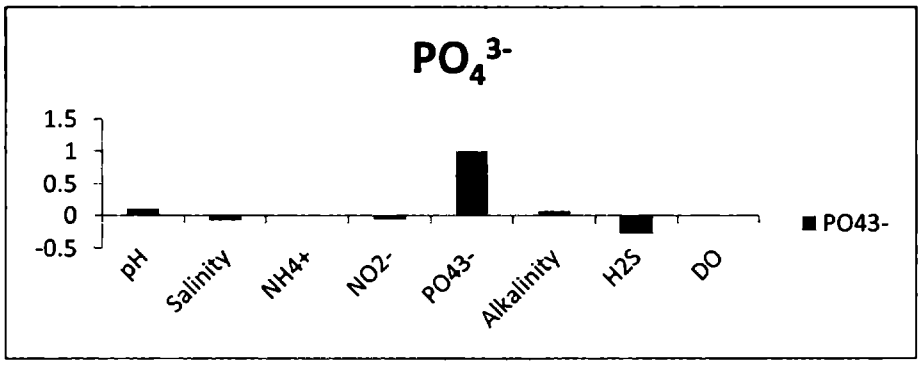
a) Total Correlation

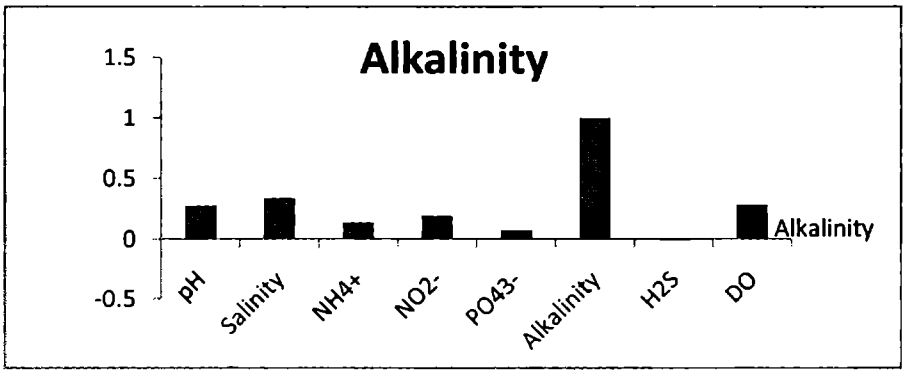


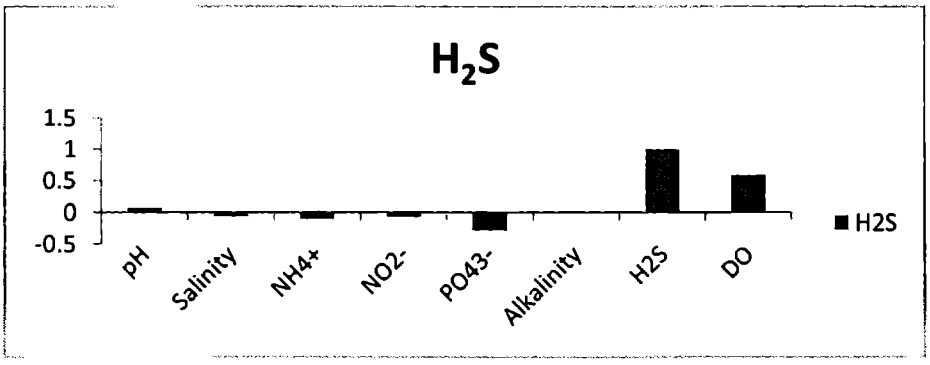


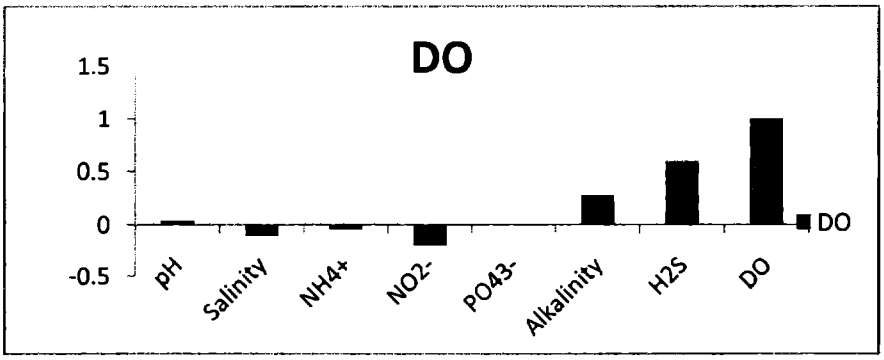



NO_2^-
1.5
1
0.5
0
-0.5
pH
Salinity
NH4+
NO2-
PO43-
Alkalinity
H2S
DO
NO2-


PO_4^{3-}
1.5
1
0.5
0
-0.5
pH
Salinity
NH4+
NO2-
PO43-
Alkalinity
H2S
DO
PO43-

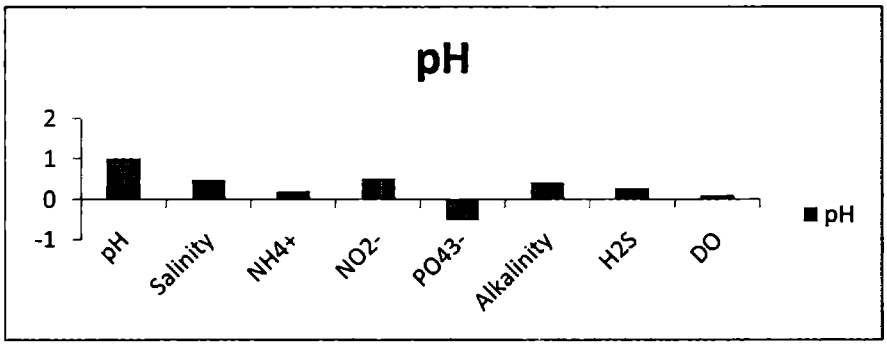

Alkalinity
1.5
1
0.5
0
-0.5
pH
Salinity
NH4+
NO2-
PO43-
Alkalinity
H2S
DO
Alkalinity

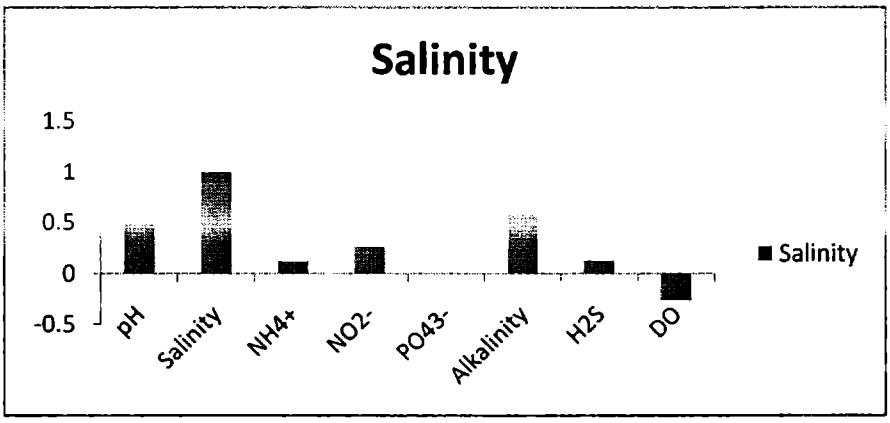

H_2S
1.5
1
0.5
0
-0.5
pH
Salinity
NH4+
NO2-
PO43-
Alkalinity
H2S
DO
H2S

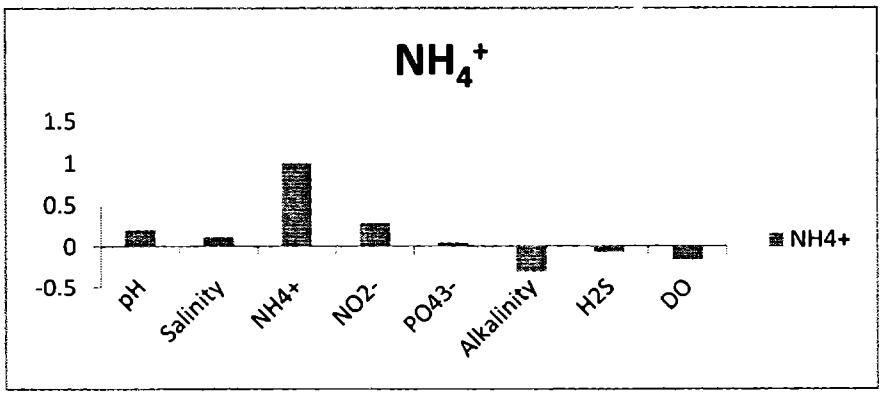


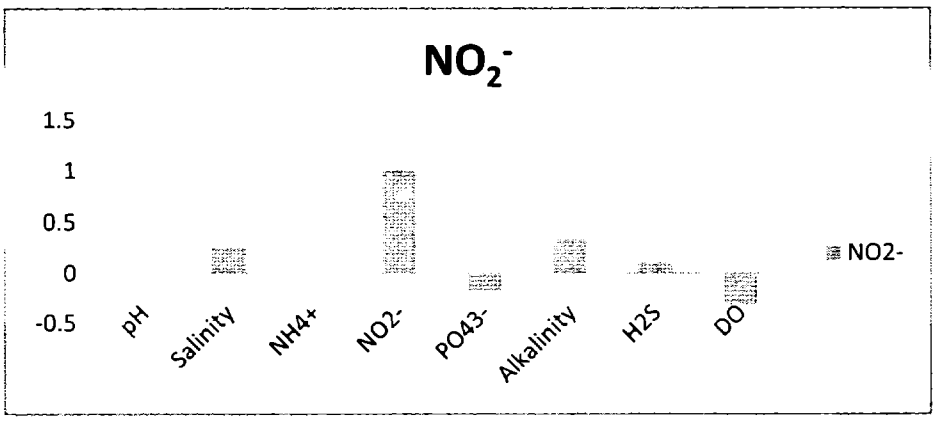
b) Seasonal

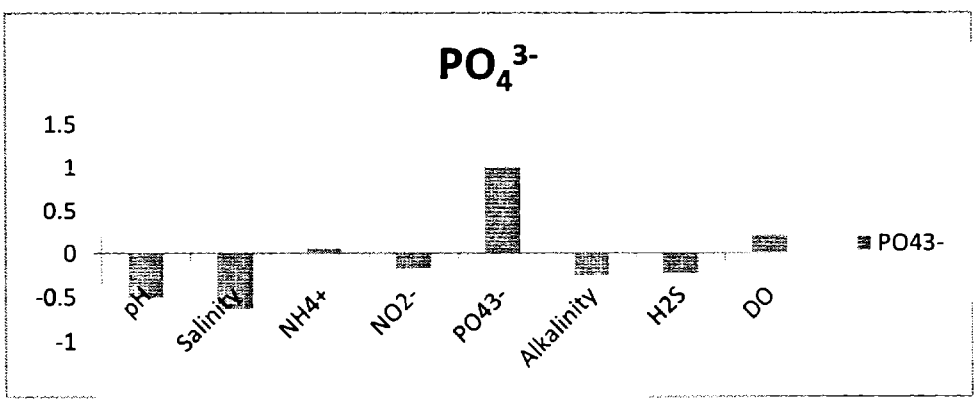
Premonsoon

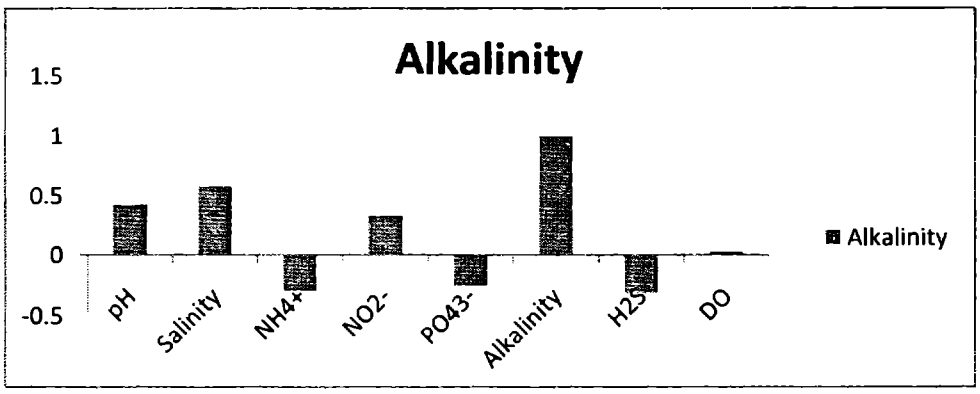


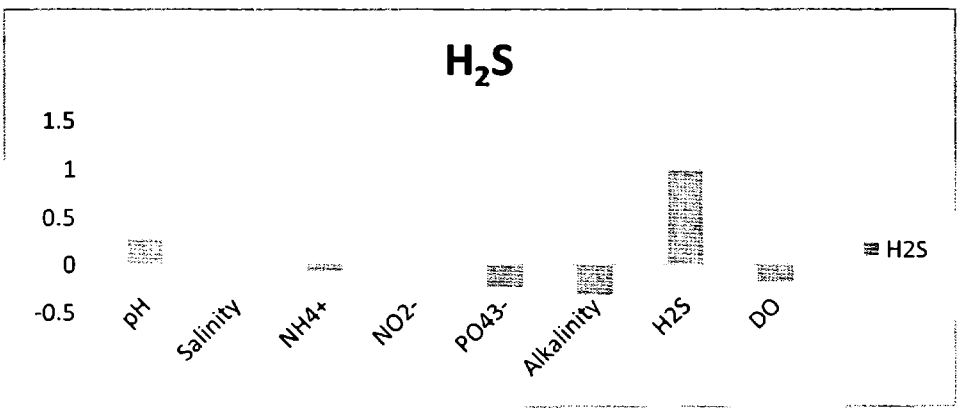


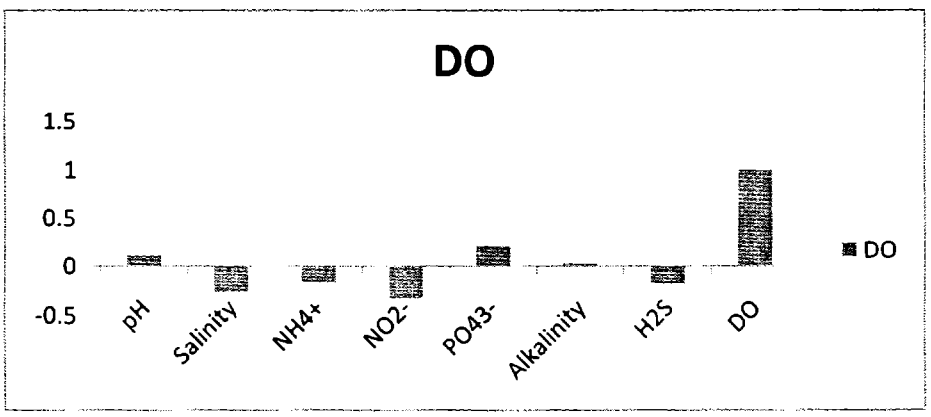

NH_4^+
1.5
1
0.5
0
-0.5
pH
Salinity
NH4+
NO2-
PO43-
Alkalinity
H2S
DO
NH4+


NO_2^-
1.5
1
0.5
0
-0.5
pH
Salinity
NH4+
NO2-
PO43-
Alkalinity
H2S
DO
NO2-

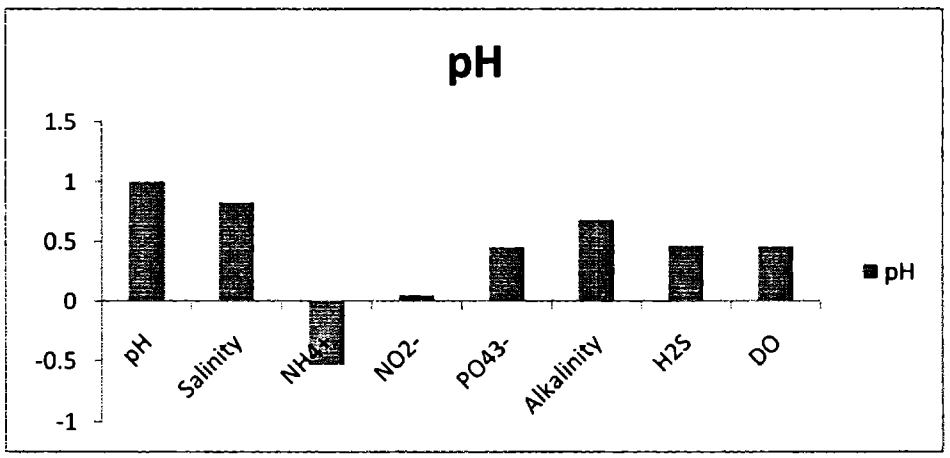

PO_4^{3-}
1.5
1
0.5
0
-0.5
-1
pH
Salinity
NH4+
NO2-
PO43-
Alkalinity
H2S
DO
PO43-

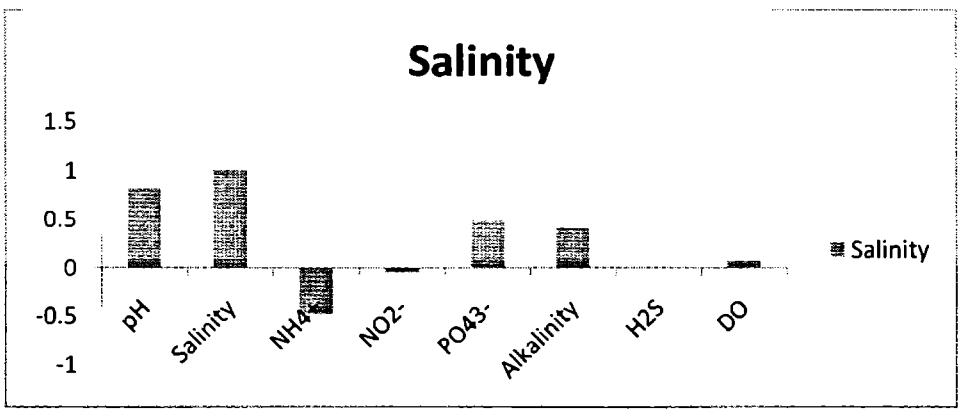

Alkalinity
1.5
1
0.5
0
-0.5
pH
Salinity
NH4+
NO2-
PO43-
Alkalinity
H2S
DO
Alkalinity

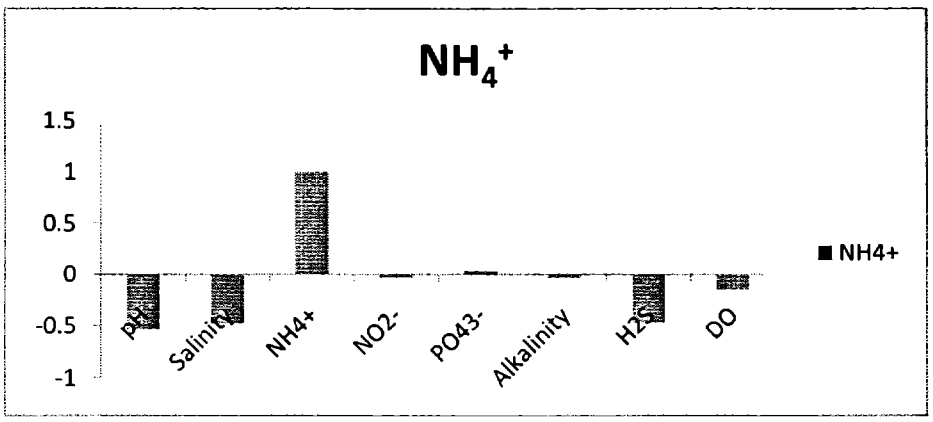

H2S
1.5
1
0.5
0
-0.5
pH
Salinity
NH4+
NO2-
PO43-
Alkalinity
H2S
DO
H2S

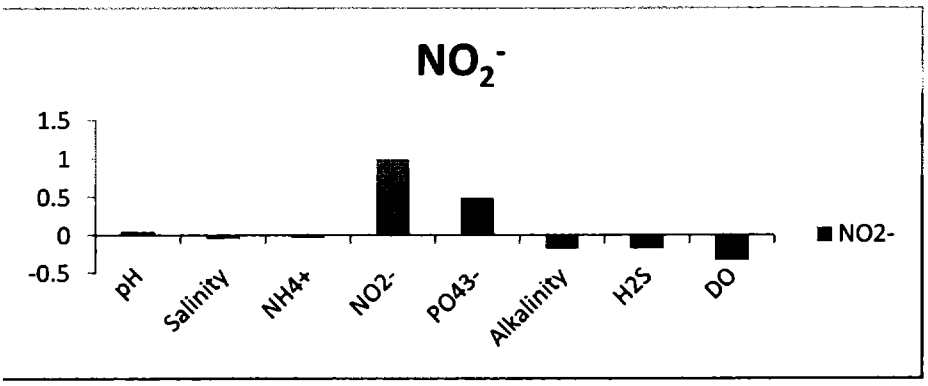

DO
1.5
1
0.5
0
-0.5
pH
Salinity
NH4+
NO2-
PO43-
Alkalinity
H2S
DO
DO

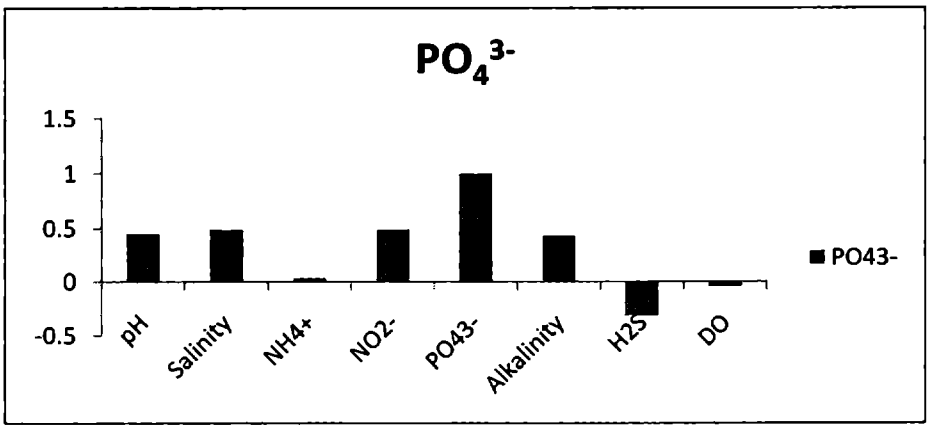
Monsoon

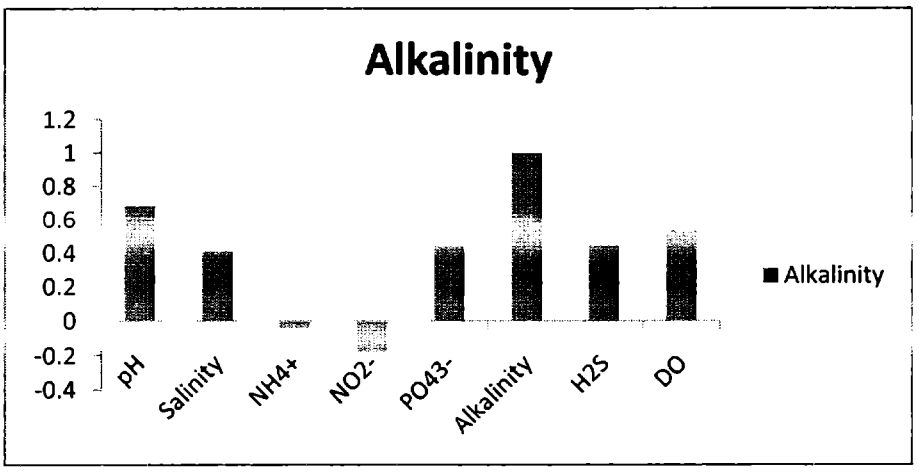

pH
1.5
1
0.5
0
-0.5
-1
pH
Salinity
NH4+
NO2-
PO43-
Alkalinity
H2S
DO
pH

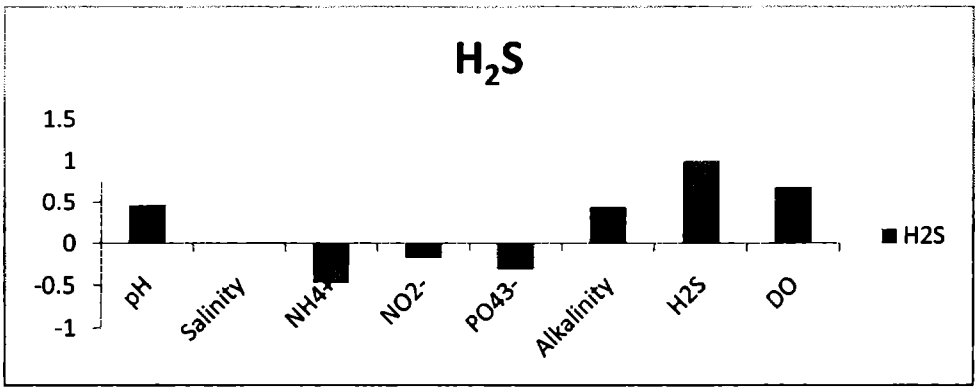

Salinity
1.5
1
0.5
0
-0.5
-1
pH
Salinity
NH4+
NO2-
PO43-
Alkalinity
H2S
DO
Salinity

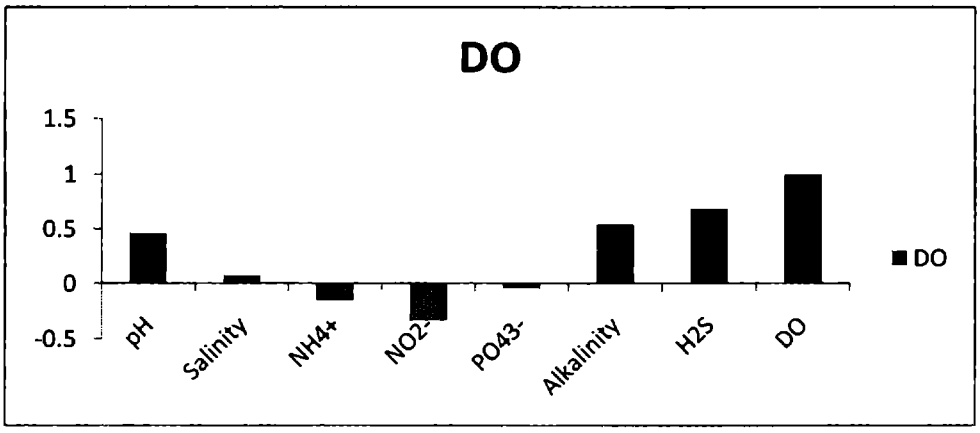

NH4+
1.5
1
0.5
0
-0.5
-1
pH
Salinity
NH4+
NO2-
PO43-
Alkalinity
H2S
DO
NH4+


NO_2^-
1.5
1
0.5
0
-0.5
pH
Salinity
NH4+
NO2-
PO43-
Alkalinity
H2S
DO
NO2-

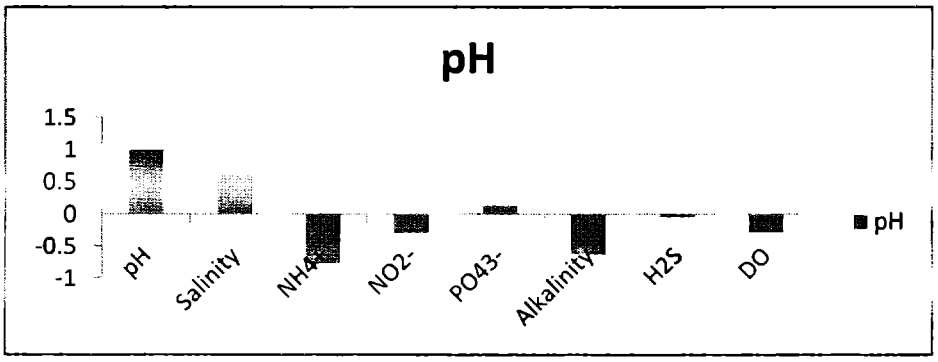

PO_4^{3-}
1.5
1
0.5
0
-0.5
pH
Salinity
NH4+
NO2-
PO43-
Alkalinity
H2S
DO
PO43-

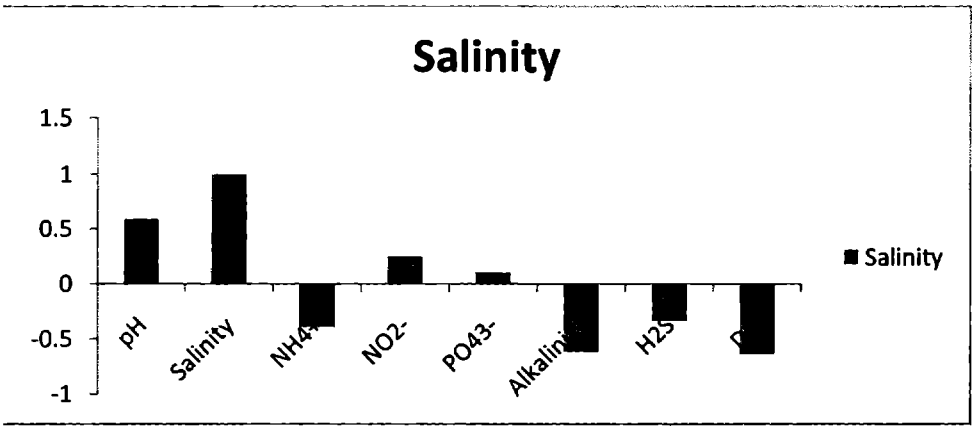

Alkalinity
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
pH
Salinity
NH4+
NO2-
PO43-
Alkalinity
H2S
DO
Alkalinity

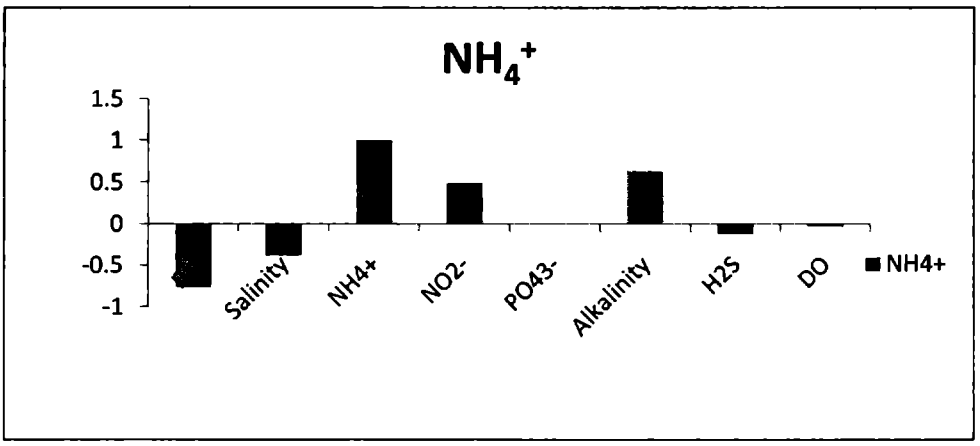


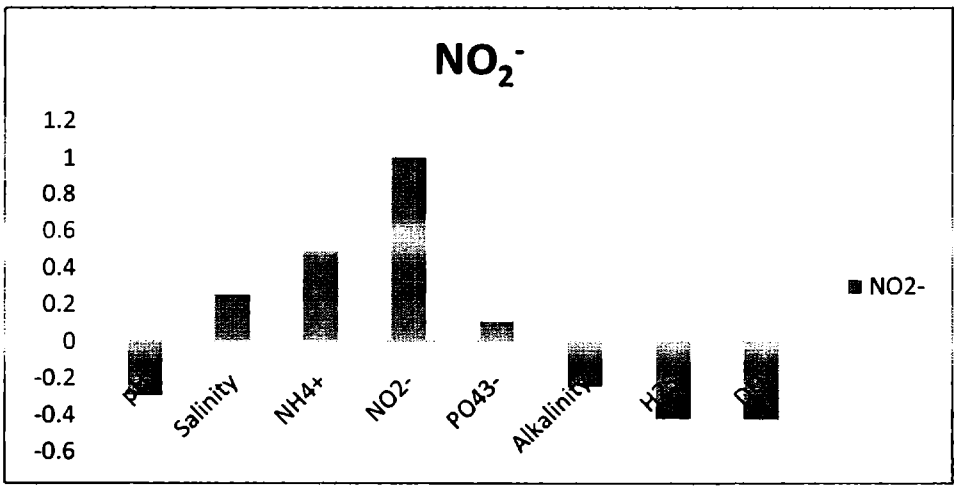


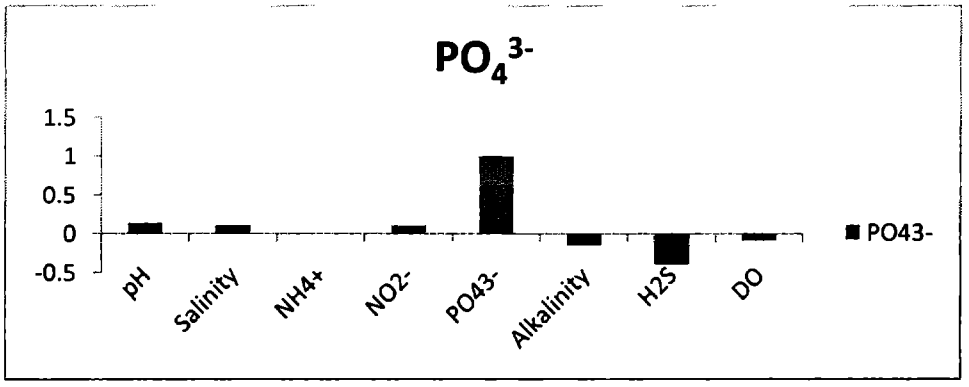
Post Monsoon

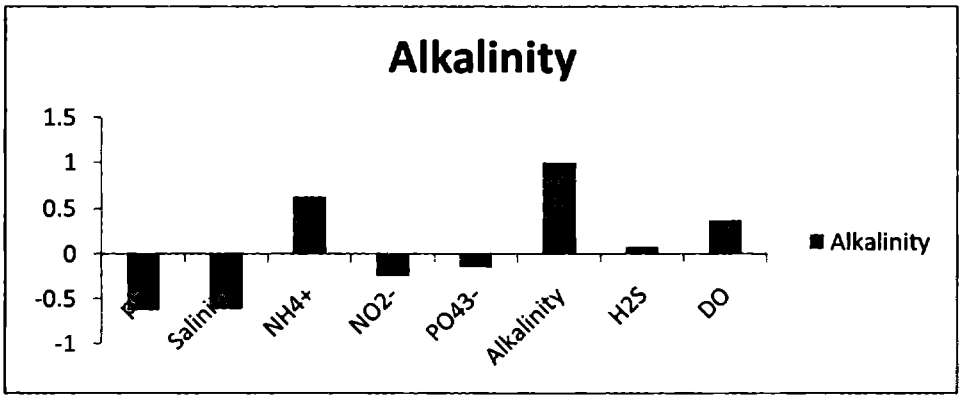


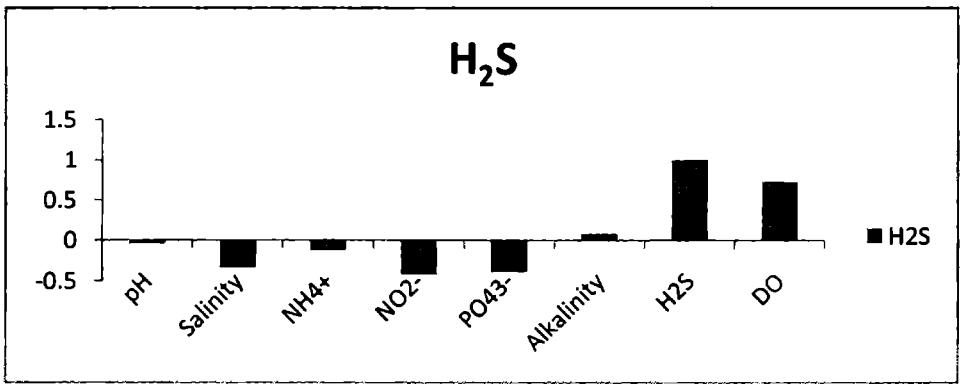

Salinity
1.5
1
0.5
0
-0.5
-1
pH
Salinity
NH4+
NO2-
PO43-
Alkalinity
H2S
DO
Salinity

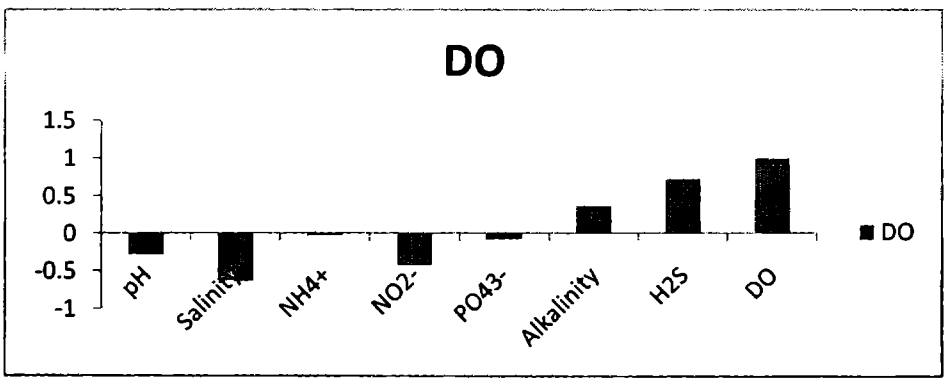

NH4+
1.5
1
0.5
0
-0.5
-1
Salinity
NH4+
NO2-
PO43-
Alkalinity
H2S
DO
NH4+


NO2-
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
Salinity
NH4+
NO2-
PO43-
NO2-


PO_4^{3-}
1.5
1
0.5
0
-0.5
pH
Salinity
NH4+
NO2-
PO43-
Alkalinity
H2S
DO
PO43-


Alkalinity
1.5
1
0.5
0
-0.5
-1
pH
Salinity
NH4+
NO2-
PO43-
Alkalinity
H2S
DO
Alkalinity


H_2S
1.5
1
0.5
0
-0.5
pH
Salinity
NH4+
NO2-
PO43-
Alkalinity
H2S
DO
H2S


DO
1.5
1
0.5
0
-0.5
-1
pH
Salinity
NH4+
NO2-
PO43-
Alkalinity
H2S
DO
DO

Two Way Anova

pH

Source of V	DF	SS	MS	F	P
Season	2	1.424	0.712	2.959	0.083
Station	4	3.087	0.772	3.207	0.043
Season x S	8	1.523	0.19	0.791	0.619
Residual	15	3.61	0.241		
Total	29	9.644	0.333		

Salinity

Source of V	DF	SS	MS	F	P
Season	2	2135.639	1067.819	30.339	<0.001
Station	4	457.608	114.402	3.25	0.042
Season x S	8	130.363	16.295	0.463	0.863
Residual	15	527.939	35.196		
Total	29	3251.549	112.12		

Dissolved NH_4 +

Source of V	DF	SS	MS	F	P
Season	2	476.297	238.149	0.845	0.449
Station	4	2811.352	702.838	2.494	0.087
Season x S	8	1984.798	248.1	0.88	0.554
Residual	15	4226.985	281.799		
Total	29	9499.432	327.567		

Dissolved $N0_2$

Source of V	DF	SS	MS	F	P
Season	2	22.443	11.222	0.811	0.463
Station	4	66.408	16.602	1.2	0.351
Season x S	8	76.303	9.538	0.689	0.696
Residual	15	207.58	13.839		
Total	29	372.735	12.853		

Dissolved PO_4^{3-}

Source of V	DF	SS	MS	F	P
Season	2	88.336	44.168	0.232	0.796
Station	4	1531.962	382.99	2.012	0.144
Season x S	8	1329.609	166.201	0.873	0.559
Residual	15	2855.924	190.395		
Total	29	5805.831	200.201		

Two Way Anova (Cont---)

Alkalinity

Source of V	DF	SS	MS	F	P
Season	2	22.895	11.447	5.599	0.015
Station	4	4.716	1.179	0.577	0.684
Season x S	8	10.86	1.358	0.664	0.715
Residual	15	30.666	2.044		
Total	29	69.136	2.384		

H_2S

Source of V	DF	SS	MS	F	P
Season	2	13.142	6.571	1.02	0.384
Station	4	24.911	6.228	0.967	0.454
Season x S	8	47.914	5.989	0.93	0.52
Residual	15	96.647	6.443		
Total	29	182.613	6.297		

Dissolved Oxygen

Source of V	DF	SS	MS	F	P
Season	2	2.934	1.467	0.36	0.703
Station	4	8.449	2.112	0.518	0.724
Season x S	8	25.902	3.238	0.795	0.616
Residual	15	61.119	4.075		
Total	29	98.404	3.393		

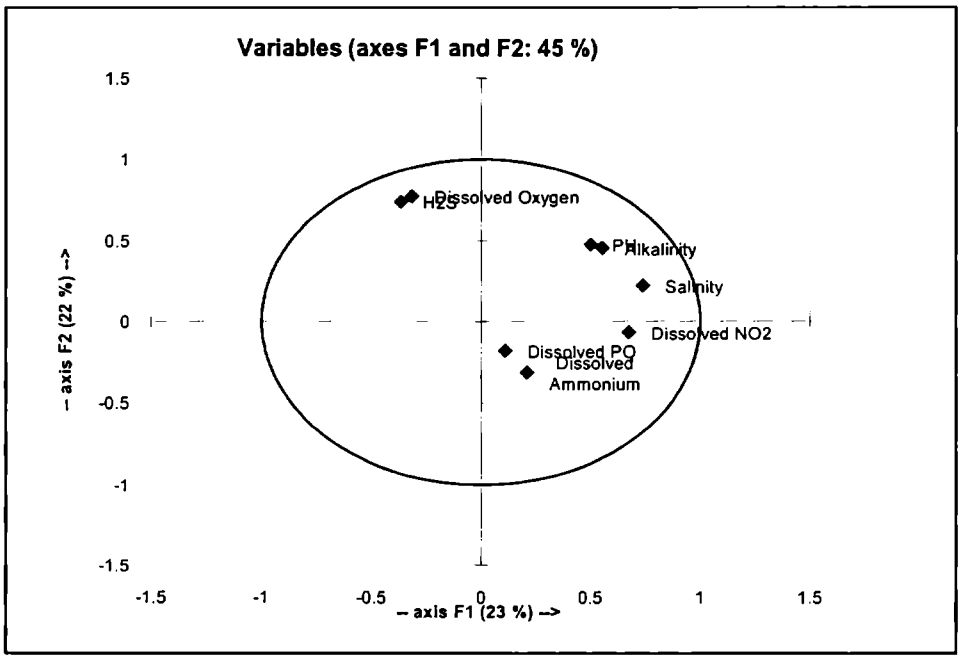
Means of Hydrography Parameters (Station wise)

Report									
Station		pH	Salinity	Dissolved NH_4^+	Dissolved NO2	Dissolved $PO4^{3-}$	Alkalinity	H2S	Dissolved Oxygen
	Mean	7.5	13.57	21.85	0.39	16.56	3.01	3.13	2.82
	Std. Deviation	0.58	11.71	12.53	0.34	11.36	1.87	2.58	2.25
	CV	7.78	86.32	57.36	87.2	68.57	61.97	82.59	79.79
1	Median	7.49	8.59	16.95	0.22	14.3	3.9	2.52	2.17
	Mean	7.78	14.4	31.33	0.5	13.18	2.46	5.04	3.13
	Std. Deviation	0.64	11.44	22.21	0.36	9.2	1.41	3.46	2.18
	CV	8.21	79.45	70.88	72.4	69.81	57.39	68.7	69.85
2	Median	7.61	13.42	29.04	0.44	12.28	2.57	3.55	2.62
	Mean	7.46	8.09	39.24	2.9	24.74	2.55	3.1	2.2
	Std. Deviation	0.46	8.31	19.17	2.52	17.25	1.45	1.17	1.1
	CV	6.17	102.83	48.85	86.86	69.71	56.85	37.94	50.27
3	Median	7.56	6.45	37.78	1.85	18.52	2.29	3	2.1
	Mean	8.36	20.17	15.77	3.97	16.75	2.17	4.29	1.61
	Std. Deviation	0.42	10.87	16.2	7.38	18.47	1.95	2.06	0.99
	CV	5.03	53.89	102.72	185.97	110.24	89.51	48.19	61.6
4	Median	8.17	17.89	13.01	1.34	12.15	2.23	4.57	1.28
	Mean	7.72	12.15	13.48	0.55	2.68	1.82	5.24	2.66
	Std. Deviation	0.42	10.17	7.58	0.44	1.59	1.23	2.69	2.44
	CV	5.41	83.73	56.21	79.22	59.43	67.39	51.36	92
5	Median	7.54	11.11	12.46	0.51	2.44	1.59	4.57	1.56
	Mean	7.76	13.67	24.34	1.66	14.78	2.41	4.16	2.48
	Std. Deviation	0.58	10.59	18.1	3.59	14.15	1.54	2.51	1.84
	CV	7.43	77.44	74.37	215.97	95.71	64.2	60.36	74.27
Total	Median	7.61	11.52	19.46	0.65	12.28	2.29	3.43	2.04

Means of Hydrography Parameters (Station wise)

Report									
Station		pH	Salinity	Dissolved NH_4^+	Dissolved NO2	Dissolved $PO4^{3-}$	Alkalinity	H2S	Dissolved Oxygen
1	Mean	7.5	13.57	21.85	0.39	16.56	3.01	3.13	2.82
	Std. Deviation	0.58	11.71	12.53	0.34	11.36	1.87	2.58	2.25
	CV	7.78	86.32	57.36	87.2	68.57	61.97	82.59	79.79
	Median	7.49	8.59	16.95	0.22	14.3	3.9	2.52	2.17
2	Mean	7.78	14.4	31.33	0.5	13.18	2.46	5.04	3.13
	Std. Deviation	0.64	11.44	22.21	0.36	9.2	1.41	3.46	2.18
	CV	8.21	79.45	70.88	72.4	69.81	57.39	68.7	69.85
	Median	7.61	13.42	29.04	0.44	12.28	2.57	3.55	2.62
3	Mean	7.46	8.09	39.24	2.9	24.74	2.55	3.1	2.2
	Std. Deviation	0.46	8.31	19.17	2.52	17.25	1.45	1.17	1.1
	CV	6.17	102.83	48.85	86.86	69.71	56.85	37.94	50.27
	Median	7.56	6.45	37.78	1.85	18.52	2.29	3	2.1
4	Mean	8.36	20.17	15.77	3.97	16.75	2.17	4.29	1.61
	Std. Deviation	0.42	10.87	16.2	7.38	18.47	1.95	2.06	0.99
	CV	5.03	53.89	102.72	185.97	110.24	89.51	48.19	61.6
	Median	8.17	17.89	13.01	1.34	12.15	2.23	4.57	1.28
5	Mean	7.72	12.15	13.48	0.55	2.68	1.82	5.24	2.66
	Std. Deviation	0.42	10.17	7.58	0.44	1.59	1.23	2.69	2.44
	CV	5.41	83.73	56.21	79.22	59.43	67.39	51.36	92
	Median	7.54	11.11	12.46	0.51	2.44	1.59	4.57	1.56
Total	Mean	7.76	13.67	24.34	1.66	14.78	2.41	4.16	2.48
	Std. Deviation	0.58	10.59	18.1	3.59	14.15	1.54	2.51	1.84
	CV	7.43	77.44	74.37	215.97	95.71	64.2	60.36	74.27
	Median	7.61	11.52	19.46	0.65	12.28	2.29	3.43	2.04

CLUSTER ANALYSIS



Chapter 4

Sedimentary Characteristics

4.1 Mangrove sediments – an over view

Mangrove ecosystems are one of the major types of natural wetlands in tropical and subtropical regions, flooded by fresh water as well as by salty water. Mangroves play an important role in the socio economic development of the regions where it is found. These include protection of shoreline against soil erosion, preventing siltation, thus saving shipping lanes and coral reefs, providing shelter to a variety of birds, reptiles, amphibians and fishes. They provide resources such as wood, medicine, honey, tannins and fodder. The quality and health of the ecosystem can be inferred from the richness and species diversity of benthic and in faunal organisms. Organic and inorganic contaminants reaching directly or indirectly the coastal waters are derived from both natural and anthropogenic sources. The coastal ecosystems potentially pose ecological risks to many marine organisms. Therefore, eco toxicological studies are needed for a better understanding of toxic effects induced by contaminants including metals (Kwok et al., 2008). Mangrove ecosystem has a number of characteristics not found else where. The ecosystem associated with mangroves has special adaptations to live in a salty and often anaerobic environment. These include specially designed root system for plants, salt exclusion mechanisms etc. In highly saline areas the mangroves will appear as patches with stunted vegetation, but in favourable environment, the canopy may reach up to a height of 30-40 meters, extending kilometers along the coastline in pristine and untouched environment. Forest structure and species diversity will vary from coast to coast. Coastal areas are under tremendous pressure arising out of enhanced anthropological activity. Mangroves are often at the receiving end of these inevitable processes, so and so that they are being destroyed for agriculture, tourism, aquaculture and various type of structural works.

Due to their proximity to industrial activity, persistent pollutants such as trace metals accumulate in mangrove sediments. Mangrove sediments can also filter trace metals and other pollutants before they enter the sea (Saifulla, 2002). The effectiveness of mangrove ecosystems to receive and retain pollutants is well documented. Chemical, physical and biological processes taking place within the sediments, which vary seasonally and geographically determine the effectiveness of the mangrove ecosystem as a pollution sink. Repeated re-suspension of contaminated fine grained sediments by river currents and wind generated waves in the bay, periodic channel dredging and passage of large maritime vessels are some of the processes that influence the deposition of toxicants. Sediments are also important carriers of trace metals in the hydrological cycle because the metals are partitioned between the surrounding water and the sediment. Mangrove sediments contain a greater amount of trace element than other shore line sediments, perhaps due to greater clay/silt fraction. Mangrove sediments are anaerobic, rich in organic matter and sulphides. Many mangrove ecosystems are close to urban developments. Biomarkers such as fatty acids and sterols allow the sources of organic matter to be identified (Perran, 2004). Higher percentage of organic content, mud and relatively higher total phosphorous and total nitrogen content were reflected in the greater height of vegetation and higher number of puematophores and seedlings (Zapata, 2004). Organic matter present in mangrove sediments undergoes microbial degradation which generally removes all oxygen from sediments below the surface layer. This creates ideal condition for bacterial sulfate reduction. At night when photosynthetic oxygen production ceases, H_2S diffuses from sediments to the overlying water precipitating the dissolved metals as sulphides. Because of this, the level of trace metal in sediments often reflects the quality of the aquatic system of mangroves. The presence of metal sulphides can identified by pink, blue-green and green mat of photosynthetic bacteria on the sediment surface. The sources and pathways of metals can be deduced from the chemical availability of metals in sediments. The weathering trends and the sources of

pollution can also be inferred from the geochemical characteristics of the sediments (Selvaraj, 2004).

The mangrove roots help in the trapping of particulate matter which involves the aggregation of cohesive particles (Wattayarkorn et al., 2000). The characteristic root system of Avecennia projecting as pnuematophores effectively traps floating detritus and hinders tidal flow so that the suspended mud and clay particles settle out. Mangrove roots can also influence the chemistry of mangrove sediments which in turn depend on the plant species. In avicennia dominant sediments, higher redox potential is observed than those dominated by Rhizopora. Oxygen transport by the roots of *Aviecennia* to below ground organs, followed by oxygen transfer to sediments is responsible for this. Mangrove vegetation also contributes to metal retention by physical stabilization of sediments and metal binding to rhizosphere sediments. The surface sediments of mangroves is enriched in nitrate and phosphorous by the fecal matter within mangrove area, as well as by the foliage decay. The abundance of N fixing *Azotobacter* spp and *Rhizobium* strains of bacteria which convert nitrogen to nitrate is responsible for the high nitrate content of mangrove sediments. Significant amounts of nutrients brought in by flood waters are also trapped by mangrove sediments (Lakshmi and Unni, 2002). Vertical sections of the sediment can give a record of the level of contamination over a period of time, provided that the pollutants are persistent and the sediment structure has not been disturbed by activities such as dredging. Increased sedimentation may influence the health, abundance and distribution of benthic animals leading to loss of mangrove habitats. Anoxia, changes in sediment geochemistry, grain size, variations in faunal movement, impacts on suspension feeders and primary productivity, due to enhanced turbidity may also result from sedimentation. Sedimentation can smother pnuematophores, causing death of vegetation. As the mud content increased, a decrease in species diversity and total vegetation density was observed (Thrush et al., 2003b). Taller, single stemmed trees were reported in newly formed sediments, while multi stemmed trees were reported

in older sediments. Sea level rise in mangrove dominated coasts may cause large flux of particulate matter to coastal areas due to enhanced sediment erosion (Zapata, 2004).

4.2. Total Organic Carbon

Mangroves are highly productive ecosystems fringing about 60-75% of the coastal areas of the tropics (Dittamar, 2001). About 1/3 of their production is represented by plant litter mainly in the form of leaves, branches, twigs and wood. Microalgae on the sediment surface, epiphytes on branches, lower trunks and prop root deposited phytoplankton and sea grass exported from the coastal zone outside the mangrove, all contribute to the benthic detritus pool of mangroves. Mangroves contain trees and plants of different physiology and hence the accumulation and degradation of organic matter will be markedly different. The bulk of the organic carbon storage of shelf sediments is in the mangal systems because of the woody materials. Mangrove sediments are generally made up of well sorted silt and clays with variable quantities of fine fibrous root matter and spongy wood material. Terregenous organic matter is heterogenous in nature composed consisting of soil and plant debris (Gorden et al., 2003), peats, as well as discharge of organic matter from anthropogenic sources (Meziane and Tsuchiya, 2002).

Due to slow decomposition, the residence time of the carbon in the mangals will be larger. During the first 10-14 days, of decomposition, about 30-50% of organic carbon is leached as dissolved organic carbon out of which the major fraction may be composed of tannins and other inhibitory phenolic compounds. About 60-90% of leachable fraction is mineralized and incorporated into microbial biomass environment (Chambers et al, 2000). It is a measure of organic matter preserved in sediments which can quantified by the total organic carbon. The amount of organic matter found in sediment is a function of the amount of various sources reaching the sediment surface and the rates at which different types of organic matter are degraded by microbial

processes during burial. The organic content of mangrove sediments is usually high with carbon contents typically varying from 2-15% dw. A major fraction of this is exported to adjacent waters and has a marked effect on the food webs in the coastal waters. Mangroves also similarly export a substantial amount of dissolved organic matter and particulate organic matter. During ebb, organic matter and nutrient rich pore waters flow from mangroves to the estuary due to transformation of terrestrial DOM to POM (Dittmar et al., 2001).

The extent of organic matter export from mangroves depends on factors such as tidal range, topography, sediment chemistry, community structure etc. The accumulation of organic carbon supports micro flora and meiobenthic and macrobenthic communities. Organic material settled in the sediments provides substrates for heterotrophic energy transformations and nutrient regeneration. The pathways of energy and nutrient flow through these benthic compartments are complex. Increased organic matter decomposition associated with nutrient loading could inhibit coupled nitrification – denitrification rates. Since mangrove leaves have a high content of lignin derived phenols, which leach out from leaves during early diagenesis, a high lignin content might be present in mangrove derived organic matter. Organic matter derived exclusively from marine primary producers does not contain lignin. The amount of organic carbon is important in soil classification and chemical characterization. Many soil bacteria utilize organic carbon as energy source. Soils whose organic carbon is > 6% and those rich in labile materials (i.e. reactive organic matter) are likely to exhibit greater microbiological activity than mineral soils. Organic matter such as humic acids and organic acids from root exudates are also thought to play an important role in the buffering capacity of soils. The ability of organic carbon especially humic compounds to adsorb trace metals through chelation is well documented. Inputs of organic carbon to estuaries can cause nutrient enrichment and enhance autochthonous production and increased heterotrophic activity leading to oxygen depletion (Vant et al., 1998). The amount of organic carbon present, along with the oxygen content also plays a role in

converting the soil to a highly anaerobic state. Total C and N in the top 40- cm of mangrove sediments is known to increase linearly with distance from the estuary (Chen& Twilly, 1999).

Results and discussion

The total organic carbon content varied between 0.1297 mg/g and 2. 423 mg/g among the different stations. Stations 1 and 2 maintained a consistent organic carbon value of 1.5 mg/g and above during all seasons. These stations had the highest mangrove cover among all the stations. Station 4 which had the least mangrove cover recorded low organic carbon values. This supports the observation that the organic carbon content of mangrove sediments is reported to be high and is dependent on litter fall and burial (Dittmar et al, 2001). All mangrove stations recorded a low organic carbon value in monsoon. The monsoon season was marked with heavy rainfall, river discharge and the flooded conditions are not favourable for the accumulation of organic matter (Anila Kumari, 2001). During the rainy season, the water table is high and the whole depth profile will be anoxic. The total amount of organic matter decreases due to lesser burial of organic materials. Lower rates of decomposition and greater flushing of organic matter during monsoon season will further reduce organic carbon accumulation in sediments. Highest organic matter content was observed at station 3 during post monsoon period. This may be due to the accumulation of bird droppings, sewage and foliage in station 3, which must have under gone decomposition leading to a higher sedimentary organic carbon value. Other factors responsible for accumulation of organic matter are heavy drainage with abundant organic matter, and high temp (25-30^{o}C). Also station 3 had a high % of clay fraction during post monsoon setting geomorphology conditions favouring organic carbon accumulation. Station 5, which is a non mangrove station with a higher sandy texture showed the least organic carbon content in monsoon. Sediment carbon and nutrient concentrations decreases with increasing grain size as organic matter adsorbs better onto mineral surfaces and has a high affinity for fine-grained sediment (Hedges et al, 1995). Variation in phytoplankton

productivity, species composition and size distribution will also alter the carbon cycling of the ecosystem (Riedel et al, 2003). The elevated organic carbon values at stations 1,2&3 during pre monsoon period is due to low rain fall, reduced river discharge and stagnant condition leading to a sharp rise in the organic carbon content. It may also be due to higher productivity due to the upwelling.

In total correlation and seasonal correlations, total organic carbon showed positive correlation with tannin and lignin, protein as well as exchangeable ammonium. In station wise correlations, at station 1, total organic carbon correlated with exchangeable ammonium; at station 2 it showed negative correlation with tannin and lignin and positive correlation with exchangeable ammonium, while at station 4 there is positive correlation between total organic carbon and tannin and lignin. Carbohydrates undergo rapid degradation at the sediment water interface in the young mangroves, or in the litter in the older ones. These carbohydrates may have been subjected to selective preservation by adsorption on to clay minerals. Conversely, lignin-derived phenols are usually more in mangrove sediments as a consequence of their rather refractory character. The negative correlation between total organic carbon and tannin and lignin reflects the loss of carbohydrate during the early stages of diagenesis leaving behind the tannin and lignin (Marchand et al., 2008). Tropical moist forests can vary considerably in their carbon stocks depending on the abundance of the large, densely wooded species that store the most carbon (Baker et al., 2004). The sediment organic matter pool is therefore mostly derived from a mixture of source materials as a result of the intense mixing by currents. Carbon sources in coastal areas are characterized by a large variability in their composition and degradability, ranging from labile sources such as phytoplankton and benthic microalgae to less degradable sources such as macrophyte material and terrestrial C transported by rivers. The identity and importance of the source materials that drive mineralization in sediments likely depends on a combination of their relative amounts and degradability. Bacterial mineralization can have a large

impact on the amount, composition, age and lability of organic matter and can be sustained both by aquatic primary production and by terrestrial C, prior to its export into the coastal zone or ocean (Boschker et al., 2005). TOC found in sediments is sorbed to the mineral, clay phase of the sediment, and it has been shown that this greatly reduces the availability for bacterial degradation. The availability of the organic matter is largely determined by the rate at which the sorbed substrates are released from the mineral phase. Higher levels of refractory organic carbon enhance nitrification rates. The recalcitrant fraction of organic carbon is considered to favor enhanced nitrification rates by reducing the utilization pressure on ammonium between heterotrophs and nitrifiers (Straus and Lamberti, 2000). Heterotrophic nitrification can control the nitrification process (Ahmad et al., 2008)which may be the reason for the positive correlation between total organic carbon and exchangeable ammonium. At stations 3 and 5 there exists a positive correlation between total organic carbon and protein. Plant-derived organic matter was better preserved under permanently anoxic environments. Soil organic matter decomposition was found to cause an increase in microbial products, including proteins (Fernando et al, 2009) must have lead to the positive correlation between protein and total organic carbon at stations 3 and 5. Two way Anova showed significant variations station wise with $P<0.001$.\

4.3 Tannins and Lignins

Tannins and lignins are aromatic polycyclic phenolic compounds, which accumulate in the sediments during the degradation of organic matter derived from plants. Tannins are polyphenols that occur only in vascular plant tissues such as leaves, needles, bark, heartwood, grasses, seeds, and flowers. They

are derived originally from monosaccaharides and are composed of poly hydroxy aromatic acids such as gallic and ellagic acid.as well as polyhydroxy flavanoid units. Tannins exist primarily in condensed and hydrolyzable forms. Condensed tannins consist of oligomers and polymers of flavanoid

compounds. Hydrolyzable tannins, on the other hand, are made up of sugars (primarily glucose) and gallic acid. These flavanoids are thought to provide protection against uv radiation and microbial attack (Killops and Killops, 2005). Tannins constitute up to 20% of the leaf tissue that is a major form of terrigenous organic matter cycling in these systems. Since tannins are a major component of leaf tissue and bark, they can have a significant impact on the bulk properties of organic mixtures, such as aromaticity, organic carbon:nitrogen ratios, phenolic OH, color, and reactivity Unlike carbohydrates, lipids, amino acids, and pigments—which are ubiquitous in organic matter and have both marine and terrestrial sources—tannins (along with lignin and cutin) are uniquely terrestrial. They act as chelators of metal ions present in sediments (Pautou, 2000). A tannin polymer (either condensed or hydrolyzable) has a plethora of hydroxy groups to form hydrogen-bond with proteins and amino acids and to complex with metals. Interestingly, a condensed tannin must be sufficiently large before significant protein complexation takes place—monomers, dimers, and other small oligomers apparently are not able to form enough cross-bridges to strongly complex with proteins. The ability to complex with proteins and amino acids leads to another geo chemically significant trait of tannin mentioned previously—inhibition of organic matter degradation. A high concentration of tannins and lignins in sediments is known to have a toxic effect on the heterotrophic microbial population, thereby reducing the productivity of the region. Their antimicrobial action is similar to that of quinines (Christian, 2003). Concentrations ranging from 325 to 3000 mg L^{-1} have been reported to be inhibitory to methanogenic bacteria. In addition to complexing bacterial exoenzymes and directly slowing degradation, tannin may also bind up the nitrogen source used by degraders for growth. Tannin control nitrogen release from litter and less effective organic matter degradation takes place when tannins are present and hence they are known as feeding deterrents

(Christian, 2003). The latter is of particular concern to forestry because of its impact on young trees in recent clear cuts and the overall decline in site

quality. Concentrations of 1-2% tannin have been shown to reduce the overall decomposition of organic materials applied to soil. This is due to low consumption by detritus feeder. Tannins make the plants less palatable to herbivores (Killops and Killops, 2005). They also inhibit seed germination and growth. At the right concentration, tannins are literally toxic to their environment (Rey et al, 2000). At 15 mg L^{-1}, tannins have been known to cause fish kills. In fresh water, tannins control the niches of crustaceans and mosquitoes (Patou, 2000). Because of tannin's redox and photochemical sensitivity, it may be possible to use tannins as an indicator of the environmental history of associated organic matter. For instance, tannins present in anoxic sediments may be able to tell us whether the sediments have been under constant or intermittent anoxia. Mangrove plants show high values for polyphenols, especially lignin derived phenols, indicating that they are store houses for phenolic compounds.

Lignin is a biopolymer made up of polyphenolic compound formed by condensation reactions between three main building blocks, namely coumaryl, coniferyl and sinapyl alcohols which are biosynthesized enzymatically from glucose. Lignin comprises 20 to 30% of vascular tissue. They are found abundantly in cell walls associated with hemi celluloses, forming a network around cellulose fibres in maturing xylem and play a supportive role to the woody core of terrestrial plants. The soil derived organic matter deposited in nature contains lower levels of recognizable biochemicals such as lignin. Lignins are broken down by lignin peroxidases which show non specificity, with their only substrate being H_2O_2. Lignin derived structures are highly photolabilie (Christian, 2003). Although fungi are important in the degradation of lignins, no lignin has been found in fungi (Killops and Killops, 2005). Organic matter derived exclusively from marine primary producers does not contain lignin (Dittmar et al, 2001). Low molecular size lignin moieties may initiate aggregation of aromatic rings to higher molecular weight humic substances (Haiber et al., 2001b). Lignin as the source of humic substance

precursors leads to high aromatic content in the humic substances (Christian, 2003). Deposition of reduced quantities of lignin in the soil leads to a consequent decrease in water colour (Seppa and Weckstrom, 1999). Lignins are useful biomarkers in the study about terrestrial organic carbon which is comprised of biological sources, relic forms of carbon such as coal, kerogen, and various other petroleum fractions (Ronald Benner, 2004). Microbial mineralization of terrestrial organic carbon is dependent on a number of factors such as pH, exposure to solar radiation, changes in redox potential of the system, photochemical transformations as well as physical reworking of sedimentary deposits. Lignin signatures can also be used to distinguish recently fixed terrestrial organic carbon from relic organic carbon.

Results and discussion

The tannin and lignin concentration of the sediments studied did not show any specific seasonal variation pattern. There was a lowering of tannin and lignin concentration in the month of August at all the mangrove stations. Water logging causes the soil to be under predominantly reducing conditions. Redox conditions of the soil control the precipitation and dissolution of a number of elements. This in turn affects the bioavailability of compounds (Olle Selinus, 2005). The highest value of tannin and lignin (14.24 mg/g) was found at station 3, in the month of June. Mangrove plants shed their leaves throughout the year and phenolics will be leached out from leaves during early diagenesis and thus a high lignin content might be present in mangrove derived organic matter. Effluents may also be a factor for increasing the phenolic concentration of mangrove swamps. Elevated concentrations of lignin may also be due to the delivery of coarse terrigenous material to region as well as contributions from lignin rich plant debris (Gordon & Goni, 2003). Coarse plant fragments such as woody debris contains higher levels of lignin than non- woody and soil derived organic matter (Goni & Thomas, 2000). The polysaccharide (i.e. cellulosic) components of lignocellulose are generally degraded about twice as fast as the lignin component, indicating that mangrove detritus becomes relatively enriched in lignin-derived carbon with

time. While cellulose and lignin can readily be degraded in oxic environments, these compounds are only degraded slowly under anoxic conditions. Lignin, for example, has a half-life of more than 150 yr in anoxic mangrove sediment (Dittamer and Lara, 2001). The burial and storage of old and refractory organic carbon in mangrove sediments can be observed visually as lignified and humified (spongy) litter fragments deep into the sediment. The lowest concentration of 0.182 mg/g was recorded at station 5 in the month of December. This may be due to the preferential degradation of tannin and lignin to other forms of carbon. Another reason may be due to hydrodynamic sorting, lignin poor fine particles such as soil derived fine clays may be mobilized to this area. There is also the possibility of a relatively moderate increase in $CaCO_3$ content which can be linked to lowering of tannin and lignin loadings in the sediments. Also when the organic matter is composed mainly of soil derived organic matter, it is characterised by lower lignin content (Gorden and Goni, 2004).

Tannin and lignin showed negative correlation with exchangeable ammonium at stations 1,2 and 3. Tannin content of mangrove leaves especially in *Rhizopora* leaves is high. Tannins will inhibit the growth of bacteria. As the tannin content of leaves decreases with time, the nitrogen content of leaves will increase (Gonsalez et al, 2006) which will be reflected in the sediment content also. With the lowering of tannin content, the activity of decomposing bacteria will increase. Stations 1, 2and 3 have higher silt and clay fractions. Higher the % of silt and clay, higher is the bacterial population and diversity (Sesstisch et al., 2001). With total organic carbon, tannin and lignin showed negative correlation at station 2 and positive correlation at station 4. The negative correlation between total organic carbon and tannin and lignin reflects the loss of carbohydrate during the early stages of organic matter diagenesis leaving behind the tannin and lignin (Marchand et al., 2005). Bacterial activity is responsible for most of the carbon recycling in mangrove

sediments. Mangrove tree root exudates fuel many bacterial activities in mangrove sediments. Spatial variations in bacterial populations were possible

related to several sediment conditions, including amount of clay, concentration of ammonium, and pH. Bacteria will probably only utilize a fraction of the TOC as their substrate as the various source materials are characterized by differences in degradability or accessibility. Carbon mineralization may be partially sustained by non-local sources also (Holmer et al., 2004). Mangrove sediments are in general relatively rich in organic carbon. Since most mangrove forests occur along sedimentary coastlines in large estuaries and deltas, large quantities of suspended organic carbon brought in by tides or rivers are deposited along with local input from mangrove detritus (Victor et al., 2004). All organic matter that is not exported by tidal action enters the sediment where it is consumed, degraded and chemically modified. The degradation of organic matter in mangrove sediments is mediated by both aerobic and anaerobic microbial processes using a variety of electron acceptors. A fraction of mangrove detritus escapes degradation and is permanently buried within the mangrove sediments or adjacent ecosystems. While some mangrove forests largely retain detritus within their sediments (i.e. as degradation or burial) a considerable fraction is exported.

The positive correlation between total organic carbon and tannin at station 4 shows that the organic matter remaining in sediments is composed of slow degrading materials. Mangrove detritus becomes relatively enriched in lignin-derived carbon with time (Marchand et al., 2005). While cellulose and lignin can readily be degraded in oxic environments, these compounds are only slowly degraded under anoxic conditions. Very high positive correlation exists between exchangeable ammonium and tannin and lignin at station 5. Sediments can trap organic matter from litter as well as from water flowing through it. The efficiency of sediment systems in trapping suspended material from the water column likely depends on a range of factors such as the

particle size, salinity, tidal pumping and the areal extent of the intertidal zone (Kitheka et al., 2002).The origin of the organic fraction in the water column is highly variable, and may include a mixture of marine or freshwater plankton terrestrial matter, litter and seagrass-derived material. Station 5 has sandy texture and poor canopy of trees. The trapping efficiency by root systems that retards forces of erosion seems to be a key factor in the burial process, which is absent here. In areas with slow sediment accretion, most of the organic matter is rapidly removed by tidal currents, eaten by crabs or degraded by aerobic microorganisms before any burial occurs. The accumulation of organic carbon and nutrients at this station will be low and this is reflected in the low amount of tannin and lignin as well as exchangeable ammonium at this station and this explains the positive correlation between the two parameters existing at the station. Two way anova showed significant variations station wise with $P<0.001$.

4.4 Exchangeable ammonium

Increased human population coupled with aquatic sewerage systems and the development of intensive agriculture and aqua culture have resulted in a significant change in the quantities of nutrients reaching the mangroves (Ayukai and Volanski, 2000; Trot and Alongi, 2000). Inputs from terrestrial run off (terrigeneous sediments) generally are considered the major nutrients source that support mangrove development. Mangrove sediments are a sink for dissolved inorganic N. Most of the inorganic N remained in sediments in the organic pool or was removed by plant uptake. In mangrove sediments the dissolved inorganic N is trapped in the first few centimeters of the sediment surface. Nitrogen existing in soils can be subdivided into organic and inorganic nitrogen. Organic nitrogen exists in a large variety of compounds such as proteins, amino acids etc in both living and non living things. The major form (99% or more) of total nitrogen in soils is bound up in organic form. Organic nitrogen accumulated in mangrove detritus from the water column via microbial activity. The breakdown of organic matter by heterotrophic organisms (mineralization) is the source of organic nitrogen which is often

very slow in anaerobic soils; so the total nitrogen level remains relatively constant with time. The inorganic forms i.e. $NH4^{+}$, NO_3^{-}, NO_2^{-} are the only forms that can be directly utilized by plants. N limitation may be an important process that controls the fate of inorganic nitrogen. The presence of litter in mangrove sediments establishes different nutritional constraints on N transformations in sediments. Nitrogen deficient leaf litters may help to serve as a mechanism for nutrient conservation. Nutrient concentrations of the soil appear to limit the growth production and species distribution of mangrove vegetation. The limiting nutrient may vary from one habitat to another (Kathiresan and Bingham, 2001). Nitrogen immobilization in sediments can eventually contribute to the burial of N in mangrove ecosystem. The nutrient cycling starts with the fall of leaves. Since a significant amount of litter is buried in the mangroves, nutrients immobilised by living vegetation are also incorporated into the sediments. The litter is colonized initially by fungi followed by bacteria. The breakdown and decomposition of mangrove litter is accelerated by the feeding activities of invertebrates such as crabs, shrimps and fishes. Microbes on decomposing litter itself accumulate significant amounts of nutrients from the flooding waters as well as those leached out from freshly fallen leaves. With litter burial these are also incorporated into the sediment. Recycling of organic materials by bacterial mineralisation and invertebrate excretion is an important mechanism supplying nutrients to estuarine and coastal ecosystems. Prolonged exposure to heavy nutrient input can reduce the capacity to trap nutrients permanently. The mangroves tolerate high levels of N and P (Trot and Alongi, 2000) and they utilize these to enhance tree production and the production of primary producers (Bouillon et al., 2002). Mangrove leaves decomposed faster in low latitudes, indicating atemperature dependence for decomposition. High nutrient loadings are known to lower oxygen content, water clarity, and affect consumer populations (Dauer, 2000) and potentially reduce the primary production of sediment.

Ammonium is a major component in the N loading to coastal areas. Nitrogen immobilization is mediated by microbial conversion of inorganic nitrogen

(NO_3^- and NO_2^-) into organic forms during decomposition of organic matter. Ammonium fuels nitrification. Strong competition also exists for available NH_4^+ among decomposers, plant roots and nitrifiers. Increased ammonium uptake may occur due to high rates of nitrification, increased plant uptake or sediment retention of ammonium (Stephan et al., 2001). Ammonium is also usually the dominant form of biologically available nitrogen in reduced, waterlogged marsh sediments as in most water logged soils; nitrite and nitrate are rapidly reduced to N_2 and are usually very low in concentration. Ammonium is therefore the only measurable amount of inorganic nitrogen. Ammonification results in the production of ammonia from the breakdown of organic nitrogen. This is performed by heterotrophs ranging in size from bacteria to fish. Nearly all organic nitrogen compounds are broken down via this pathway. As the primary excretory product of protein catabolism, ammonium accounts for most of the nitrogen excreted by invertebrates. Besides the ammonium originated from the decomposing organic matter, hydrolysis of urea is an important source of ammonium, especially when there is an inflow of domestic waters.

Ammonium volatilization in mangrove sediments could account for nitrogen losses of 10-20%. But in the pH range 6.5-8.2, the amount of volatilization may be insignificant. The uptake of nitrogen by sediments increased during seasons of high river discharge. Lignin probably does regulate nitrogen mineralisation either directly because it is a poor substrate or indirectly because it may render good substrates unavailable for use by microbes. Mangrove sediments removed NO_2^- and NH_4^+ from tidal waters throughout the year suggesting that these sources of inorganic N may support both direct and coupled denitrification in mangrove sediments. Soils with high C:N ratios tend to favor net immobilization of N during decomposition, while those with low C:N favors net mineralisation. Nitrification rates in mangrove sediments are low due to high concentration of tannins in pore waters, which can inhibit the growth and activity of nitrifying bacteria. Studies show that NH_4^+ was gradually immobilized in sediments and was not available for nitrification.

Some of the immobilized nitrogen in the early stages of litter decomposition may be recycled by ammonification and used in plant uptake (Riedel and Sanders, 2003). Nitrification of ammonium is also considered as a significant source of oxidized inorganic nitrogen in mangrove ecosystems which may fuel denitrification, leading to considerable loss of nitrogen. In anoxic Mn rich sediments, the nitrification was found to be insignificant. But in MnO_2 rich sediments NO_3^- was found, showing that ammonia was anoxically oxidised by MnO_2. In mangrove ecosystems the vegetation influence of nitrogen utilization is also noticed. These may include uptake of nutrients by trees, transformations of nutrients by epibiont communities on the submerged prop roots, as well as microbial processes carried out by them(Krista,2004).

Results and discussion

Nitrogen is mainly present as ammonium in sediments. Stations 1 to 3 showed increased values in pre monsoon and post monsoon. When water level was low ammonification value was high (Chen and Twiiley, 1999). When there is no over lying water present, there can be no dissolved output from the sediments resulting in an increased concentration of dissolved substances that have a source with in the sediments such as ammonium. High value for NH_4^+ indicated that most of inorganic N was dominated by NH_4^+ in sediments. The amount of ammonium in marsh sediments changes in response to the net effect of several processes such as microbial mineralisation, dissimilatory nitrate reduction to ammonium, microbial assimilation, nitrification, advection, diffusion, and plant uptake. Labile organic matter present in sediments will also be used up for denitrification (Mortimer et al., 2004)

The exchangeable ammonium was comparatively lower at stations 4and 5 during all seasons. Factors such as pH, temperature organic carbon and competition for ammonium can regulate nitrification (Krishanan and Bharati, 2009) and control the amount of ammonium present in sediments. The total organic carbon at stations 4and 5 were low during all seasons. The

ammonium absorptive capacity of sediments depends on its ion exchange capacity, which in turn depends on the organic matter and clay content of the sediment. Sediments at these stations also had lower clay content which justifies the observation. The low ammonium absorption in the mangrove sediments is due to competition with cations, especially iron. Fe (III) has higher affinity for binding sites than Fe (II). Organic coatings may block ion exchange sites on clay surfaces. Low ammonium absorption on sediments also coincided with high phosphate adsorption. Low pH values reduce the ammonium adsorption capacity. The studies carried out on mangrove sediments of the four stations showed that exchangeable ammonium was low in monsoon. During monsoon there is the possibility of more oxygen reaching the sediments due to mixing of oxygen rich water and unsettled nature of sediments. Ammonium regeneration in pore water during daytime leads to release of ammonium from sediments (Ziegler and Benner, 2000). Ammonium oxidation coupled to reduction of manganese occurs in anaerobic environments, which may also be the reason for low ammonium values (Deflandre et al., 2002).

At stations 1 and 2, there exists a positive correlation between exchangeable ammonium and total organic carbon and a negative correlation between exchangeable ammonium and tannin and lignin. The negative correlation existing between tannin and lignin and exchangeable ammonium at station 3 was very high. Station 4 showed no correlation with exchangeable ammonium, while station 5 had a high positive correlation. The above observations may be understood from the following explanation. Aerobic and anaerobic microbial respiration processes oxidize most of the organic carbon produced or deposited in mangrove sediments. Aerobic respiration occurs near the sediment surface, around crab burrows and along oxic root surfaces. Nitrogen fixation is a major bacterial activity in mangroves (Rojas et al., 2001). Nitrification of organic matter serves as a significant link between nitrogen mineralization. Nitrification also depends on NH_4^+ regeneration rates, which in turn is positively influenced by temperature. The presence of organic carbon

compounds may diminish the rate and the yield of nitrate formed, by diverting nitrogen from the nitrifiers to the heterotrophs proliferating at the expense of easily assimilable carbon but this depends mainly on the magnitude of C: N ratio and the quality of organic compound (Straus and Lamberti,2000). There is a close relationship between heterotophic microorganisms, nutrients, trees and marine organisms that control the mechanisms of nutrient recycling in mangroves. This recycling preserves most of the necessary nutrients for the natural sustainability of these ecosystems (Holguin et al, 2001). Tannins which are abundant in mangrove environment have a strong affinity to soils (Kaal et al, 2005) and have protein-binding ability, influencing nitrogen dynamics in ecosystems. Tannin–protein complexes have been shown to be recalcitrant to microbial degradation (Kraus et al, 2003). But tannins undergo structural modifications during degradation of foliage, accompanied by a decrease in the protein binding capacity (Maie et al 2003). Insoluble tannin–protein complexes degrade slowly under exposure to sunlight, releasing previously bound proteins into the aquatic environment. Therefore, the tannin–protein complexes may serve as a long-lasting source of N in such ecosystems sychronising the supply of N and its uptake by mangroves. Microbial fixation of nutrients on degrading plant residue will also contribute to maintain N in mangrove forests (Tremblay and Benner, 2006).

4.5. Proteins

Mangroves are highly productive marine ecosystems where bacteria actively participate in bio mineralisation of organic matter and bio transformations of minerals. Soil organic matter decomposition will cause an increase in microbial products including proteins (Ferreira, 2009). Sugars and proteins are generally believed to be susceptible to microbial degradation and thus can be quickly incorporated into food webs. Mangrove leaves and wood are degraded primarily by a large variety of microorganisms and later by higher organisms (Holguin et al, 2001). The detritus of mangroves is rich in proteins. Enzymatic activity is a key step in the degradation of high molecular weight

organic matter. Most these activities are believed to be carried out by bacteria, thereby playing a crucial role in the nutrient dynamics and energy flow of the ecosystem. Tree exudates can fuel the bacterial activity and soil particle size influence the bacterial biomass and structure of the bacterial community. Soils composed mainly of clay and fine silt particles showed a greater diversity of bacteria than those with larger particles (Sessitsch et al., 2001). Nutrients in sediments also contributed to the variability and distribution of bacteria. Bacterial concentration is known to increase in the wet season than in the dry season perhaps due to the increase in dissolved oxygen. But oxygen production by algae and microalgae in waters might increase the bacterial population in warm season. The heterotrophic community of mangroves contains a large population of nitrogen fixing bacteria which might be suppressed because of oxygen produced. Another group of organisms called protists which are known to be present in mangrove environment also play an important role in the decomposition of organic matter. They pervade various solid substrates and have been isolated from mangrove leaves and aid in the decomposition process by secreting many extra cellular enzymes. Peptide degrading enzymes leucine and valine aryl amidase were isolated from many strains of these organisms and the exo enzymatic activities of amino peptidase accounted for more than 30% of the total enzymatic activity (Raghu Kumar, 2002). In sediments a large portion of organic matter available for microbial decomposition occurs as polymers including proteins. The origin of proteins can be due to massive macrophytic production, the microfloral community through lysis, as well as extra cellular enzymatic activity, proteinaceous releases by macrophytic rooting tissues, and epipelic algal populations. The contributions of each of these may vary seasonally. The protein existing in sediments can also represent a significant source of nitrogen for microflora. The utilization of protein by the micro flora represents a recycling of nitrogen by exploitation of nitrogen sources not directly available to the plant community. The protein degradation is light dependent and also related to algal mat on the sediment surface. Proteolytic

activity is reported to support the amino acid degrading population not directly involved in the proteolytic processes.

The long term survival of labile proteins in mangrove sediments may result from their interaction with refractory organic matter present in sediments. Interaction of proteinaceous materials with humic substances via physical adsorption on its surface, entrapment within its 3-D structure and chemical bonding can help preserve proteins in sediments for long periods of time (Zang et al, 2000). The highly branched structure of humic acids will help the proteinaceous material encapsulated in its structure to be resistant to chemical hydrolysis (Riboulleau et al, 2002). Polymers such as tannin which are are mostly water-soluble and highly reactive, exhibit protein-binding ability, influencing nitrogen dynamics in ecosystems. Tannins form microbially recalcitrant complexes with proteins (Kraus et al. 2003). However, (Maie et al, 2008) showed that the molecular structure of tannins was modified during degradation of foliage, accompanied by a decrease in the protein binding capacity. For this reason, it could be expected that bio labile proteins can be re-released into the water column through the digenetic alteration of insoluble tannin–protein complexes. Proteins were released gradually from tannin–protein complexes incubated under light conditions but not under dark conditions, indicating a potentially buffering role of tannin–protein complexes on dissolved organic nitrogen recycling in mangrove estuaries.

Results and discussion

Sediments contain a mixture of proteins and peptides at various states of degradation (Keil et al, 2001). At station 1 the protein content varied between 2.778 and 19.3 mg/g, at station 2 it varied between 8.59 and 17.29 mg/g. At station 3 the variation was between 6.56 and 15.73 mg/g while at station 4 it was 0.028 and 1.066 mg/g while at station 5 it was between 0.015 and 0.322 mg/g. During pre monsoon the protein content varied between 0.023 and 19.3 mg/g, during monsoon the variation was between 0.015 and 15.68 mg/g, and during post monsoon it was between 0.028 and 15.73 mg/g. There was a

lowering of protein content at the onset of monsoon at stations 1,3, 4 and 5, while at station 2 there was an increase. The protein content showed an increase in with rise in temperature. The organic rich sediments accumulated high amount of proteins in non monsoon months. Bacterial communities play a pivotal role in the bio mineralization of organic matter in sediments (Holguin et al, 2001). The spatial distribution of microorganisms in a silty-loam soil was determined mainly by the placement of clay and organic carbon. Soil organic matter decomposition will cause an increase in microbial products including proteins (Ferreira, 2009). Stations 4 and 5 which had less foliage showed low protein content. Protein correlated with tannin and lignin, total organic carbon and exchangeable ammonium during pre monsoon and post monsoon seasons. During monsoon it correlated only with total organic carbon. The mean of protein during pre monsoon was 8.29 mg/g, for monsoon 5.34 mg/g and during post monsoon 5.27 mg/g. The mean of protein at station 1 was 9.10, at station 2, 12.51, at station 3, 9.33, at station 4, 0.44 and at station 5, 0.12 mg/g. In cluster analysis protein formed a cluster with tannin and lignin and total organic carbon. Two way anova showed significant variations of protein for stations with $P<0.001$ for total correlation data.

4.6 Trace metals

Metal accumulation in sediments is of great concern all over the world as it travels along the food chain and is detected in the various tissues of consumable species (Ozturk et al., 2009). Mangrove ecosystems can act as sinks for anthropogenic contaminants. Mangrove sediments are anaerobic, reduced, rich in sulphides and organic matter (Lindsey and James, 2005). Due to these inherent physical and chemical properties, mangrove sediments have an affinity to immobilize heavy metals within their anaerobic sediments. The occurrence of heavy metals in mangrove sediments is observed all over the world (Tam and Wong, 2000). Heavy metals are natural constituents of rocks and soil and enter the environment as a consequence of weathering and erosion. They are among the most serious pollutants within the natural

environment due to their toxicity, persistence and accumulation (Mac Farlane, 2000). Anthropogenic activity frequently results in elevated local metal concentration even where dispersal is rapid and local contamination is normally evident. Metals associated with fine atmospheric particles (<2.5um) may remain aloft for several months, traveling considerable distances. Such emission from the industrial centers of the developed world has contaminated even the Polar Regions.

Metal concentrations present in polar ice profiles correlate with past industrial activity. Many metals are biologically essential but all have the potential to be toxic above certain threshold concentration. Following industrialization, unnatural quantities of trace metals particularly metals such as Pb, As, Cd, Cu, Hg, Ni, Zn etc have been released into the environment. Mangrove ecosystems are often subject to anthropogenic impacts especially metal pollution due to their proximity to urban development. Urban and industrial run-offs, untreated domestic sewage, storm water, road run off, inputs from shipping and agricultural activities are some of the sources causing metal pollution in mangrove sediments. Studies have shown that mangrove forests maintain their sediment metal load predominantly under forms with a low potential for biotic uptake (Machado and Silva, 2002). Temporal and spatial patterns of nutrient and trace element loadings are complex and bioavailability and toxicity of metals are affected by geochemical as well as anthropogenic activities (Riedel et al., 2000). Also, potential interactions among stressors such as nutrients and trace metals can affect the food web of the system. Contaminants such as trace metals can alter productivity and species compositions of primary producers. The chemical states of heavy metals and their bio availabilities are strongly dependent on environmental factors such as pH, salinity, temperature, redox potential etc (Miramand, 2001, David and Johanna, 2000). Trace metals may mimic nutrients thus producing competition for uptake and utilization of macronutrients. Trace element limitation or interference by a second trace element may cause poor utilization of macronutrients. Trace element enrichment may alter phytoplankton community with altered trace element requirement and sensitivity than the

original group. Alterations of phytoplankton communities can affect higher tropic levels which graze upon them and recycle trace elements (Riedel and Sanders, 2003). Nutrient enrichment is known to reduce dissolved trace elements and enhance the concentration of sedimentary trace metals.

Once introduced into the marine environment, trace metals have the potential to affect sediment nutrient cycling, cell growth, regeneration, reproductive cycles, photosynthetic potential and behaviour of marine organisms (David and Johanna, 2000). Kidney and liver of marine organisms are known to contain the highest concentration of metals. Microbial biomass and enzyme activities decrease with heavy metal pollution (Yim and Tam, 1999). The mobility and bioavailability of metals present in soils depend on the physico-chemical properties of both the metal and the soil. In comparison to sandy soils, soils which have high organic and clay mineral contents are able to accumulate large quantities of metals due to an abundance of soil matrix of cation exchange surfaces and organic ligands capable of complexing with metal ions. The extent and nature of the organic fraction is strongly influenced by the activity of soil microorganisms. In unpolluted soil ecosystems these organisms typically account for more than 90% of chemical decomposition of organic matter. When the activity of microorganisms is disrupted the ability of soils to accumulate and retain metals will be affected. A reduction in the rate of decomposition will reduce organic matter accumulated in soil surface, increasing the number of potential metal binding sites. However a reduction in the microbial biomass in soil matrix increases the mobility of metals previously accumulated within and adsorbed onto the surfaces of soil microorganisms. Bacterial activity within soils and aquatic sediments is capable of affecting mobility of metals directly via bio transformation and indirectly by generating localized gradients. The ability of certain bacteria to methylate metals is of particular importance, given the greater toxicity and bioavailability of such compounds. For example: the uptake and accumulation of Hg by bean plants was increased by a factor of ten when methyl mercury was supplied in place of inorganic Hg. The high toxicity associated with alkyl

metal compounds is partly accounted for the ease with which they are taken up and accumulated in the biota.

Since the metals present in the soil solutions and easily extractable fraction are most available to plants, factors increasing the concentration of metals in these phases will greatly increase their bioavailability. The grain size, organic carbon content as well as diagenetic history can be important in influencing trace metal concentration and bio availability. These profiles are also important in influencing trace metal concentration in sediment depth profiles. Because of the relationship between metal mobility and pH, residence times for metals in calcareous soils exceed those associated with acidic soils. Mangrove sediments are known to concentrate heavy metals 3 to 5 times the magnitude of that present in the overlying waters. The trace metal content of sediments is often to a large extent a function of its biochemical and mineralogical characteristics. These metals are mainly held in mineral lattices and particle surfaces. Knowledge about concentrations and partitioning of trace metals in inter tidal sediments will enhance our understanding of bio accumulation and biological effects of trace metals in inter tidal environments. Filter feeders and burrowing organisms are particularly at risk from sediment bound trace metals.

Trace metals can be transferred from soils and accumulated in mangrove plant tissues which can cause long term damaging effects on plants (Lindsey and James, 2005). Bio magnification with trophic levels along food chains can also occur. The concentration of trace metals is found to be highest in summer suggesting that these values may be closely related to increase in bacterial activity during summer than an increase in anthropogenic output. Trace metals are known to be associated with a variety of forms of organic matter, namely living organisms, organic detritus and organic coatings on mineral grains. The complexation of metals with humic and fulvic acids is well recognized. The bioavailability and hence toxicity of metals may be affected by the presence of these chelating ligands (Killops and Killops,

2005). The formation of metal organic complexes can detoxify metals such as Cu and Pb. However the formation of lipophylic organometallic complexes can increase the uptake and toxicity of the metals. The stability of metal complexes formed with these organic substances has been established in a number of experimental and ranked in the following order, i.e.Cr> Fe> Al> Pb> Cu> Ni> Cd> Zn> Mn> Ca> Mg. The formation of stable organic complexes can have effects on the chemical behaviour of the metal, preventing the formation of insoluble precipitated complexes and increasing the potential mobility of the metal, which ay be leached out of down the soil profile. Since the metals present in the soil solutions and easily extractable fraction are most available to plants, factors increasing the concentration of metals in these phases will greatly increase their bioavailability. The burden of heavy metals is now a serious environmental concern (Cochen et al., 2001). Geochemical fractions such as Fe, Co, Cr, Cu, Mn, Ni, Pd and Zn were detected in the coastal sediments of central south-west coast of India, in and around Cochin, the second biggest city along the west coast of India (Balachandran et al., 2003). Concentration of dissolved and particulate trace metals and their partitioning behavior between the dissolved and particulate phases in southern upstream part of the Cochin estuarine system were studied (Unnikrishnan and Nair, 2004).The research work presented here shows the level of contamination in the sediments of mangroves around Cochin. As the mangrove habitats are of great ecological value in terms of nutrient regeneration, primary production, habitats for fish and birds (Cacodor and Vale, 2001), it is vital to know their level of contamination as it has an impact on the living organisms of the area. The variations of the following metals were studied. The results and discussions of the findings are given below.

4.6.1 Iron

Iron is the most useful metal of material civilization. It is an essential trace element required by both animals and plants. It is essential to oxygen transportation of the blood of all vertebrates and some invertebrates, in

addition to electron transport and substrate oxidation and reduction. Iron is an essential component of several cofactors including haemoglobin and the cytochromes. In biological systems, the oxidation states of iron are primarily limited to +2, +4 and +4(ferryl) states. The primary oxidation states of iron are Fe^{2+} and Fe^{3+}. Under anoxic conditions Fe^{2+} state predominates. Nature controls the reactivity of iron by exploiting the oxidation state, redox potential, and electron spin state of iron (Beard, 2001). Lacto ferrin an iron binding protein, has the ability to inhibit bacterial growth and viral infections by functioning as an immune modulator for activating the defense system of the host(Kruzel and Zimecki, 2002). Iron if present as a free ion might be detrimental to cells (Kehres and Maguire, 2003). Iron activated enzymes such as heme oxygenase is required for diverse processes such as cellular signaling, in mammals, acquisition of iron by bacterial pathogens and synthesis of light harvesting pigments in cyano bacteria(Wilks,2002). Transcription is the preferred process by which plants and lower eukaryotes maintain iron homeostasis. Iron is also essential for translation of messenger RNA of iron regulatory proteins required to maintain iron homeostasis as well as the uptake, storage and usage of iron by cells (Eisenstein, 2000). Ferretins, the iron storage proteins found in bacterial, plant and animal cells is controlled by the level of iron in the cell(Andrews, 2003). Clinical symptoms of iron toxicity include hepatic, cirrhosis, diabetes, heart failure, arthritis and sexual dysfunction (Olle, 2005).

Total environmental flux of iron is enormous. Its principle use is to alloy it with carbon, in the production of steel and cast iron. Since iron is the fourth most abundant element in the earth's crust, natural weathering accounts for a large amount of iron present in the environment. Iron readily complexes with sulphates in sediments. This is of considerable significance because other elements are likely to be adsorbed by the resulting complex. In anoxic sediments iron is predominantly associated with organic sulphides. In reduced sulphidic sediments oxy hydroxides of iron and manganese dissolved permitting arsenic, copper and zinc sulphides to precipitate. The proportion of Fe-Mn hydrous oxides is highly variable and depends on water depth and

redox reactions within the sediments. Since iron plays such an important role in the fate of trace metals and nutrients, a breach in the iron redox cycle may ultimately lead to the mobilization of toxic agents in the environment. Although it is of little direct toxicological significance, it often controls the concentration of other elements and also has the potential to reduce the toxic effects of other metals. Iron is known to enhance the concentration of iodine in soils and Fe^{3+} ions are reported to oxidize iodine under acidic and alkaline conditions (Olle, 2005). Because iron is found in such high concentrations in the environment, it is also plentiful in freshwater marine plants. Fe^{3+} is moderately toxic to many species of aquatic plants. Iron precipitates are periodically deposited on the bottom of lakes and rivers. These agents especially $Fe(OH)_3$ and Fe_2O_3 then form gels and flocs that can suffocate benthic organisms and any planktonic species with gills. This treatment may occur near industries with poor waste treatment facilities.

Results and discussion

The mangrove sediments of Cochin appear to act as a sink for iron during all seasons. It varied between 10ppm and 397ppm. Higher accumulation of Fe was observed during pre monsoon, while the values in the monsoon and post monsoon were lower and was in agreement with observations else where(Krishnan et al.,2007). The maximum Fe concentration was recorded at station 2 during the post monsoon season and the minimum at station 4 during the monsoon season. Stations 1 and 2 recorded high values for Fe during all seasons while stations 4 and 5 showed the reverse trend. Station 3 showed a considerable lowering of iron concentration in monsoon. In fact there was a lowering of Fe concentrations at all stations during monsoon. This may be due to the low residence time of water as well as dissolved organic matter in the stations leading to poor mineralization and accumulation of Fe in sediments. Processses such as bio turbation, re-suspension and erosion are known to affect the metal concentrations in sediments(Belluci etal,2002). Similarly all stations except station 2 had the highest Fe concentration during pre monsoon. This is because organic matter in the mangrove ecosystems

may be remineralised microbially and bound organically in the mangroves itself by primary and secondary producers, thus becoming sedimented in mangroves during post monsoon season. The degradation of organic matter in sediments is mediated by both aerobic and anaerobic processes using a variety of electron acceptors (Bouillon et al, 2007a). Station 2 had the highest Fe concentration during post monsoon. During post monsoon increase in H_2S concentration and a lowering of dissolved oxygen favoring anaerobic conditions was also observed at station 2. In oxygen depleted zones Fe(III) becomes the main electron acceptor for microbial respiration and reduction of Fe(III) is observed. In anaerobic environments sulphate reduction produces dissolved sulphide which can then react with the dissolved Fe^{2+} as well as the Fe(II) produced from Fe(III) precipitating FeS, which becomes incorporated in the sediments. The lowering of pH at station 2 during post monsoon supports the reduction of sulphate. Station 5 had low iron concentration during all season. This may be due to the sandy nature of station 5. The concentration of Fe and Mn showed inverse relationship but the variation in the concentration of iron and the concentration of manganese seem to follow a similar pattern showing a mutual correlation between iron and manganese concentration in sediments. The mobility and availability of metals in a floodplain soil can be significantly reduced by the formation of metal sulphide precipitates which is initiated by microbial sulphate reduction, at quite low redox potentials (Mansfeldt, 2004). The degradation of organic matter and the transformation of Fe hydroxides to Fe sulphides and siderite ($FeCO_3$) in the anoxic layer also causes a reduction in the total adsorption capacity of the solid sediment phase for trace metals.

In total correlation, Fe shows high correlation with Mn, Ni and Cu. Both Fe and Mn are redox sensitive metals and are involved in the electron exchange reactions of the environment. Diagenetic behavior similarities possibly contributed to a correlation between Fe and Mn. Fe/Mn oxides and hydroxides are able to trap metals such as, Cu, Ni, and Zn and along with organic matter and clay minerals by acting as an important sorbing phase for trace metals such as Ni, Cu and Zn (Naylor *et al.*, 2006). The stability of Fe

and Mn oxides and hydroxides are largely dependent on soil pH and redox conditions. Micro organisms may act as catalysts to bring about redox changes in metals such as Fe, Mn and Cu , which in turn will bring about a change in redox potential of the sediment (Simpson et al,2000). Increase in redox potential of the sediment will increase the affinity between Fe and Mn oxides and metals such as Zn, Pb as well as Ni (Kashem and Singh, 2001). The behavior of Ni was found to be closely related to the behavior of Fe and Mn(Du Liang et al,2007 b). The formation and re-oxidation of sulphides is also an important factor that controls the overall metal concentration in inter tidal sediments. Considering the season wise correlation, in pre-monsoon Fe correlates negatively with sand and positively with clay. This indicates that the amount of Fe present is dependent on the clay fraction in pre-monsoon. Iron correlates with all metals except Cd in pre- monsoon. The correlation of Fe with all other metals other than Cd is supported by the fact that all the metals except Cd form a cluster with Fe. In pre-monsoon, ascending salinity promotes Cd desorption from sediments (Du Laing et al. 2002). Solubility of metals such as Cd increases with increase in salinity to the reduction in the binding between metals and humic acids. Cd uptake from water also decreases with increase in salinity. The low concentration of Cd in mangrove sediments sediments during pre- monsoon may be due to these facts.

In monsoon, iron correlates negatively with sand, and positively with silt. This shows that in monsoon concentration of silt is the determining factor for Fe accumulation in sedments. This may be true because monsoon flow of water carries a large amount of silt from riverine discharge. Very high correlations exist between Fe and Mn, Zn and Ni. Cu also shows good correlation with Fe. In monsoon when water flow increases, the sediment will be exposed to more oxic conditions due to its unsettled nature arising out of re-suspension due to more turbulent flow conditions. The aqueous medium showed an alkaline pH in monsoon. In the oxic environment the FeS and MnS are oxidized. The metals adsorbed or co-precipitated on Fe and Mn sulphides under these conditions are rapidly oxidised, due to their relative solubility in oxic conditions (Caetano et al., 2002). A general decrease in metal concentration with the

lowering of Fe concentration was displayed by sediments in monsoon. In post –monsoon Fe shows negative correlation with silt and positive correlation with clay. Similarly it correlates extremely well with Mn and Cu as well as with Ni. In post monsoon the percentage of clay increased at all stations. In post monsoon there will be flooding coupled with reduced flow rates which will favour the accumulation of fine grained sediments and organic matter (Rinklebe, 2005). Fe/ Mn hydroxides along with organic matter and clay minerals can provide an important sorbing phase for trace metals such as Ni and Cu. There is an increase in Fe concentration during post-monsoon, which is the trend followed by metal such as Mn, Ni and Cu also, which results in good correlation between Fe and these metals. Anova showed significant stationwise variations in Fe concentrations with $P<0.001$.

4.6.2 Manganese

Most of the manganese reaching the oceans are from natural sources. Anthropogenic discharges are relatively small. The major anthropogenic sources are coal burning and incineration of municipal wastes. Processing of iron ores containing significant amounts of manganese constitute a major source of manganese. Manganese is an essential micro nutrient for plants and animals as it forms part of several important enzyme systems involved in protein and energy metabolism and in muco polysaccharide formation. In higher plants and algae, a cluster of Mn^{2+} ions is involved in the oxygenic photosynthesis where water is oxidized (Barber, 2003). The major pathway for manganese excretion from the body is through bile. The Mn^{2+} and Mn^{4+}states are the most important ones in the aqueous systems. Manganese is relatively nontoxic and often ameliorates the hazards posed by other metals owing to competition for uptake or binding sites. Mn^{2+}acts by saturating extracellular metal binding sites thereby restricting sorption by other metals. Its deficiency in humans has been implicated with several diseases like diabetes, rheumatoid arthritis, nervous instability, convulsions, disorders of behavior and growth in infants, and children. The major concerns about manganese in drinking water are its objectionable taste and its capacity to stain plumbing

and laundry. The high reduction potential of Mn^{2+} enables the cells to tolerate very high cytoplasmic concentrations of free Mn^{2+} (Kehres & Maguire,2003). Although oral absorption of manganese in the diet is slow and incomplete, inhaled manganese is rapidly absorbed through the lungs. It is a systematic poison when inhaled in excess amounts. Chronic manganese poisoning (manganism) leads to psychiatric disorders characterized by irritability, difficulty in walking, speech disturbances and compulsive behavior including running, fighting and singing. If the condition persists, a Parkinson like disease will develop. In countries where manganese carbonyl compounds are used as antiknock agents, Parkinson's disease may develop due to the neuro toxicity of manganese observed in such patients (Olle, 2005). Liver cirrhosis is also frequently observed. Victims of manganese poisoning tend to recover slowly, even when removed from exposure. The redox cycle is the most important factor that controls the fate of manganese in water columns. The oxygen concentration in water sediment interface often approached zero especially during summer which causes the reduction of Mn^{4+} to Mn^{2+} which being soluble is then transported upwards in the water column. The oxygenated water results in the re oxidation of Mn^{2+} to Mn^{4+} which then settles to the bottom and the cycle gets repeated again.

Results and discussion

Mn shows a dynamic behavior in mangrove sediments (Gueiros, 2003). The concentration of manganese at all stations was akin to variations in Fe concentrations. This shows that there is a close relationship between the concentrations of these two metals in the environment. Both these metals can undergo redox transformations easily. The redox processes takes place mostly due to abiotic processes. These metals are important in the carbon cycling and controlling redox conditions of the environment. The concentration of Mn varied between 0.22 and 1.56ppm at the different stations. All the stations except station 2 showed a decrease in Mn concentration during monsoon. Mn showed highest concentration at all stations during post monsoon. Enhanced metal concentration in the

sediments is localized and usually accompanied by marked enrichment in organic C, Kjeldahl N and humic acids. The concentration of Mn is influenced by the concentration of Mn oxide in sediments (Naylor et al, 2006). The availability of metals is dependent on the clay content and organic matter of the soil, with the metal content increasing with lowering of clay content (Rosselli et al, 2003). The clay content at all stations was high during post monsoon. In post monsoon metal concentration followed the order Cu > Fe>Mn> Zn> Ni> Cd> Pb. Mn oxide is required to oxide FeS in anaerobic sediments (Schippers & Jorgensen, 2001). The depletion in Mn during monsoon at stations 3, 4 and 5 may be due to the bacterial decomposition of organic matter using Mn oxide as oxidant. It may also be due to greater translocation of Mn to mangrove plant parts as Mn that decreased in the roots with simultaneous increase in leaves (Valerie and Feller,2005).

In total correlation Mn showed high correlation with Fe, Ni and Cu. During pre-monsoon, Mn shows positive correlation with sand and positive correlation with clay, Fe, Ni, Pb and Cu. During monsoon, negative correlation exists between Mn and sand, while high positive correlation exists between Mn and silt, Fe, Zn, Ni and Cu In post- monsoon, negative correlation exists between silt and Mn, while positive correlation exists between Mn and clay, Fe, Ni and Cu. Analysing the station wise correlation, at station 1, positive correlation exists between sand Cu and Mn , while clay, Zn, Pb and Cd showed negative correlation with Mn. Station 2 exhibited the same correlation pattern between Mn and sand, Zn as well as Cd as shown by station 1. At station 3, clay and Cd correlated negatively with Mn, but metals such as Fe, Zn, Ni, Pb and Cu as well as sand correlated positively. In station 4, clay and sand showed negative correlation with Mn whereas metals such as Fe, Zn, Ni and Cd correlated positively with the last one showing very high correlation. At station 5, Mn correlated positively with silt, Fe, Zn, Ni, Pb and Cu.

The general trend in station wise correlations was that, at stations 3, 4 and 5, Mn showed positive correlation with the metals Fe, Zn and Ni. Stations 3,4 and 5 are close to boating activity. The antifouling paints which are used in

boats must have contributed to the deposition of Zn in these sediments (Nimisha and Turner, 2009). Affinity between Fe and Mn oxides and Zn will increase with increasing sediment redox potential. The behavior of Ni was found to be closely related to the behavior of Fe and Mn. At stations 1 and 2, Mn showed negative correlation with Zn. This may be due to the oxidation of brackish sediments under acidic or near neutral pH which causes dissolution of Zn but not Mn. Short periods of air exposure followed by renewal of overlying water will also result in a large increase in the Zn flux from the sediments(Simpson et al,2002). Cd correlated negatively with Mn at stations 1 and 3. This may be because of weak pyratisation of Cd compared to Mn at these stations. Similarly Mn showed positive correlations with Cu at stations 1, 3 and 5. CuS bound to FeS and MnS are more stable due to their slow oxidation kinetics (Caetano et al., 2002). Inundation time also had significant effects on Cu and Zn accumulation (Speelmans et al., 2007).

4.6.3 Zinc

Zinc is an essential trace element as it is involved in a number of significant biological processes. Zinc is called Nature's Lewis acid and use this property to easily coordinate with N and O donors and is characterized by fast ligand exchange. A large fraction of the Zn entering the oceans is derived from aerial deposition (Neff, 2002). Zinc has a catalytic, co catalytic (Sterling et al,2001, Mc Call, 2000) and structural role (Yang and Zhou, 2001) regarding enzymes. It is known to be a co factor of nearly 300 enzymes. Zinc is the primary physiological inducer of metallothionein, a super family of proteins involved in redox reactions (Coyle and Phicox, 2002) and its deficiency is known to cause malfunctioning of the immune system. It also plays a vital role in viral infections (Chaturvedi et al, 2004). The significant role played by zinc in gene expression is also well established (Ladom ery and Dellaire, 2002). Since Zinc is an essential micronutrient for marine animals, they are able to regulate the Zn concentration in sediment and seawater. Fish species are found to be most tolerant to Zn (Neff, 2002). Increasing zinc solubility was noted upon oxidation of brackish contaminated sediment at acid and near neutral pH

levels. Significant linear relationship was observed between sediment Zn level and those accumulated in mangrove plants like *Avicennia* and thereby Zn is considered as the most mobile metal and hence accumulated in greatest amount in leaf tissue (Macfarlane, 2002).

Results and discussion

Zinc concentration varied between 0.22 and 1.71 ppm. Stations 1, 2 and 3had high Zn concentrations compared to stations 4 and 5 during all seasons. The concentration of Zn decreased considerably at station 2, 4 and 5 during monsoon with station 4 recording the zinc lowest concentration. Frequent short periods of air exposure followed by renewal of overlying waters resulted in large increase in the zinc flux from sediments. Fluxes were greater in the presence of sediment dwelling organisms (Simpson et al,2002). Zoumis et al.,(2001) has reported that association of zinc from strong bound oxidisable fractions to weaker bound carbonate and exchangeable fractions during sediment oxidation significantly enhanced the dissolved zinc concentration, thereby reducing the sediment bound zinc concentration. Presence of capping materials such as zeolite or sand can reduce zinc fluxes from the sediment (Simpson et al,2002). Zinc exists as ZnS in anoxic sediments because of the availability of SO_4^{2-} in these environs. ZnS increasingly associates with large molecular humic substances with decreasing redox potential. Sulphide bound metals are unlikely to be oxidized in short term due to their slow oxidation kinetics (Caetano et al, 2002). The maximum zinc concentration of 1.71 ppm was observed at station 3 during post monsoon. During post monsoon, station 3 had higher organic carbon content as well as tannin and lignin content which enhances the slow releases of Zn from sediments. Decaying plant material caused litter accumulation which will contribute to the binding of metals by adsorption, complexation and chelation (Alvim and Lourenço,2000). Micro organisms in the rhizosphere of wetland plants can accumulate metals (Decho, 2000). Organic matter directly affects the metal fate because micro organisms feeding on the organic matter will catalyse a series of redox reactions in the presence of electron acceptors. The extra cellular microbial

polymeric secretions in inter tidal systems play a significant role in the binding and concentration of metals (Kunito et al., 2001). In total correlation Zn correlated positively with Fe, Ni, Pb and Cu. The high correlation between Fe, and Zn and Ni suggests that these metals are retained in the sediments associated to iron oxides/hydroxides. In season wise correlations, Zn correlated with clay, Ni, Pb, Cu and Cd during pre-monsoon. Anthropogenic enrichment for heavy metals occurs naturally in silt and clay-bearing minerals of terrestrial and marine geological deposits. In monsoon, it correlated positively with Fe, Mn, Ni and Cu. The significant correlation of metals with Fe indicates the adsorption of these metals on to the oxyhydroxides with Fe (Jonathan et al., 2004). Positive correlation exists between Zn and Ni, Pb, Cu and Cd during post monsoon.

Considering the station wise correlations between metals and sedimentary texture, at station 1, Zn exhibits positive correlation with silt and Cd and negative correlation with sand, Fe, Mn, and Cu. At station 2, positive correlation exists between Zn and silt, clay, and Ni. Negative correlation exists between Zn and sand, Fe, Mn and Cu. Zn occurs as ZnS anoxic sediments, but Zn is only weakly pyritised compared to Mn (Billon et al., 2001). At higher sulphide concentrations the formation of soluble bi- and polysulphide complexes increased the total metal concentrations in the solution. Organic matter does not complex Zn and Cd to an appreciable extent in the presence of bi sulphides giving rise to the negative correlation. At station 3, a trend opposite to that at station 2 is seen in the case of correlation between Zn and sand, clay, Fe, Mn and Cu. With Ni the same continued to be maintained with Zn as in station 2. Cd exhibited negative correlation with Zn. In station 4, clay, Fe, Mn Ni and Cd retained the same trend of correlation with Zn as in station 3 and sand followed the trend shown in station 2. Heavy metal ions accumulate in sediments because of the deposition of metal-enriched allochthonous particles or the adsorption of dissolved heavy-metal ions from the water column. Most contaminants are transported as fine-grained suspended matter which has large surface area. According to Binkley and Fisher (2000), the cations that balance the charge of the anions interact

strongly with the solid phase of the soil, principally with the cation exchange complex. .At station 5 which is a non mangrove site, Fe, Mn , Ni and Cu followed the same pattern as in station 3. Cd exhibited a positive correlation, while sand maintained a negative correlation with Zn. Cu and Zn enrichment is observed in areas having considerable boating activity. Cation forming elements such as Cu, Zn, etc. are likely to be involved in oxidation and reduction reactions with each other as part of complex cycle involving trace metal enrichment in sediments, which explains the varying correlations between Zn and Cu.

4. 6.4 Nickel

Ni ranks 23rd in the order of abundance among elements and can be found in all soils. Natural sources of nickel include weathering of minerals, rocks and geothermal emissions. The concentration depends on the type of soils and its location with the normal concentration range varying between 5 to 500 mg/kg. Soils derived from sandstones, limestone or acid igneous rocks contained less than 50 mg/kg or more. Ni is used extensively in plating and alloy manufacture, as catalyst in oil refining, in nuclear power plants, gas turbine engines, cryogenic containers and pollution abatement equipment. Nickel is also a naturally occurring element found in a number of mineral ores including Ni sulphides, oxides and silicates. It is present in the enzyme urease and as such is considered to be essential to plants and some domestic animals. The essentiality of Ni to man has not been demonstrated extensively (Teo and Chen, 2001). Its properties such as strength, corrosion resistance, high ductility, good thermal and electric conductivity and catalytic properties enhance its commercial importance and applications. However, Ni-related health effects such as renal, cardiovascular, reproductive, and immunological effects have been reported in animals. Toxicity of Ni to rainbow trout has been reported (Pane et al., 2003). Its toxic effects in man are related to dermal, lung and nasal sinus cancers. Ni compounds attack histones and produce carcinogenic effect (Zoroddu et al., 2002). Nickel is introduced into the marine environment through effluents from various industries. The normal uptake of

Ni in humans is known to vary between 0.3 to 0.6 mg/day through diet and sometimes Ni enters the biological system through inhalation. Most of the Ni ingested will be eliminated via excretory products. Ni is known to affect reproduction and growth in animals. Nickel toxicity affects the life stages and egg survival of fishes, causes gill damage, leading to reduced gas diffusing capacity and biochemical changes (Abbasi and Soni, 1998). Increased concentration of Ni will cause a significant reduction of oxygen consumption at the sediment water interface and an increase in oxic zone in sediments. Creation of new oxygen consumption regions in sediments were also observed in the presence of elevated sedimentary nickel concentration. This phenomenon is due to the mobility of microorganisms to the deeper layers of the sediments to escape the toxicity of the metal. This microbial migration is similar to those shown by cyano bacteria in the presence of UV radiation (Viret et al, 2006).

Results and discussion

The concentration of Ni in polluted waters including mangroves is reported to vary on an average between 40- 100 ppm with surface sediments showing Ni enrichments due to anthropogenic inputs. Nickel in a polluted site showed a concentration as high as 27.3 ppm in sediments (Lindsey et al,2005). Highly polluted mangrove sediments showed higher values as in Indus delta of Pakistan, where sediments concentration of nickel ranged between 90.32 and 152.03ppm (Saifullah et al., 002). Ni in the sediments of Cochin estuary is reported to vary between 0.35 to 10.30ppm (Jayasree and Nair, 1995). In the present study it varied between 0.10 to 0.62ppm, which is lower than the concentration of all the metals analysed except lead. Monsoon showed a lowering of Ni in sediments at stations 3,4 and 5 which might be due to re-suspension and erosion(Bellucci et al.,2002) while at stations 1and 2 there was an increase which might be due to recent input from anthropogenic sources. In pre monsoon and post monsoon stations 1, 2 and 3 had high values of nickel concentrations. Metal speciation studies have indicated that Ni is reported to be associated with residual and reducible phases. Metals

bound to these phases will behave differently in sedimentary and diagenetic environment and have different potentials for remobilization and biological uptake when compared with that of metals which are present in oxidisable phases. The high values of Ni might be due to reducing conditions or due to high clay fraction present during pre-monsoon and post monsoon seasons (Saifulla et al.,2002).

In total correlation, Ni correlated well with all the metals except Cd. Good correlation exists between Ni and Fe, Mn and Cu. In pre-monsoon Ni correlated positively with all the metals except Cd. High correlation exists between Ni and Fe, Pb and Cu. In monsoon, Ni correlated positively with all the metals except Pb and Cd. During monsoon also high correlation exists with Fe, Mn, Zn and Cu. Negative correlation exists between sand and Ni while a positive correlation is seen between Ni and silt. During post monsoon Ni correlated positively with all the metals including Cd. High correlation exists between Ni and Mn as well as with Cu. Considering the station-wise correlation, Ni correlated positively with clay and negatively with Fe and Pb. At station 2, there exists negative correlation between Ni and Fe, Mn, Pb and Cu, while the correlation is positive between Ni and silt, clay, Zn and Cd. At station 3, Ni showed positive correlation with sand, Fe, Mn, Zn, Pb and Cu, while negative correlation is observed between Ni and clay and Cd. At station 4, Ni correlates negatively with sand, clay, Pb, Cd, and Cu and positively with silt, Fe, Mn and Zn. At station 5, Ni correlated negatively with sand, and positively with silt, Fe, Mn, Zn, Cu. The mean concentration of Ni during pre monsoon was 0.36ppm, in monsoon 0.31 ppm and in post monsoon 0.38ppm. The mean concentration of Ni at the different stations were 0.47ppm at station 1, 0.57 ppm at station 2, 0.40ppm at station 3, 0.14 ppm at station 4, and 0.16ppm at station 5. Anova showed that significant variations exist in the stationwise concentration of Ni with $P<0.001$.

4.6.5 Lead

Lead is more ubiquitous than most other toxic metals. The principal anthropogenic source of lead in the environment are gasoline additives mainly tetraethyl lead that enter the atmosphere in the form of unburned alkyl lead vapours and as lead halides. Other major sources of lead contamination in the air includes burning of fossil fuels, cement manufacture, metallurgical industries, lead pigments in paints lead storage batteries and cables, sedimentation rainfall containing atmospheric lead, urban storm water run off, paper, rayon, chemical and fertilizer plants, all contribute to lead contamination. Drinking water may be appreciably contaminated by lead from the use of lead and PVC pipes. Glazed ceramic food ware is another source of lead pigment. Battery industries and mine storage also cause lead pollution. Pollution due to lead in coastal areas near industrial sites can be 5 to 10 times than those prevailing 50 years back(Valdes,2005). For most people the major source of lead intake is food. Generally lead levels in the soil range from 5-25mg/kg, in ground water from 1 to 60ug/l and somewhat lower in natural surface water and in air under 1ug/g which may be higher in areas with higher motor traffic. Organic lead compounds such as tetra alkyl lead can penetrate the skin and absorb into the body tissues more rapidly than inorganic lead compounds. Lead is a cumulative and slow acting protoplasmic poison, which inhibits haeme synthesis, disrupts kidney function, replaces Ca in bones (Mohapathra and Ranga rajan, 2000) and readily enters the central nervous system. The lead level in blood is considered as the best indicator of lead poisoning. Levels higher than 0.008 mg/100ml are dangerous and damage the central nervous system, especially in children (Olle, 2005) as they have a greater ability to absorb ingested lead and also have a greater susceptibility to the metal because of their fast growth rate. At 40-50ug/dl, children may exhibit hyperactivity, decreased attention span and a slight lowering of IQ scores. When the blood level is over 809ug/dl, encephalopathy may occur. There are damages to the arterioles and capillaries, resulting in stupor, coma and convulsion. Lead also adversely affects reproductive

functions mainly through gamete toxicity resulting in sterility, abortion and neonatal deaths.

Lead typically complexes with sulphides and Fe-Mn hydrous oxides in sediments. Lead sulphides are common in anaerobic sediments. Lead typically desorbs from sediments and suspended solids in estuaries owing to competition with chlorides, producing an appreciable increase in residues in the water column. Adsorption plays a key role in the fate of lead complexes. Although desorption of lead is a slow process, sediment bound lead may ultimately appear in the pore water and be recycled to the overlying water. The process can be reversed by a sudden decrease in the pH or by a change in the ionic composition of the solution. Anions such as humic acid, nitrilotriacetate, glycine, tartrate and phosphate enhanced the adsorption of lead by soils especially at low pH values. The majority of lead complexes in water are not subjected to photolysis. Volatilization may remove compounds such as tetramethyl lead which are volatile. Among submerged macrophytes, rooted species are found to accumulate lead to a greater extent than plants without roots. Although marine invertebrates and fishes bio accumulate Pb from water in proportion to its concentration in solution it is not efficiently transferred through marine food webs (Neff, 2002).

Results and discussion

Pb showed very low concentration compared to other metals. It varied between 6.3 and 530 ppb among the different stations. The concentration of Pb is high at stations 1&3. Station2 also showed high lead concentration except in monsoon when the concentration was the least observed concentration in the analytical sequence. Enrichment of trace metals may be due to biogenesis, terrigenous and authigenic sources. But both stations 2&3 are close to vehicular transport, pointing to the role of atmospheric deposition as an important factor for the lead concentration at these stations. Lead has a tendency to concentrate in the water surface micro layer especially when surface organic materials are present in thin films. In water lead is probably complexed with organic ligands(Susana et al,2005) giving soluble colloidal

and particulate compounds. Clay materials can remove lead from solution. The % of clay in the sediments of stations 1,2 and 3 are is high which might be another factor for elevated lead concentrations at these stations. During post monsoon station 5 recorded a six fold increase in lead concentration. The rainfall during north east monsoon season must have brought in contaminants from the industrial areas on the banks of the river Periyar which empties itself in the Cochin estuary. Rivers flowing close to urban areas may bring pollutants downstream to estuarine sediments from where they are incorporated into mud banks resulting in abundant elevated metal concentration. Also, in post monsoon the fishing activity intensifies in Cochin, along with the whole of the coastal belt of Kerala. Numerous fishing boats traverse the waters surrounding station 5. High concentration of Pb in the surface sediments is mainly associated with anthropogenic activities(Xu et al,2009).

In total correlation lead shows significant correlation with Zn, Ni and Cu. In pre-monsoon lead showed correlation with all metals except Cd. The correlations were high in the case of Ni and Cu. Negative correlation exists between lead and sand. Monsoon data displayed that Pb correlated positively with clay and Cd and negatively with sand. During post monsoon high correlation exists with Zn and Cd. At station 1, lead shows negative correlation with Mn, Ni and Cu and positive correlation with clay. Lacerda (2004), showed that the mobile fraction of metals tends to migrate in the sediment through interstitial water until it comes in contact with oxygen. Thus precipitation of hydrous metal oxides will occur. The precipitates of these metals are no longer soluble and are therefore incorporated into the sediment. Lead shows high concentration at station 1 suggesting dissolved uptake from water column. Contrary to this low concentration of metal such as Mn, Ni and Cu is observed at station 1, due to remobilization of metals when anoxic sediments due to disturbances caused by human activities or bio turbation, when oxidation of previously metal sulphide species takes place (Hegde et al,2009). At station 2, lead shows negative correlation with silt, Ni and Cd while positive correlations of lead were observed for Fe and Cu. Wolanski

(2006) has reported that when the sediment submerged at high tide, Fe oxides are converted into hydrated forms and provide a large surface area for reactions of metals ion, which may be the reason for positive correlation of Fe and Pb. At station 3, lead shows positive correlation with sand silt and all metals except Cd, while negative correlations were observed between lead and Cd as well as between lead and clay the latter being more significant. Cation forming elements such as Cu, Zn, etc. are more likely to be involved in oxidation and reduction reactions with each other as part of complex metal cycle in sediments.

Station 4 showed negative correlation between Pb and Fe, Mn and Ni, and positive correlation with Cu and Cd. Pb shows high correlation with Cu at station 4. Marchand et al., (2006) stated that in estuarine sediments, copper and manganese have been identified as pyrite co-precipitates because of pyrite dissolution. In contrast, cadmium and lead are believed to be attached by other sulfides or oxides because only significant amount of these metals dissolved. This is because these trace metals are involved in sorption or co-precipitation with amorphous FeS (Calloy et al., 2002). At station 5, lead shows high positive correlation with silt, Fe, Mn Ni and Cu with the latter three being higher. According to Ray *et al.* (2006) and Jonathan et al. (2004), the significant correlation of metals with Fe indicates the adsorption of these metals on to the oxyhydroxides with Fe. Pb showed significant negative correlation with sand. This indicates that Pb is accumulated well in the silt fraction at station 5. Trace metals may be incorporated into sulfide minerals by adsorption, precipitation or ion exchange. The studies of metal adsorption on sulfide minerals suggest that the adsorption is dominated by the surface hydroxyl groups. The surface interactions of metals with sulfide minerals are likely to influence the fate and transport of metals in anoxic environments. Sediment pore-water represents the mediator fluid in the exchange of the components between sediment and water. A steep gradient in ionic strength in sediment pore water destabilizes the colloidal materials causing it to flocculate (Andrews, 2004). Salt flocculation plays an important role in metal accumulation of fine grained materials. Grain size also plays a significant role

in determining elemental concentrations in sediment (Pekey, 2006) with adsorption potential increasing exponentially with a decrease in particle size. Two way anova indicated that variations of Pb between stations and between seasons were not significant.

4.6.6 Copper

Copper reaches the aquatic environment through wet or dry deposition, mining activities, land runoff, industrial, as well as domestic activities and agricultural waste disposal. Industries such as pulp and paper mills, petroleum refining, rayon process, brass rod and wire industries and copper molls. Even industries like soft drinks and flavouring syrup, ice cream, laundry and fur dressing and drying are known to cause copper pollution. Sewage effluents, fertilizers, and pesticides used in agriculture are other important sources, which make environmental concentration of copper go up. Copper is considered the most toxic metal to a wide spectrum of marine lif; hence its value in antifouling preparations (Trannuma et al., 2004). Copper is sorbed onto sediments resulting in devastating residue levels. Sediments receiving effluents from metal mining industries and smelters are quoted to containing levels up to 2350 ppm of copper. As a nutrient, copper is essential for plants, animals and humans and is a constituent of many metalloenzymes and respiratory pigments. Copper participates in the formation of blood and the utilization of Fe in haemoglobin synthesis (Miramand et al,2001), the synthesis and cross linking of elastin and collagen in the aorta and major blood vessels and in the oxidation process by its presence in many oxidative enzymes. Copper containing enzyme ceruloplasmin plays a role in iron homeostasis (Hellman and Gitlin, 2002). Copper dependent proteins are also known to carry out other functions such as hormone signaling, oxidation of phenols, super oxide dismutation etc (Frausto da Silvaand Williams, 2001). Though normally bound to proteins, Zn can remove copper from its binding site and lead to the formation of highly reactive hydroxyl radicals which can interfere with important cellular processes (Chaturvedi et al., 2004).

Toxicity of copper to aquatic biota varies with pH, hardness of water, presence of other metals, and presence of various species of copper and organic matter. Decreases in sediment pH contributes to the mobilization of exchangeable species of copper leading to its greater uptake(Macfarlane et al,2003). Copper toxicity may partially eliminate certain species of algae from waters. The larvae and younger stages of aquatic invertebrates are more sensitive to copper than adults. Fish musculature is a major path through which heavy metals enter the human body. Mineral rich food stuffs, legumes, nuts, grains and fruits act as important sources of copper. The deficiency of copper has been associated with anemia, demineralization of bones and amyelination of central nervous system of the newborn. The Menkes disease characterized by de pigmented hair, physical and mental retardation, hypothermia and eventually death has been linked to copper deficiency (Olle, 2005). Copper concentration in various fishes from coastal waters of Cochin varied from 1.43 to 35.49 ug/g dry wt. Decrease in pH contributes to the mobilization of metals as exchangeable species in mangrove sediments, allowing greater copper available for uptake. P-type Cu transporting ATPases are thought to play a role in preventing accumulations of copper ions to toxic levels in plants

Results and discussion

Mangrove sediments of Kerala are reported to contain varying amounts of copper depending on the pollution load, proximity to industries and deposition of sediments etc. The mangroves of Quilon, Kerala are reported to contain a very high concentration of copper 652-845 ug/g air dried weight. In Kumarakom it varied between10 to 44 ug/g and in Veli 62-256 ug/g respectively (Fernandez and Tresa,1997). Sediments become chemical archives of heavy metal accumulations, which can provide valuable information in resolving the source and sink of heavy metal pollution (Cundy et al., 2003; Jha et al., 2003). Copper in mangrove sediments of the study sites varied between 96 and 410 ppm in pre monsoon, while in monsoon it varied between 66. 43and 301ppm and in post monsoon it varied between

168 and 424ppm. The variations in copper concentrations in sediments with changing seasons can arise due to inundation time which had significant decreasing effects on Cu accumulation. The redox potential of sediment is of major importance in the accumulation of copper in sediments(Speelmans et al., 2007).

All stations showed an increase in Cu concentration during post-monsoon. The burial flux of heavy metals in sediments is dependent on environmental factors, such as sedimentation rate, sediment porosity, microbial activity, bioturbation rates and bottom water oxygen conditions (Schenau et al., 2005). Copper can be immobilized in the sediment as both copper-sulfides and copper-oxides. Though copper forms metal-sulfides it can additionally form oxides and adsorb onto hydrous-oxides. The increased Cu concentration may be due to the presence of easily oxidisable fractions of Cu during post monsoon. Cu enrichment of sediments contaminated with boating activity is observed due to Cu pyrathone being present in anti fouling paints. Cleaning, maintenance, grounding, flaking from various underwater structures are the causative factors of the above said enrichment (Nimisha and Andrew, 2009). There was a lowering of Cu concentration during monsoon at all stations except at station 4. Increased acidity of the sediments will cause leaching of metals from sediments. Similarly agitation of sediment and mixing with oxygenated water will also enhance oxidative degradation of organic matter and could solubilise considerable amounts of metals like Cu. Dissolution will release metals associated with the oxide phases to the overlying water column and to benthic biota. Bacteria and phytoplankton can bind a high concentration of metals such as copper. This uptake by biota is significant with respect to the impacts on food web (Rossi et al, 2008). Metals can be released from metal-sulfides, iron hydroxide complexes and organic matter, by changes in the chemical properties of the sediments. The conversion of iron hydroxides to FeS and $FeCO_3$ in anoxic sediments will also cause a lowering of trace metal adsorption capacity of sediments. Continuing microbial oxidation can gradually release metals bound to organic matter. Once

released the metals are available to be taken up by flora and fauna and can be washed out of the marsh.

Cu showed high positive correlation with Fe, Mn, Zn and Ni. It also correlated well with Pb and clay when the total metal correlations are considered. During pre –monsoon, Cu shows positive correlation with clay, Fe, Mn, Zn, Ni and Pb the last one being quite high. In monsoon, Cu has positive correlation with silt, clay, Fe, Mn, Zn, and Ni. During post monsoon positive correlation is observed between Cu and clay, Fe, Mn, Zn, Ni and Cd. The seasonal correlations show that there is a consistent correlation of Cu with Fe, Mn, Zn and Ni during all the three seasons. Geochemical metals such as Fe and Mn are usually abundant in sediments. Pyritisation of iron minerals will lead to these metals to be effectively immobilized in sediments as long as the sediment conditions remain reducing. At station 1, Cu correlates positively with Mn and negatively with Zn, Cd and clay. At station 2, negative correlation exists between Cu and Fe, Zn, Ni, ,Cd and silt, whereas Pb shows positive correlation with Cu. At station 3, Cu shows positive correlation with Fe, Mn, Zn as well as Ni and negative correlation with Cd, which is the reverse of that observed at station 2. At station 4, Cu correlates only with Pb. At station 5, again it correlates positively with the metals Fe, Mn, Zn, Ni as seen in station 3and additionally with Pb. The negative correlation between Cu and Cd may be due to weak incorporation of Cd into pyrite and hence may remain in more labile phases during early diagenesis. Another reason may be because of greater tendency of Cd to form soluble sulphide species and to remain in solution than Cu. Two way anova showed that station wise variation of Cu is significant($P < 0.001$).

4.6.7 Cadmium

Cadmium is one of the notorious heavy metal pollutants as it is a potential bio-toxic heavy metal that is readily absorbed by plants and reaches the human chain (Susana et al,2005). Cadmium pollution is mainly due to anthropogenic

factors. Cadmiun accumulation has been found in large areas of estuaries due to emissions from municipal waste incinerators, car exhausts, sludge or urban composts, peticides and fertilizers. It is usually found associated with Zinc. Cadmium finds wide applications in Ni- Cd battery, pigment manufacture, galvanizing, plastic manufacture, alloy manufacture etc. It is a non- essential element for plants and animals. The amount of cadmium in sediments is related to the amount leached into water(Neff,2002). Concern about its toxicity began to increase with the incident of Itai-Itai disease in Japan due to cadmium poisoning. In human beings exposure to increased cadmium levels is known to cause deterioration of bones, weakening of joints, extreme pain and in severe cases the joints broke under the most ordinary of diseases. Factors such as pH and hardness may effect the amount of biologically active forms of Cd, while other factors like DO, and temperature may influence the tolerance capacity of the organisms.

Cadmium exposure causes swelling, vacuolization and degeneration of mitochondria leading to reduction in ATP and chlorophyll in green algae. Cadmium toxicity in fish is mainly caused due to gill damage leading to anoxia. Certain bivalves such as *S. plana* are known to have a greater tendency to bio accumulate cadmium in tissues (Ni et al,2000 ; Neff 2002). In marine environments the concentration of cadmium is found to be much higher in the low salinity zone(Willy Baeyens, 1998). This may be due to the fact that cadimium bound to organic matter in the particles as in solution left the suspended matter at low salinity. The percentage of dissolved Cadmium is reported to increase from about 3% to 70% at the estuarine mouth. High organic carbon and carbonate content along with high iron hydroxide precipitates are known to enhance the concentration of cadmium in sediments (P. P.Mohan, 1997). Cd sorption and desorption is influenced especially by pH, sorption time and aqueous cadmium activity, while Mg^{2+} concentration and electrostatic factors appears to be of minor importance. Cadmium deposited in the soil readily enters the plants and incorporates into the food chain. It is retained in the body a, especially in the liver and kidneys and is excreted very slowly. Kidney damage causes conditions such as proteinuria

and calciuria. Biological monitoring of Cadmium is done by measuring cadmium in blood and urine. The latter may be detected only after renal damage which often is fatal. Metal binding proteins such as metallothioneins are considered central in the intracellular regulation of cadmium (OlleSelenius, 2005).

Results and discussion

The cadmium concentrations varied between 1.43ppm and 97.77ppm among the various stations. High concentration of cadmium was found in monsoon at stations 1 and 3. Significant correlation has been reported between cation exchange capacity, clay and organic matter content(Du Liang et al., 2007a). Electro positively charged elements can be attracted to negatively charged surfaces of organic matter, clay particles, iron and aluminium oxides which determine their ion exchange capacity. High cation exchange capacity reduced metal mobility and availability and increases metal cation retention in sediments. The pH of the medium was alkaline in monsoon. The salinity also decreases which favours better retention of cadmium in sediments. The concentration of Cd during post-monsoon and pre-monsoon was less. The least concentration of cadmium was observed during post monsoon. The mobility and availability of cadmium in oxidized, sulphidic sediments is affected by salinity(Du Laing et al, 2008(b)). Increase in salinity caused faster release of cadmium from cadmium sulphide during the oxidation of reduced sediments (Gerringa et al, 2001). Soluble Cadmium was found to increase with increase in salinity, with desorption of metal from sediments taking place (Milward and Liu, 2003). Chloride complex formation and ion exchange are the primary stimulants for the release of cadmium. Cd primarily exists as CdS in anoxic sediments, due to the availability of considerable amounts of sulphide in these environs. It is found to be more mobile in oxidized sediments. Changes in valence state with variations in sedimentary redox states is less significant for cadmium when compared to other metals like Fe and Mn. Binding forms of Cd, change from stronger bound oxidisable fractions to weaker bound carbonate and exchangeable fractions during

sediment oxidation, which significantly increased dissolved Cd concentrations (Stephens et al, 2001). The Cadmium present in sediments has a significant role in the uptake of cadmium by plants and animals. In pre monsoon, as ascending salinity promotes Cd desorption from sediments, increases in total Cd concentrations in the water column and further increasing salinities is known to promote the formation of Cd chloride complexes, which seem to be less bio-available compared to free Cd^{2+} As a result, a higher Cd bioavailability and toxicity with decreasing salinity has been observed for organisms living in close contact with the water column, such as mussels (Du Laing et al. 2002). But as the sedimentary concentration of Cd is high greater amount of Cd will be desorbed and greater amount of Cd will be available for bio uptake.

Cd shows significant positive correlation with clay in monsoon and negative correlation with silt in pre-monsoon and with sand in monsoon. In pre-monsoon and post monsoon Cd correlates well with Zn and in monsoon and post-. monsoon with Pb. Cd correlates positively with Cu only in post monsoon. At station 1, Cd showes negative correlation with sand, Fe, Mn and Cu and positive correlation with silt and Zn. At station 2, Cd has positive correlation with silt and Ni and high negative correlation with Fe. Pb and Cu also has negative correlation with Cd at station 2. At station 3, Cd negatively correlates with all metals and sand and shows positive correlation only with clay. At station 4, negative correlation exists with silt, Fe, Mn, Zn, Ni and positive correlation with sand and clay. Station 5 exhibits high correlation between Cd and clay. Cd also correlates positively with Fe, Mn and Zn an observation seen contradictory to the mangrove sites. From the above observations it can be seen between Cd and Fe is common negative correlation. Pyrite is a typical mineral found in several mangrove sediments (Roychoudhury *et al.* 2003). The sedimentary characteristics of the mangroves under consideration promote a rapid leaching and oxidation of the pre-existing sulphides. The correlation indicates that the amount of Cd present is more in the solubilised form than as immobilized in sediments and

re-precipitation of Cd on Fe and Mn oxides is less. The positive correlation between Cd and clay as well as silt fractions is due to the well documented fact that fine grain sediments are the preferred source of trace metals.

Conclusion

Mangrove sediments are enriched with detritus from the ecosystem. During pre monsoon and post monsoon there is mutual correlation between sedimentary protein, TOC, tannin and lignin as well as exchangeable ammonium. In monsoon, protein correlated only with TOC. In monsoon when light and salinity levels are minimum and water has maximum turbidity, rates of pelagic respiration is enhanced and phytoplankton productivity is suppressed (Ram et al, 2003). There exists a positive correlation of TOC with tannin and lignin as well as exchangeable ammonium in monsoon. Mangrove soils are a mixture of organic and inorganic ingredients derived from an array of land and ocean based sources with proportional contributions depending on the location and geomorphology. The organic matter of mangrove soils is a rich mixture of mangrove litter, dead and live roots wood and mangrove peat with allochthonous contributions from seagrasses reef algae, plants animal waste microbial biomass and particulate organic matter(Muzuka and Shunula, 2006). Most of the organic carbon found in sediments is sorbed onto clay fraction of the sediments and this greatly reduces the availability for bacterial degradation Bacterial mineralization can have a large impact on the amount composition age and lability of organic matter (Boschker et al,2005) with benthic mineralization accounting for half the total mineralization in coastal sediments(Middleburg et al,2005). Degradability of organic matter can also be modified with time, as less available fractions remain. The positive correlation between organic matter and tannin and lignin may be due to tannin and lignin rich fractions of organic matter remaining in sediments. 2 way anova showed that station wise variations were significant for protein, total organic carbon as well as tannin and lignin. For copper station wise variations is more significant than season wise variations. For Pb and Cu both station wise and season wise variations are not significant. In cluster Analysis Fe, Mn, Cu Ni, Pb and

Zn forms one cluster underling the correlations existing between the concentrations of these metals during the period of analysis. Cd, silt and clay forms another cluster while sand by itself forms a cluster. Principle component analysis showed that protein, total organic carbon and tannin and lignin formed a cluster, while exchangeable ammonium formed another.

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Sediment Data (Bimonthly)

A. Total Organic Carbon (mg/g)

		Stn 1	Stn 2	Stn 3	Stn4	Stn5
Pre-Mon	Feb	1.456	1.53	2.289	0.247	0.246
	April	1.686	1.625	0.9047	0.2805	0.1816
Mon	June	1.557	1.187	1.67	0.1297	0.2613
	Aug	2.102	1.483	1.927	0.2019	0.2919
Post -Mon	Oct	1.547	1.427	1.388	0.442	0.2215
	Dec	1.664	1.442	2.423	0.2516	0.3519

B. Tannin and Lignin (mg/g)

		Stn 1	Stn 2	Stn 3	Stn4	Stn5
Pre-Mon	Feb	4.629	7.951	6.844	0.869	0.237
	April	2.134	5.671	4.761	0.752	0.211
Mon	June	6.455	6.407	14.24	1.044	0.746
	Aug	3.01	3.33	4.88	1.204	1.753
Post -Mon	Oct	5.154	4.331	4.974	2.187	0.985
	Dec	3.871	6.611	14.04	0.431	0.182

C. Exchangeable ammonium (µmol/g)

		Stn 1	Stn 2	Stn 3	Stn4	Stn5
Pre-Mon	Feb	2.027	3.209	3.2	0.576	0.097
	April	2.32	4.21	5.77	0.44	0.154
Mon	June	0.37	0.439	0.432	0.19	0.085
	Aug	4.01	3.33	4.88	1.204	1.753
Post -Mon	Oct	2.141	2.235	3.32	0.865	0.786
	Dec	1.833	1.061	2.23	1.296	0.234

D. Protein (mg/g)

		Stn 1	Stn 2	Stn 3	Stn4	Stn5
Pre-Mon	Feb	19.3	17.29	12.280	1.066	0.053
	April	12.37	13.620	6.568	0.322	0.023
Mon	June	4.661	15.68	4.084	0.292	0.015
	Aug	7.661	9.711	10.32	0.865	0.119
Post -Mon	Oct	7.836	8.592	6.992	0.058	0.214
	Dec	2.778	10.15	15.730	0.028	0.322

E. Texture Of Sediments

Premon		Stn 1	Stn 2	Stn 3	Stn4	Stn5
	% sand	22	14	19	24	71
	% silt	15	27	20	31	5
	% clay	63	59	61	45	24
Mon		Stn 1	Stn 2	Stn 3	Stn4	Stn5
	% sand	8	11	10	30	78
	% silt	36	34	22	22	9
	% clay	56	55	68	48	13
PostMon		Stn 1	Stn 2	Stn 3	Stn4	Stn5
	% sand	25	35	23	22	52
	% silt	21	24	28	34	33
	% clay	54	41	49	44	15

F. Metals in Sediment (Seasonal)

a) Con. of Fe (ppm)

	Pre-Mon	Mon	Post-Mon
Stn 1	371	213	311
Stn 2	378	287	397
Stn 3	259	75	211
Stn 4	86	10	82
Stn 5	78	42	83

b) Con. of Mn (ppm)

	Pre-Mon	Mon	Post-Mon
Stn 1	1.05	1	1.36
Stn 2	0.75	1.18	1.56
Stn 3	0.75	0.5	1.1
Stn 4	0.6	0.32	0.62
Stn 5	0.36	0.22	0.58

c) Con. of Zn (ppm)

	Pre-Mon	Mon	Post-Mon
Stn 1	0.67	0.74	0.63
Stn 2	0.84	0.85	0.77
Stn 3	1.46	0.44	1.71
Stn 4	0.27	0.22	0.28
Stn 5	0.47	0.38	0.46

d) Con. of Ni (ppm)

	Pre-Mon	Mon	Post-Mon
Stn 1	0.44	0.48	0.49
Stn 2	0.58	0.62	0.51
Stn 3	0.45	0.25	0.51
Stn 4	0.17	0.1	0.16
Stn 5	0.15	0.11	0.21

e) Con. of Pb (ppb)

	Pre-Mon	Mon	Post-Mon
Stn 1	288.2	233.8	162
Stn 2	407.5	6.3	309.4
Stn 3	322.2	222.8	530.8
Stn 4	67.5	113.4	105.7
Stn 5	44	39	261.1

f) Con. of Cu (ppm)

	Pre-Mon	Mon	Post-Mon
Stn 1	295.6	267.5	398.9
Stn 2	410.5	301.1	424.4
Stn 3	405.1	204.5	395.9
Stn 4	106.4	162.6	168
Stn 5	96.58	66.43	183.7

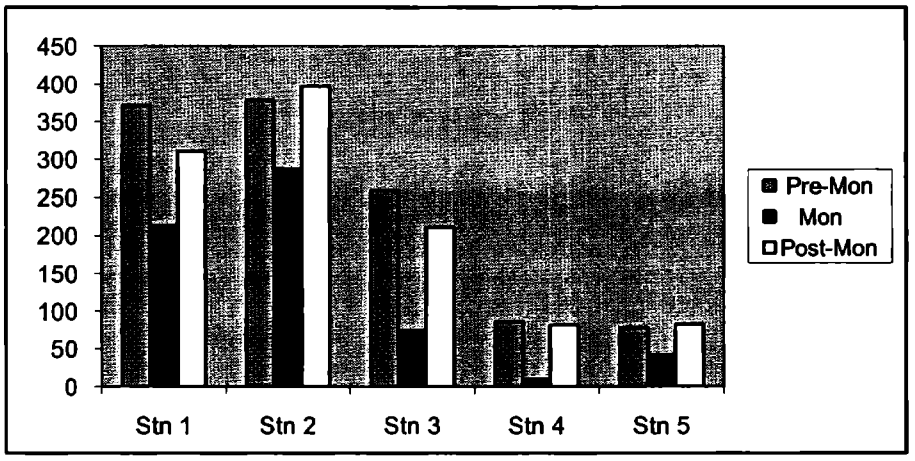
g) Con. of Cd (ppm)

	Pre-Mon	Mon	Post-Mon
Stn 1	8.88	58.93	8.86
Stn 2	8	20.8	10.07
Stn 3	24.28	97.77	20.88
Stn 4	1.762	6.669	1.43
Stn 5	15.68	3.91	6.54

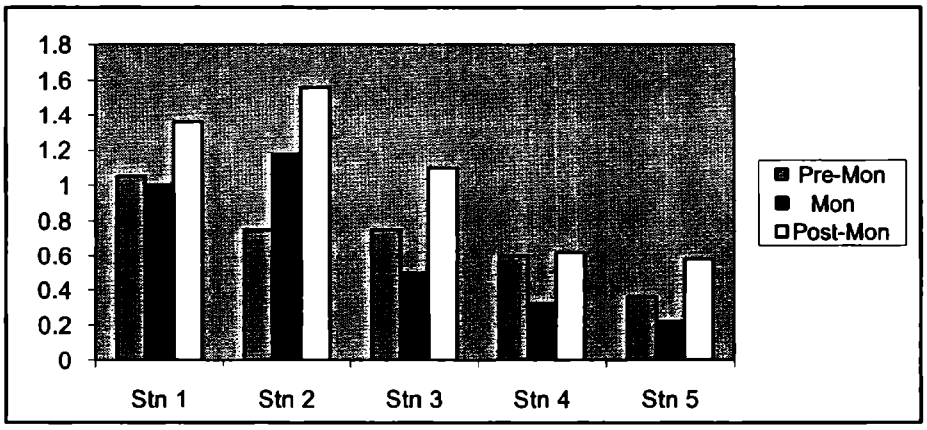
Graphs of Sediment Parameters

Metals

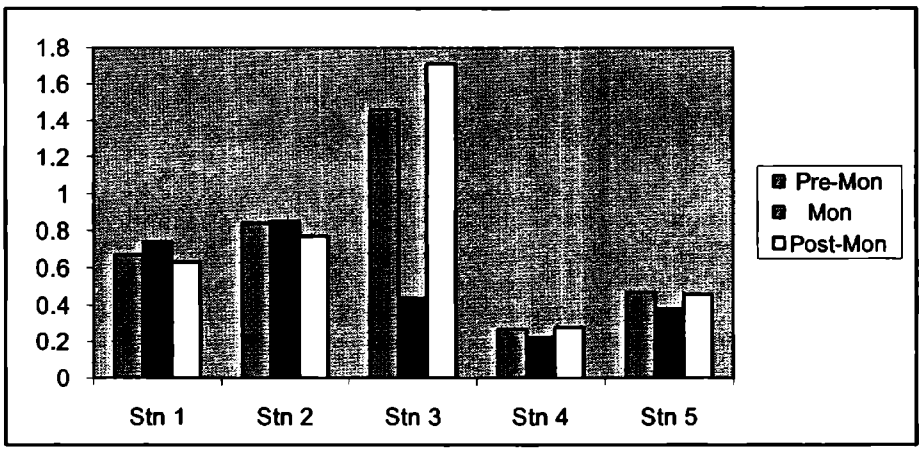
a) Con of Fe



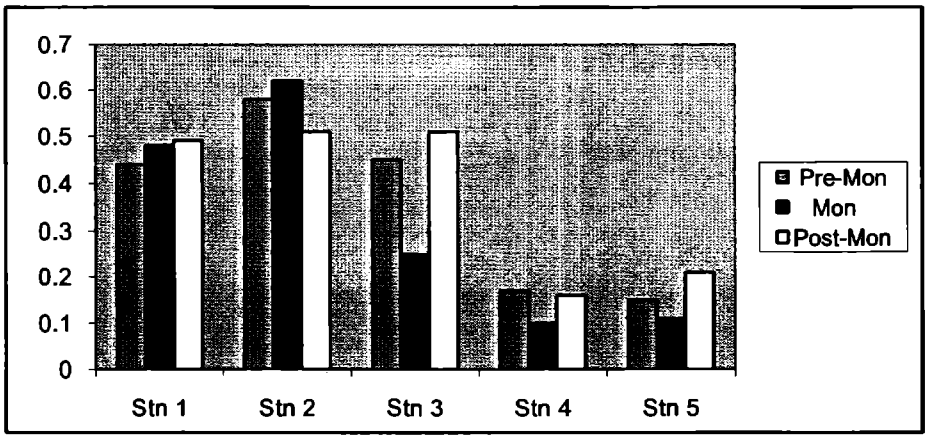
b) Con of Mn



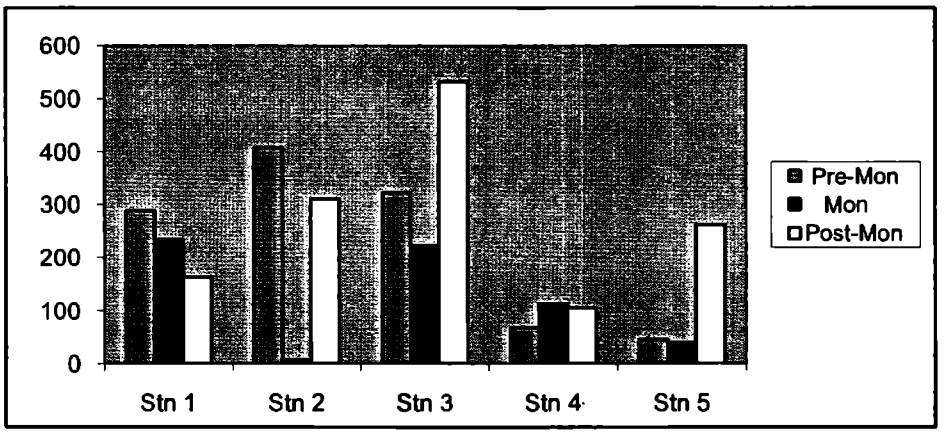
c) Con of Zn



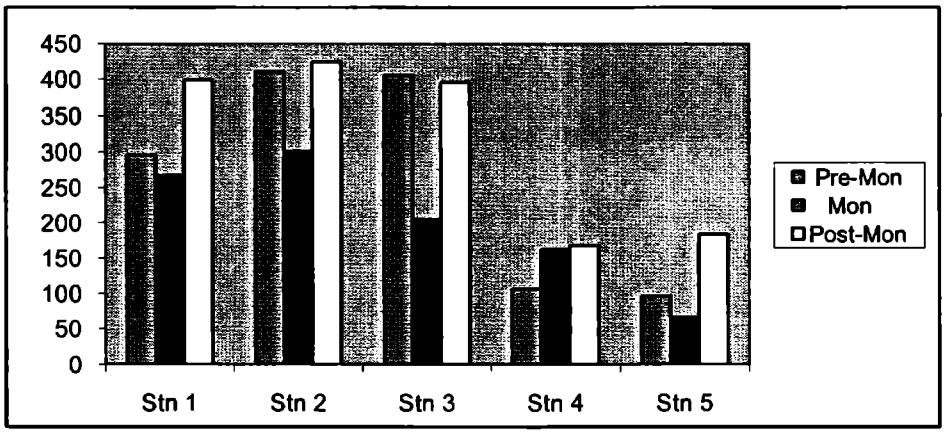
d) **Con of Ni**



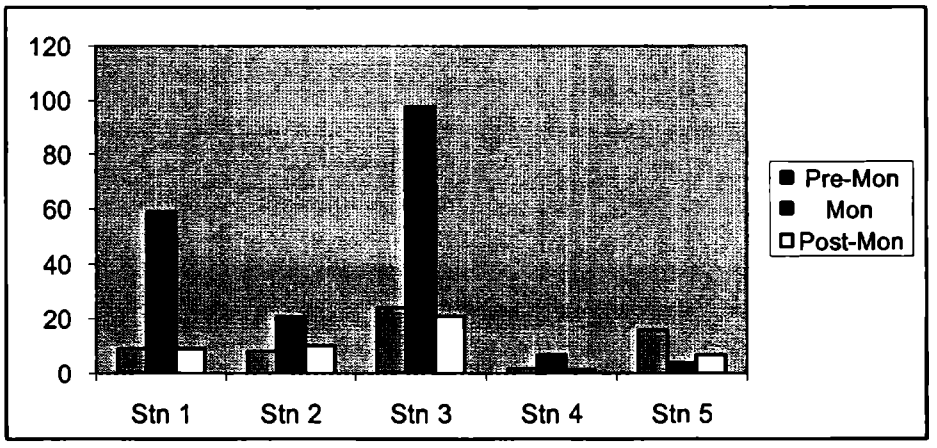
e) **Con of Pb**



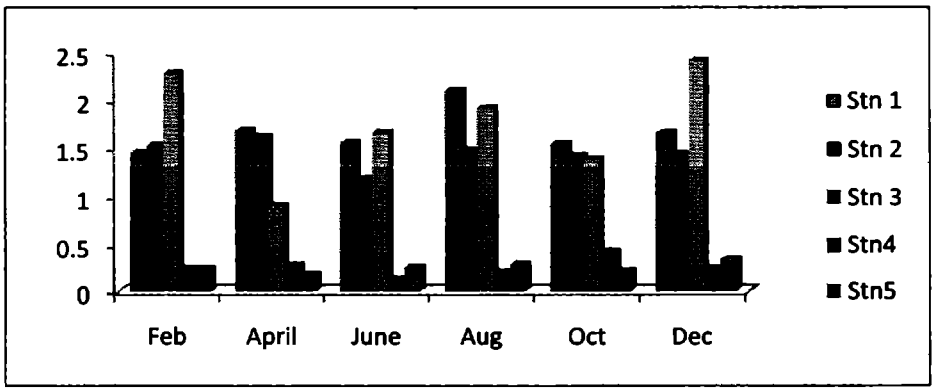
f) **Con of Cu**



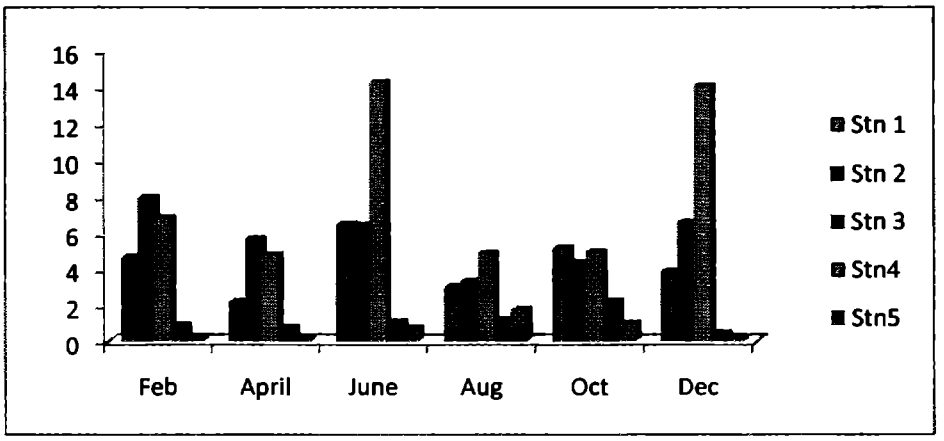
g) Con of Cd



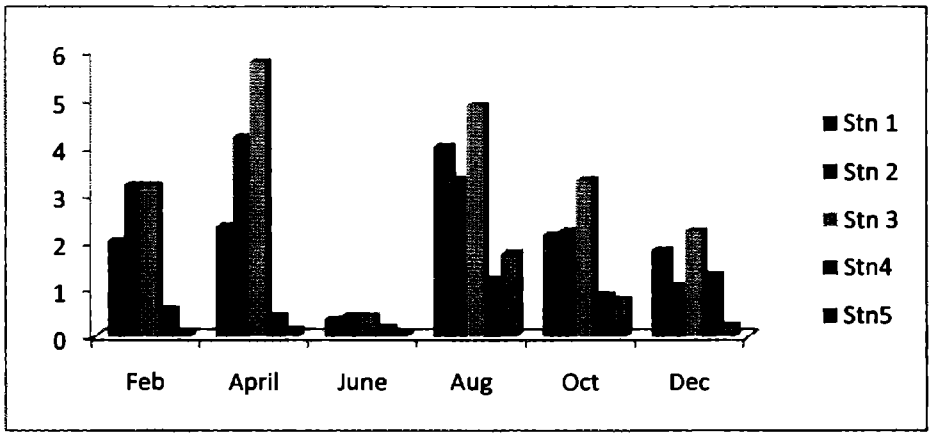
TOC



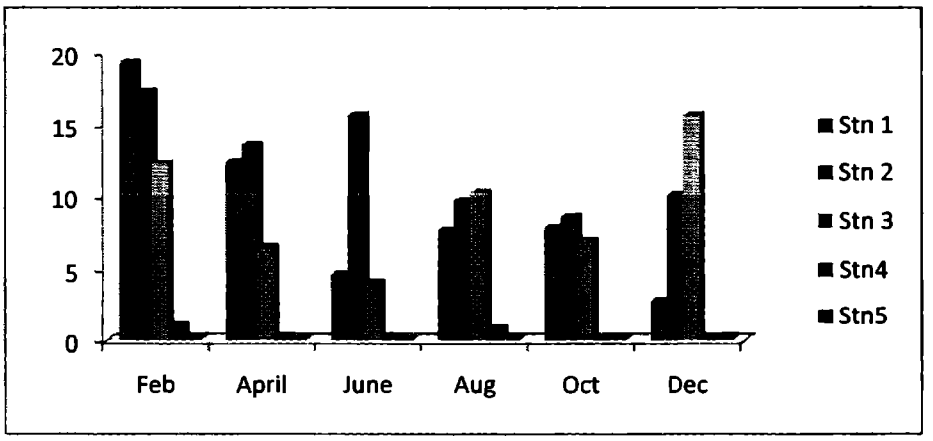
Tannin and Lignin



Exchangeable ammonium

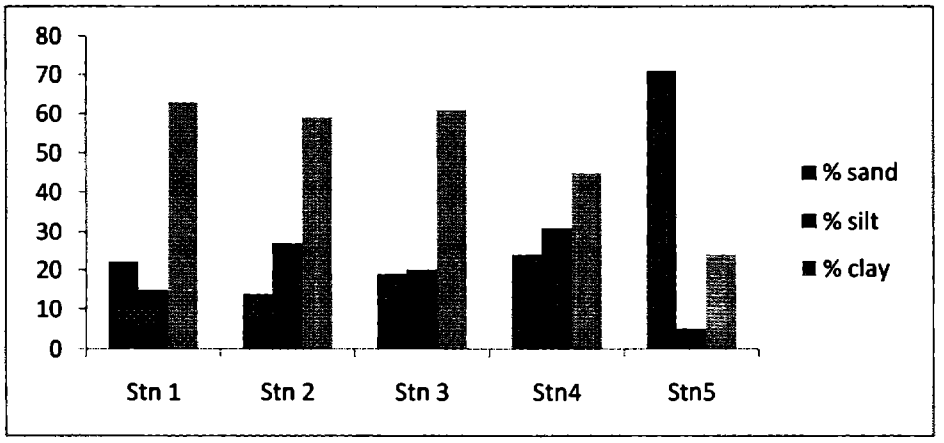


Protein

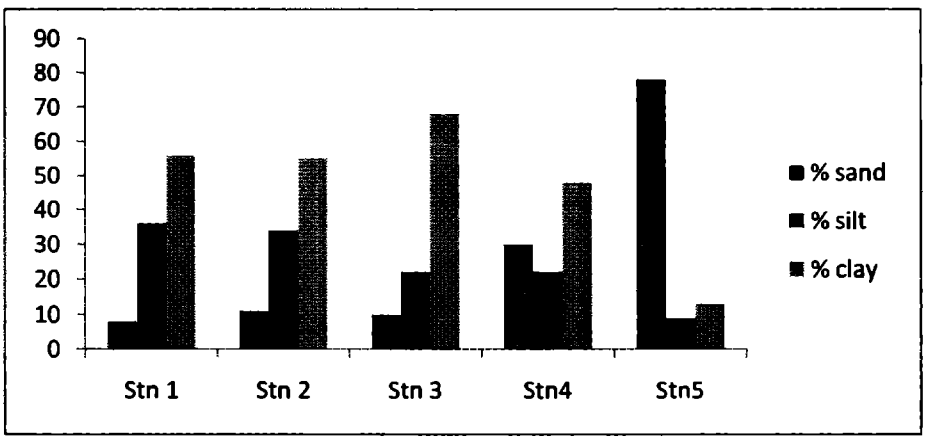


Texture of Sediments

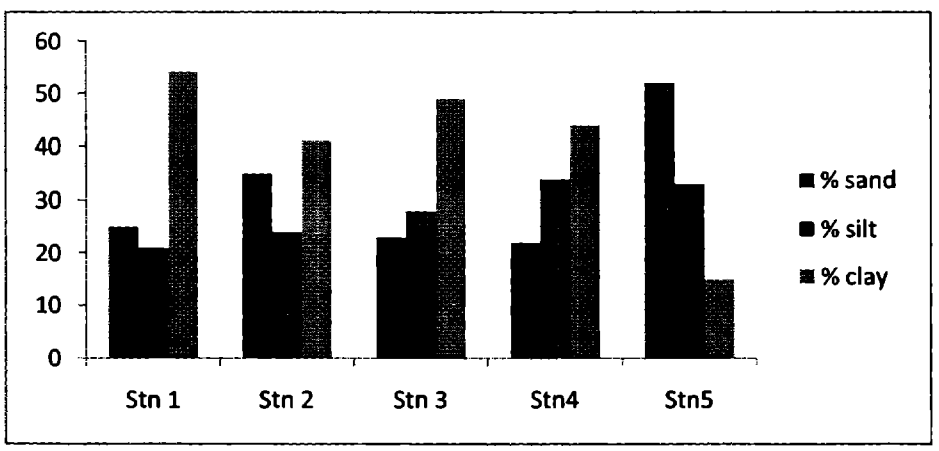
a) Pre-monsoon



b) Monsoon



c) Post Monsoon



Correlations (Total)					
		Protein	Organic Carbon	Tannin and Lignin	Ex. Ammonium
Protein	Pearson Correlation	1	.777(**)	.616(**)	.534(**)
	Sig. (2-tailed)		0	0	0.002
	N	30	30	30	30
Total Organic Carbon	Pearson Correlation	.777(**)	1	.749(**)	.590(**)
	Sig. (2-tailed)	0	.	0	0.001
	N	30	30	30	30
Tannin and Lignin	Pearson Correlation	.616(**)	749(**)	1	0.27
	Sig. (2-tailed)	0	0	.	0.149
	N	30	30	30	30
Exchangeable ammonium	Pearson Correlation	.534(**)	.590(**)	0.27	1
	Sig. (2-tailed)	0.002	0.001	0.149	.
	N	30	30	30	30
** Correlation is significant at the 0.01 level (2-tailed).					

Correlations(Premonsoon)					
		Protein	Total Organic Carbon	Tannin and Lignin	Exchangeable ammonium
Protein	Pearson Correlation	1	.864(**)	.828(**)	0.581
	Sig. (2-tailed)	.	0.001	0.003	0.078
	N	10	10	10	10
Total Organic Carbon	Pearson Correlation	.864(**)	1	.826(**)	.639(*)
	Sig. (2-tailed)	0.001	.	0.003	0.047
	N	10	10	10	10
Tannin and Lignin	Pearson Correlation	.828(**)	.826(**)	1	776(**)
	Sig. (2-tailed)	0.003	0.003	.	0.008
	N	10	10	10	10
Exchangeable ammonium	Pearson Correlation	0.581	.639(*)	776(**)	1
	Sig. (2-tailed)	0.078	0.047	0.008	.
	N	10	10	10	10
** Correlation is significant at the 0.01 level (2-tailed).					
* Correlation is significant at the 0.05 level (2-tailed).					

Correlations (Monsoon)					
		Protein	Total Organic Carbon	Tannin and Lignin	Exchangeable ammonium
Protein	Pearson Correlation	1	.630(*)	0.376	0.456
	Sig. (2-tailed)	.	0.021	0.205	0.117
	N	13	13	13	13
Total Organic Carbon	Pearson Correlation	.630(*)	1	.600(*)	.634(*)
	Sig. (2-tailed)	0.021	.	0.03	0.02
	N	13	13	13	13
Tannin and Lignin	Pearson Correlation	0.376	.600(*)	1	-0.012
	Sig. (2-tailed)	0.205	0.03	.	0.969
	N	13	13	13	13
Exchangeable ammonium	Pearson Correlation	0.456	.634(*)	-0.012	1
	Sig. (2-tailed)	0.117	0.02	0.969	.
	N	13	13	13	13
* Correlation is significant at the 0.05 level (2-tailed).					

Correlations (Postmonsoon)					
		Protein	Total Organic Carbon	Tannin and Lignin	Exchangeable ammonium
Protein	Pearson Correlation	1	758(**)	768(**)	.649(*)
	Sig. (2-tailed)	.	0.003	0.002	0.016
	N	13	13	13	13
Total Organic Carbon	Pearson Correlation	.758(**)	1	.868(**)	.727(**)
	Sig. (2-tailed)	0.003	.	0	0.005
	N	13	13	13	13
Tannin and Lignin	Pearson Correlation	768(**)	.868(**)	1	.582(*)
	Sig. (2-tailed)	0.002	0	.	0.037
	N	13	13	13	13
Exchangeable ammonium	Pearson Correlation	.649(*)	727(**)	.582(*)	1
	Sig. (2-tailed)	0.016	0.005	0.037	.
	N	13	13	13	13
** Correlation is significant at the 0.01 level (2-tailed).					
* Correlation is significant at the 0.05 level (2-tailed).					

Correlations (Station 1)					
		Protein	Total Organic Carbon	Tannin and Lignin	Ex. Ammonium
Protein	Pearson Correlation	1	-0.302	-0.212	0.188
	Sig. (2-tailed)		0.561	0.686	0.721
	N	6	6	6	6
Total Organic Carbon	Pearson Correlation	-0.302	1	-0.571	0.781
	Sig. (2-tailed)	0.561	.	0.236	0.067
	N	6	6	6	6
Tannin and Lignin	Pearson Correlation	-0.212	-0.571	1	-0.726
	Sig. (2-tailed)	0.686	0.236	.	0.102
	N	6	6	6	6
Exchangeable ammonium	Pearson Correlation	0.188	0.781	-0.726	1
	Sig. (2-tailed)	0.721	0.067	0.102	.
	N	6	6	6	6

Correlations (Station 2)					
		Protein	Total Organic Carbon	Tannin and Lignin	Ex. Ammonium
Protein	Pearson Correlation	1	-0.302	-0.212	0.188
	Sig. (2-tailed)	.	0.561	0.686	0.721
	N	6	6	6	6
Total Organic Carbon	Pearson Correlation	-0.302	1	-0.571	0.781
	Sig. (2-tailed)	0.561	.	0.236	0.067
	N	6	6	6	6
Tannin and Lignin	Pearson Correlation	-0.212	-0.571	1	-0.726
	Sig. (2-tailed)	0.686	0.236	.	0.102
	N	6	6	6	6
Exchangeable ammonium	Pearson Correlation	0.188	0.781	-0.726	1
	Sig. (2-tailed)	0.721	0.067	0.102	.
	N	6	6	6	6

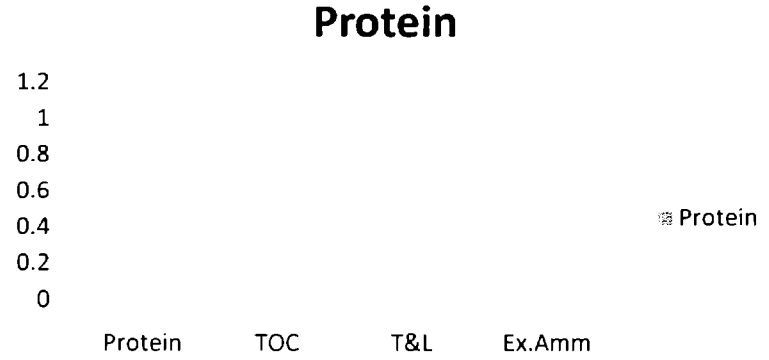
Correlations (Station 3)					
		Protein	Total Organic Carbon	Tannin and Lignin	Ex. Ammonium
Protein	Pearson Correlation	1	0.794	0.157	0.064
	Sig. (2-tailed)	.	0.059	0.766	0.904
	N	6	6	6	6
Total Organic Carbon	Pearson Correlation	0.794	1	0.473	-0.437
	Sig. (2-tailed)	0.059	.	0.344	0.387
	N	6	6	6	6
Tannin and Lignin	Pearson Correlation	0.157	0.473	1	-.855(*)
	Sig. (2-tailed)	0.766	0.344	.	0.03
	N	6	6	6	6
Exchangeable ammonium	Pearson Correlation	0.064	-0.437	-.855(*)	1
	Sig. (2-tailed)	0.904	0.387	0.03	.
	N	6	6	6	6
* Correlation is significant at the 0.05 level (2-tailed).					

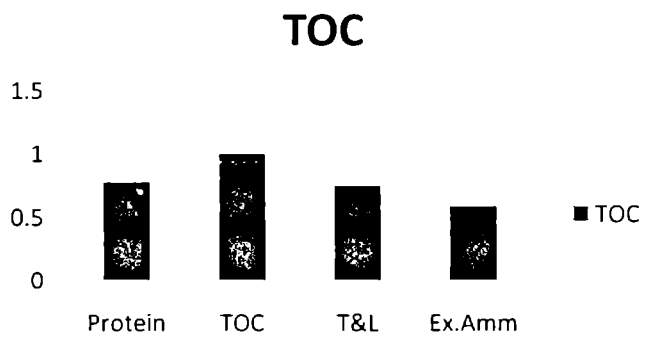
Correlations (Station 4)					
		Protein	Total Organic Carbon	Tannin and Lignin	Ex. Ammonium
Protein	Pearson Correlation	1	-0.367	-0.147	-0.069
	Sig. (2-tailed)		0.474	0.781	0.896
	N	6	6	6	6
Total Organic Carbon	Pearson Correlation	-0.367	1	0.639	0.259
	Sig. (2-tailed)	0.474	.	0.172	0.62
	N	6	6	6	6
Tannin and Lignin	Pearson Correlation	-0.147	0.639	1	-0.009
	Sig. (2-tailed)	0.781	0.172	.	0 986
	N	6	6	6	6
Exchangeable ammonium	Pearson Correlation	-0.069	0.259	-0.009	1
	Sig. (2-tailed)	0.896	0.62	0.986	.
	N	6	6	6	6

Correlations(Station 5)					
		Protein	Total Organic Carbon	Tannin and Lignin	Ex. Ammonium
Protein	Pearson Correlation	1	0.651	-0.013	0.188
	Sig. (2-tailed)	.	0.162	0.981	0.722
	N	6	6	6	6
Total Organic Carbon	Pearson Correlation	0.651	1	0.109	0.19
	Sig. (2-tailed)	0.162	.	0.837	0.718
	N	6	6	6	6
Tannin and Lignin	Pearson Correlation	-0.013	0.109	1	.920(**)
	Sig. (2-tailed)	0.981	0.837	.	0.009
	N	6	6	6	6
Exchangeable ammonium	Pearson Correlation	0.188	0.19	.920(**)	1
	Sig. (2-tailed)	0.722	0.718	0.009	.
	N	6	6	6	6
** Correlation is significant at the 0.01 level (2-tailed).					

Graphs of Correlation

a) Total Correlation

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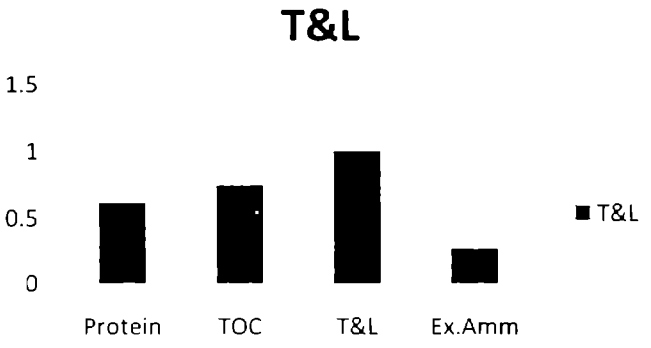
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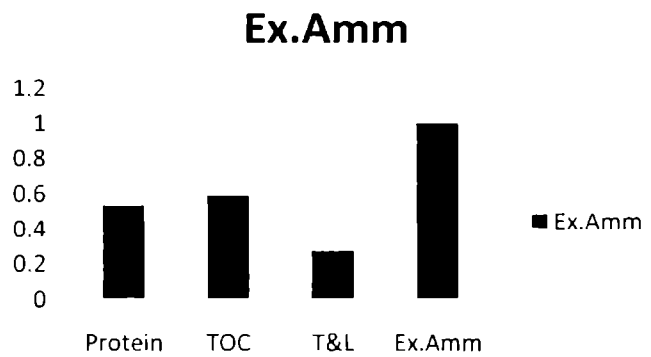
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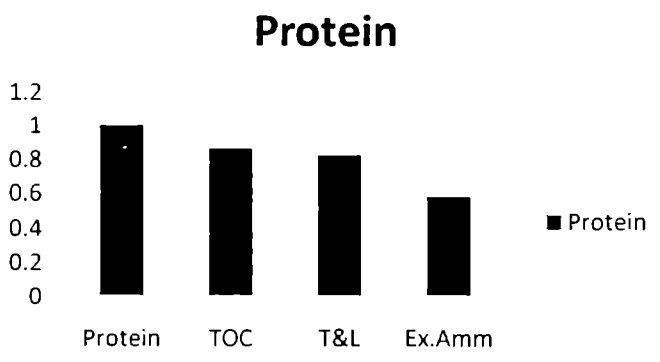
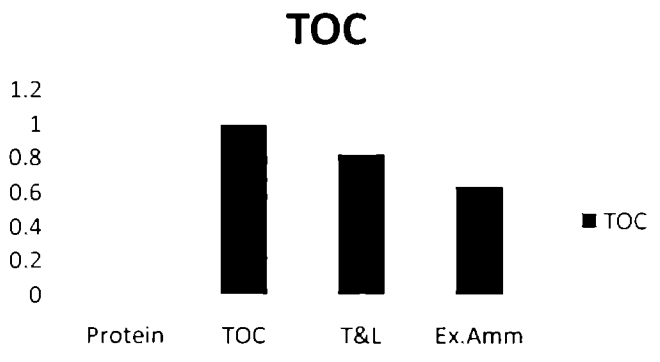
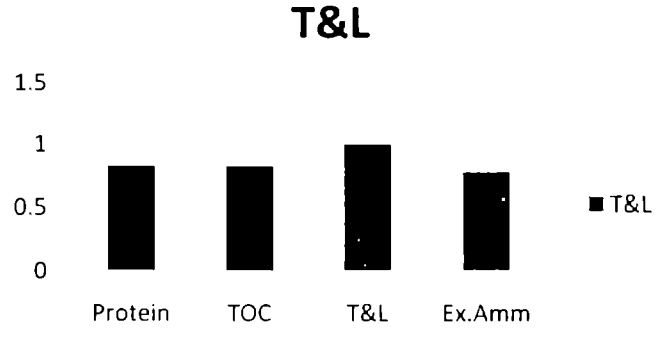
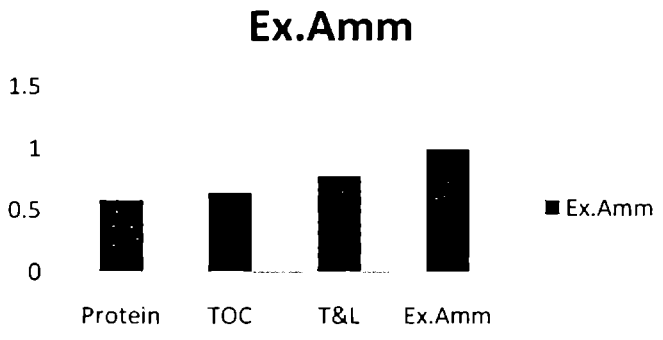
b) Seasonal

Premonsoon





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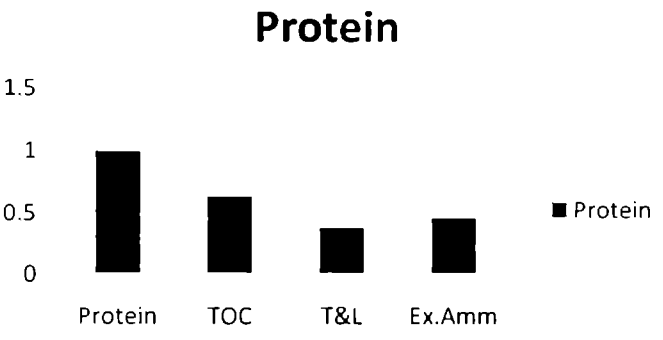
Monsoon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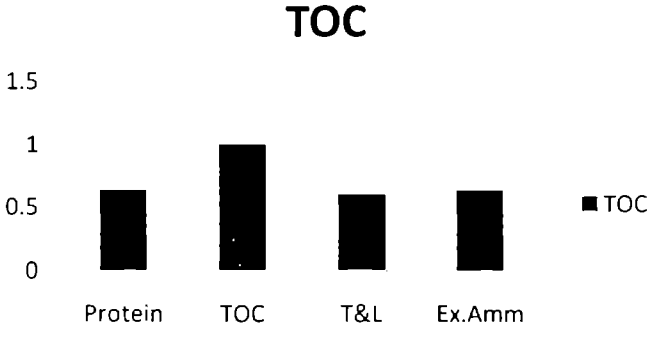
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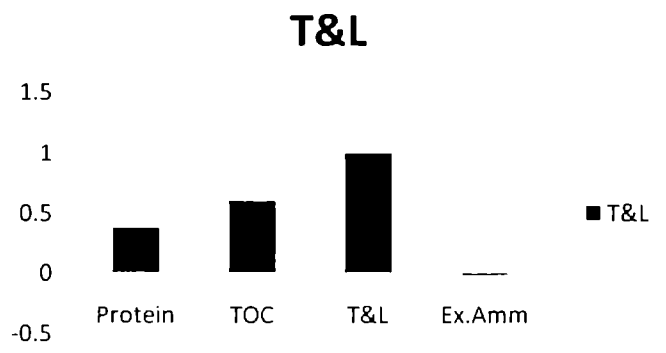
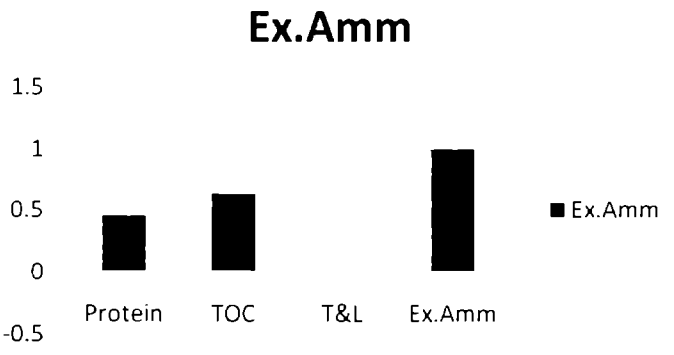
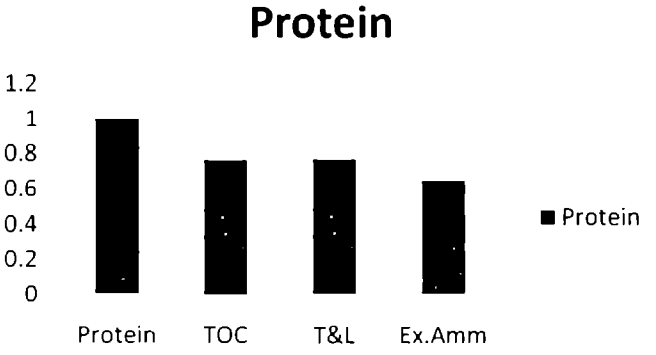
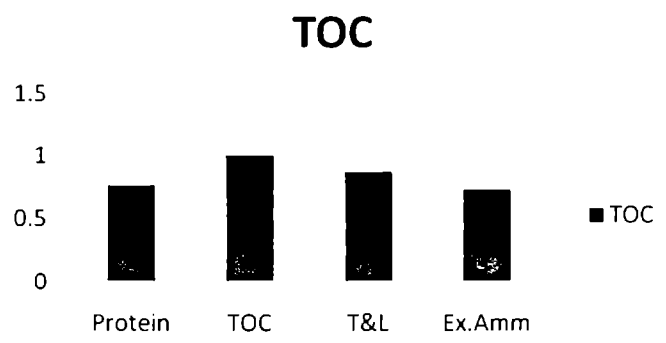




Post Monsoon

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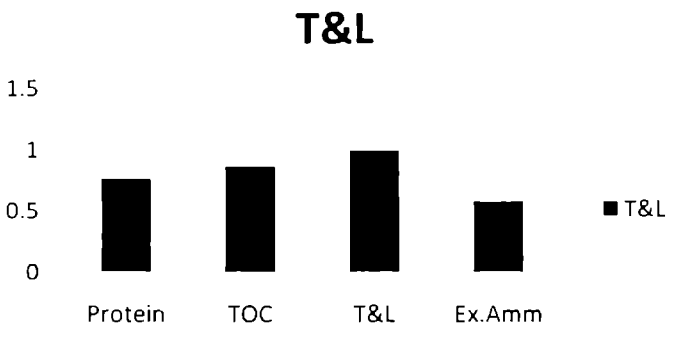
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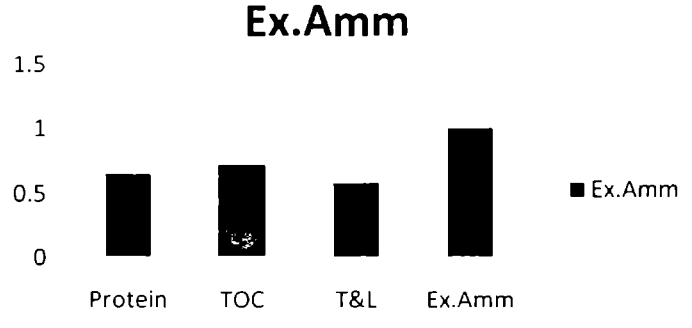
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Ex.Amm

Correlations (Total)											
		sand	silt	clay	Fe	Mn	Zn	Ni	Pb	Cu	Cd
sand	Pearson Correlation	1	.646(**)	.908(**)	-0.44	-0.469	-0.312	-.587(*)	-0.35	-.553(*)	0.412
	Sig. (2-tailed)	.	0.009	0	0.104	0.078	0.257	0.022	0.201	0.032	0.127
	N	15	15	15	15	15	15	15	15	15	15
silt	Pearson Correlation	.646(**)	1	0.266	0.102	0.33	0.094	0.315	0.176	0.232	0.095
	Sig. (2-tailed)	0.009	.	0.337	0.716	0.23	0.738	0.252	0.53	0.406	0.736
	N	15	15	15	15	15	15	15	15	15	15
clay	Pearson Correlation	.908(**)	0.266	1	0.494	0.411	0.343	.567(*)	0.345	.571(*)	0.468
	Sig. (2-tailed)	0	0.337	.	0.061	0.128	0.211	0.027	0.208	0.026	0.078
	N	15	15	15	15	15	15	15	15	15	15
Fe	Pearson Correlation	-0.436	0.102	0.494	1	.834(**)	.527(*)	.900(**)	0.501	.865(**)	0.096
	Sig. (2-tailed)	0.104	0.716	0.061	.	0	0.044	0	0.057	0	0.733
	N	15	15	15	15	15	15	15	15	15	15
Mn	Pearson Correlation	-0.469	0.33	0.411	.834(**)	1	0.483	.828(**)	0.393	.802(**)	0.025
	Sig. (2-tailed)	0.078	0.23	0.128	0	.	0.068	0	0.148	0	0.93
	N	15	15	15	15	15	15	15	15	15	15
Zn	Pearson Correlation	-0.312	0.094	0.343	.527(*)	0.483	1	.696(**)	.722(**)	.741(**)	0.102
	Sig. (2-tailed)	0.257	0.738	0.211	0.044	0.068	.	0.004	0.002	0.002	0.718
	N	15	15	15	15	15	15	15	15	15	15
Ni	Pearson Correlation	-.587(*)	0.315	.567(*)	.900(**)	.828(**)	.696(**)	1	.529(*)	.892(**)	0.117
	Sig. (2-tailed)	0.022	0.252	0.027	0	0	0.004	.	0.043	0	0.679
	N	15	15	15	15	15	15	15	15	15	15
Pb	Pearson Correlation	-0.35	0.176	0.345	0.501	0.393	.722(**)	.529(*)	1	.713(**)	0.137
	Sig. (2-tailed)	0.201	0.53	0.208	0.057	0.148	0.002	0.043	.	0.003	0.628
	N	15	15	15	15	15	15	15	15	15	15
Cu	Pearson Correlation	-.553(*)	0.232	.571(*)	.865(**)	.802(**)	.741(**)	.892(**)	.713(**)	1	0.044
	Sig. (2-tailed)	0.032	0.406	0.026	0	0	0.002	0	0.003	.	0.877
	N	15	15	15	15	15	15	15	15	15	15
Cd	Pearson Correlation	-0.412	0.095	0.468	-0.1	-0.025	0.102	0.117	0.137	0.044	1
	Sig. (2-tailed)	0.127	0.736	0.078	0.733	0.93	0.718	0.679	0.628	0.877	.
	N	15	15	15	15	15	15	15	15	15	15

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

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

Correlations (Premonsoon)											
		sand	silt	clay	Fe	Mn	Zn	Ni	Pb	Cu	Cd
sand	Pearson Correlation	1	0.792	.924(*)	-0.67	-0.748	0.407	-0.718	-0.731	-0.702	0.208
	Sig. (2-tailed)	.	0.11	0.025	0.213	0.146	0.496	0.172	0.16	0.186	0.737
	N	5	5	5	5	5	5	5	5	5	5
silt	Pearson Correlation	-0.792	1	0.498	0.172	0.253	0.004	0.284	0.294	0.26	0.515
	Sig. (2-tailed)	0.11	.	0.393	0.782	0.682	0.995	0.644	0.631	0.673	0.375
	N	5	5	5	5	5	5	5	5	5	5
clay	Pearson Correlation	.924(*)	0.498	1	0.847	.904(*)	0.58	0.842	0.854	0.834	0.026
	Sig. (2-tailed)	0.025	0.393	.	0.07	0.035	0.305	0.074	0.066	0.079	0.967
	N	5	5	5	5	5	5	5	5	5	5
Fe	Pearson Correlation	-0.673	0.172	0.847	1	0.84	0.503	.952(*)	.937(*)	0.864	0.049
	Sig. (2-tailed)	0.213	0.782	0.07	.	0.075	0.387	0.013	0.019	0.059	0.938
	N	5	5	5	5	5	5	5	5	5	5
Mn	Pearson Correlation	-0.748	0.253	.904(*)	0.84	1	0.339	0.704	0.698	0.632	0.105
	Sig. (2-tailed)	0.146	0.682	0.035	0.075	.	0.576	0.185	0.19	0.253	0.867
	N	5	5	5	5	5	5	5	5	5	5
Zn	Pearson Correlation	-0.407	0.004	0.58	0.503	0.339	1	0.661	0.704	0.831	0.8
	Sig. (2-tailed)	0.496	0.995	0.305	0.387	0.576	.	0.225	0.185	0.081	0.104
	N	5	5	5	5	5	5	5	5	5	5
Ni	Pearson Correlation	-0.718	0.284	0.842	.952(*)	0.704	0.661	1	.998(**)	.964(**)	0.176
	Sig. (2-tailed)	0.172	0.644	0.074	0.013	0.185	0.225	.	0	0.008	0.777
	N	5	5	5	5	5	5	5	5	5	5
Pb	Pearson Correlation	-0.731	0.294	0.854	.937(*)	0.698	0.704	.998(**)	1	.979(**)	0.219
	Sig. (2-tailed)	0.16	0.631	0.066	0.019	0.19	0.185	0	.	0.004	0.723
	N	5	5	5	5	5	5	5	5	5	5
Cu	Pearson Correlation	-0.702	0.26	0.834	0.864	0.632	0.831	.964(**)	.979(**)	1	0.386
	Sig. (2-tailed)	0.186	0.673	0.079	0.059	0.253	0.081	0.008	0.004	.	0.521
	N	5	5	5	5	5	5	5	5	5	5
Cd	Pearson Correlation	0.208	0.515	0.026	0.049	-0.105	0.8	0.176	0.219	0.386	1
	Sig. (2-tailed)	0.737	0.375	0.967	0.938	0.867	0.104	0.777	0.723	0.521	.
	N	5	5	5	5	5	5	5	5	5	5

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

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

Correlations (Monsoon)											
		sand	silt	clay	Fe	Mn	Zn	Ni	Pb	Cu	Cd
sand	Pearson Correlation	1	-0.871	.967(**)	-0.57	-0.706	-0.521	-0.658	0.508	-.905(*)	0.624
	Sig. (2-tailed)	.	0.054	0.007	0.319	0.183	0.368	0.227	0.382	0.035	0.261
	N	5	5	5	5	5	5	5	5	5	5
silt	Pearson Correlation	-0.871	1	0.716	0.819	.915(*)	0.771	0.863	0.275	.967(**)	0.305
	Sig. (2-tailed)	0.054	.	0.173	0.09	0.029	0.127	0.06	0.655	0.007	0.617
	N	5	5	5	5	5	5	5	5	5	5
clay	Pearson Correlation	.967(**)	0.716	1	0.377	0.525	0.338	0.485	0.579	0.782	0.727
	Sig. (2-tailed)	0.007	0.173	.	0.531	0.364	0.578	0.407	0.306	0.118	0.164
	N	5	5	5	5	5	5	5	5	5	5
Fe	Pearson Correlation	-0.567	0.819	0.377	1	.980(**)	.989(**)	.993(**)	0.123	0.854	0.131
	Sig. (2-tailed)	0.319	0.09	0.531	.	0.003	0.001	0.001	0.844	0.066	0.834
	N	5	5	5	5	5	5	5	5	5	5
Mn	Pearson Correlation	-0.706	.915(*)	0.525	.980(**)	1	.955(*)	.992(**)	0.007	.935(*)	0.209
	Sig. (2-tailed)	0.183	0.029	0.364	0.003	.	0.011	0.001	0.991	0.02	0.736
	N	5	5	5	5	5	5	5	5	5	5
Zn	Pearson Correlation	-0.521	0.771	0.338	.989(**)	.955(*)	1	.977(**)	0.069	0.807	0.198
	Sig. (2-tailed)	0.368	0.127	0.578	0.001	0.011	.	0.004	0.912	0.099	0.749
	N	5	5	5	5	5	5	5	5	5	5
Ni	Pearson Correlation	-0.658	0.863	0.485	.993(**)	.992(**)	.977(**)	1	0.047	.906(*)	0.217
	Sig. (2-tailed)	0.227	0.06	0.407	0.001	0.001	0.004	.	0.94	0.034	0.726
	N	5	5	5	5	5	5	5	5	5	5
Pb	Pearson Correlation	-0.508	0.275	0.579	-0.12	0.007	-0.069	-0.047	1	0.201	0.808
	Sig. (2-tailed)	0.382	0.655	0.306	0.844	0.991	0.912	0.94	.	0.745	0.098
	N	5	5	5	5	5	5	5	5	5	5
Cu	Pearson Correlation	-.905(*)	.967(**)	0.782	0.854	.935(*)	0.807	.906(*)	0.201	1	0.383
	Sig. (2-tailed)	0.035	0.007	0.118	0.066	0.02	0.099	0.034	0.745	.	0.525
	N	5	5	5	5	5	5	5	5	5	5
Cd	Pearson Correlation	-0.624	0.305	0.727	0.131	0.209	0.198	0.217	0.808	0.383	1
	Sig. (2-tailed)	0.261	0.617	0.164	0.834	0.736	0.749	0.726	0.098	0.525	.
	N	5	5	5	5	5	5	5	5	5	5

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

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

Correlations (Post Monsoon)											
		sand	silt	clay	Fe	Mn	Zn	Ni	Pb	Cu	Cd
sand	Pearson Correlation	1	0.272	.934(*)	-0.2	-0.281	-0.312	-0.312	0	-0.335	-0.207
	Sig. (2-tailed)	.	0.658	0.02	0.749	0.647	0.609	0.609	0.999	0.582	0.739
	N	5	5	5	5	5	5	5	5	5	5
silt	Pearson Correlation	0.272	1	-0.597	-.915(*)	-.931(*)	-0.281	-.878(*)	-0.117	-.900(*)	-0.381
	Sig. (2-tailed)	0.658	.	0.288	0.029	0.021	0.647	0.05	0.851	0.037	0.527
	N	5	5	5	5	5	5	5	5	5	5
clay	Pearson Correlation	.934(*)	-0.597	1	0.505	0.58	0.365	0.586	0.043	0.613	0.313
	Sig. (2-tailed)	0.02	0.288	.	0.386	0.306	0.546	0.3	0.945	0.272	0.608
	N	5	5	5	5	5	5	5	5	5	5
Fe	Pearson Correlation	-0.199	.915(*)	0.505	1	.993(**)	0.287	0.875	0.205	.914(*)	0.367
	Sig. (2-tailed)	0.749	0.029	0.386	.	0.001	0.64	0.052	0.741	0.03	0.543
	N	5	5	5	5	5	5	5	5	5	5
Mn	Pearson Correlation	-0.281	.931(*)	0.58	.993(**)	1	0.37	.917(*)	0.259	.950(*)	0.442
	Sig. (2-tailed)	0.647	0.021	0.306	0.001	.	0.54	0.028	0.674	0.013	0.456
	N	5	5	5	5	5	5	5	5	5	5
Zn	Pearson Correlation	-0.312	-0.281	0.365	0.287	0.37	1	0.684	.938(*)	0.627	.985(**)
	Sig. (2-tailed)	0.609	0.647	0.546	0.64	0.54	.	0.203	0.018	0.258	0.002
	N	5	5	5	5	5	5	5	5	5	5
Ni	Pearson Correlation	-0.312	.878(*)	0.586	0.875	.917(*)	0.684	1	0.562	.995(**)	0.751
	Sig. (2-tailed)	0.609	0.05	0.3	0.052	0.028	0.203	.	0.324	0	0.144
	N	5	5	5	5	5	5	5	5	5	5
Pb	Pearson Correlation	0	-0.117	0.043	0.205	0.259	.938(*)	0.562	1	0.499	.938(*)
	Sig. (2-tailed)	0.999	0.851	0.945	0.741	0.674	0.018	0.324	.	0.392	0.018
	N	5	5	5	5	5	5	5	5	5	5
Cu	Pearson Correlation	-0.335	.900(*)	0.613	.914(*)	.950(*)	0.627	.995(**)	0.499	1	0.691
	Sig. (2-tailed)	0.582	0.037	0.272	0.03	0.013	0.258	0	0.392	.	0.197
	N	5	5	5	5	5	5	5	5	5	5
Cd	Pearson Correlation	-0.207	-0.381	0.313	0.367	0.442	.985(**)	0.751	.938(*)	0.691	1
	Sig. (2-tailed)	0.739	0.527	0.608	0.543	0.456	0.002	0.144	0.018	0.197	.
	N	5	5	5	5	5	5	5	5	5	5

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

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

Correlations (Station 1)											
		sand	silt	clay	Fe	Mn	Zn	Ni	Pb	Cu	Cd
sand	Pearson Correlation	1	0.902	0.144	0.852	0.73	-0.98	-0.167	0.243	0.78	0.986
	Sig. (2-tailed)	.	0.285	0.908	0.351	0.479	0.128	0.893	0.844	0.431	0.106
	N	3	3	3	3	3	3	3	3	3	3
silt	Pearson Correlation	0.902	1	-0.558	-1	-0.363	0.797	0.577	-0.2	-0.432	0.961
	Sig. (2-tailed)	0.285	.	0.623	0.067	0.764	0.413	0.609	0.872	0.715	0.179
	N	3	3	3	3	3	3	3	3	3	3
clay	Pearson Correlation	0.144	0.558	1	0.641	-0.571	0.057	1.000(*)	0.925	-0.508	0.305
	Sig. (2-tailed)	0.908	0.623	.	0.557	0.613	0.964	0.015	0.248	0.661	0.803
	N	3	3	3	3	3	3	3	3	3	3
Fe	Pearson Correlation	0.852	0.995	0.641	1	0.263	-0.73	-0.659	0.301	0.336	0.926
	Sig. (2-tailed)	0.351	0.067	0.557	.	0.83	0.479	0.542	0.805	0.782	0.246
	N	3	3	3	3	3	3	3	3	3	3
Mn	Pearson Correlation	0.73	0.363	-0.571	0.263	1	0.852	0.552	-0.84	.997(*)	0.607
	Sig. (2-tailed)	0.479	0.764	0.613	0.83	.	0.351	0.627	0.365	0.048	0.585
	N	3	3	3	3	3	3	3	3	3	3
Zn	Pearson Correlation	-0.98	0.797	0.057	-0.73	-0.852	1	-0.034	0.432	-0.889	0.933
	Sig. (2-tailed)	0.128	0.413	0.964	0.479	0.351	.	0.978	0.716	0.303	0.234
	N	3	3	3	3	3	3	3	3	3	3
Ni	Pearson Correlation	0.167	0.577	1.000(*)	-0.66	0.552	0.034	1	0.916	0.488	0.327
	Sig. (2-tailed)	0.893	0.609	0.015	0.542	0.627	0.978	.	0.263	0.676	0.788
	N	3	3	3	3	3	3	3	3	3	3
Pb	Pearson Correlation	0.243	-0.2	0.925	0.301	-0.84	0.432	-0.916	1	-0.797	0.08
	Sig. (2-tailed)	0.844	0.872	0.248	0.805	0.365	0.716	0.263	.	0.413	0.949
	N	3	3	3	3	3	3	3	3	3	3
Cu	Pearson Correlation	0.78	0.432	-0.508	0.336	.997(*)	0.889	0.488	0.797	1	0.666
	Sig. (2-tailed)	0.431	0.715	0.661	0.782	0.048	0.303	0.676	0.413	.	0.536
	N	3	3	3	3	3	3	3	3	3	3
Cd	Pearson Correlation	0.986	0.961	-0.305	-0.93	-0.607	0.933	0.327	0.08	-0.666	1
	Sig. (2-tailed)	0.106	0.179	0.803	0.246	0.585	0.234	0.788	0.949	0.536	.
	N	3	3	3	3	3	3	3	3	3	3

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

Correlations (Station 2)											
		sand	silt	clay	Fe	Mn	Zn	Ni	Pb	Cu	Cd
sand	Pearson Correlation	1	-0.805	-0.947	0.718	0.781	-1.000(**)	-0.968	0.391	0.676	-0.468
	Sig. (2-tailed)	.	0.405	0.209	0.49	0.429	0	0.161	0.744	0.528	0.69
	N	3	3	3	3	3	3	3	3	3	3
silt	Pearson Correlation	-0.805	1	0.57	-0.99	-0.258	0.805	0.927	-0.861	-0.981	0.901
	Sig. (2-tailed)	0.405	.	0.614	0.086	0.834	0.405	0.244	0.34	0.123	0.285
	N	3	3	3	3	3	3	3	3	3	3
clay	Pearson Correlation	-0.947	0.57	1	-0.46	-0.941	0.947	0.836	-0.074	-0.402	0.159
	Sig. (2-tailed)	0.209	0.614	.	0.699	0.22	0.209	0.37	0.953	0.737	0.899
	N	3	3	3	3	3	3	3	3	3	3
Fe	Pearson Correlation	0.718	-0.991	-0.455	1	0.126	-0.718	-0.869	0.921	.998(*)	-0.951
	Sig. (2-tailed)	0.49	0.086	0.699	.	0.919	0.49	0.329	0.254	0.038	0.2
	N	3	3	3	3	3	3	3	3	3	3
Mn	Pearson Correlation	0.781	-0.258	-0.941	0.126	1	-0.781	-0.601	-0.269	0.067	0.186
	Sig. (2-tailed)	0.429	0.834	0.22	0.919	.	0.429	0.59	0.827	0.957	0.881
	N	3	3	3	3	3	3	3	3	3	3
Zn	Pearson Correlation	1.000(**)	0.805	0.947	-0.72	-0.781	1	0.968	-0.391	-0.676	0.468
	Sig. (2-tailed)	0	0.405	0.209	0.49	0.429	.	0.161	0.744	0.528	0.69
	N	3	3	3	3	3	3	3	3	3	3
Ni	Pearson Correlation	-0.968	0.927	0.836	-0.87	-0.601	0.968	1	-0.609	-0.838	0.674
	Sig. (2-tailed)	0.161	0.244	0.37	0.329	0.59	0.161	.	0.583	0.367	0.529
	N	3	3	3	3	3	3	3	3	3	3
Pb	Pearson Correlation	0.391	-0.861	-0.074	0.921	-0.269	-0.391	-0.609	1	0.943	-0.996
	Sig. (2-tailed)	0.744	0.34	0.953	0.254	0.827	0.744	0.583	.	0.216	0.054
	N	3	3	3	3	3	3	3	3	3	3
Cu	Pearson Correlation	0.676	-0.981	-0.402	.998(*)	0.067	-0.676	-0.838	0.943	1	-0.968
	Sig. (2-tailed)	0.528	0.123	0.737	0.038	0.957	0.528	0.367	0.216	.	0.162
	N	3	3	3	3	3	3	3	3	3	3
Cd	Pearson Correlation	-0.468	0.901	0.159	-0.95	0.186	0.468	0.674	-0.996	-0.968	1
	Sig. (2-tailed)	0.69	0.285	0.899	0.2	0.881	0.69	0.529	0.054	0.162	.
	N	3	3	3	3	3	3	3	3	3	3

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

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

Correlations (Station 3)											
		sand	silt	clay	Fe	Mn	Zn	Ni	Pb	Cu	Cd
sand	Pearson Correlation	1	0.553	-0.933	0.848	0.951	0.993	0.997	0.913	0.941	-0.965
	Sig. (2-tailed)	.	0.627	0.235	0.356	0.2	0.075	0.053	0.268	0.22	0.169
	N	3	3	3	3	3	3	3	3	3	3
silt	Fearson Correlation	0.553	1	-0.817	0.027	0.784	0.451	0.482	0.845	0.238	-0.315
	Sig. (2-tailed)	0.627	.	0.392	0.983	0.427	0.702	0.68	0.359	0.847	0.796
	N	3	3	3	3	3	3	3	3	3	3
clay	Pearson Correlation	-0.933	-0.817	1	-0.6	.998(*)	-0.884	-0.899	.999(*)	-0.755	0.805
	Sig. (2-tailed)	0.235	0.392	.	0.591	0.035	0.31	0.288	0.033	0.455	0.404
	N	3	3	3	3	3	3	3	3	3	3
Fe	Pearson Correlation	0.848	0.027	-0.599	1	0.642	0.904	0.889	0.557	0.977	-0.957
	Sig. (2-tailed)	0.356	0.983	0.591	.	0.556	0.281	0.303	0.624	0.136	0.187
	N	3	3	3	3	3	3	3	3	3	3
Mn	Pearson Correlation	0.951	0.784	.998(*)	0.642	1	0.908	0.922	0.994	0.79	-0.836
	Sig. (2-tailed)	0.2	0.427	0.035	0.556	.	0.275	0.253	0.067	0.42	0.369
	N	3	3	3	3	3	3	3	3	3	3
Zn	Pearson Correlation	0.993	0.451	-0.884	0.904	0.908	1	999(*)	0.858	0.974	-0.989
	Sig. (2-tailed)	0.075	0.702	0.31	0.281	0.275	.	0.022	0.343	0.145	0.094
	N	3	3	3	3	3	3	3	3	3	3
Ni	Pearson Correlation	0.997	0.482	-0.899	0.889	0.922	.999(*)	1	0.876	0.966	-0.983
	Sig. (2-tailed)	0.053	0.68	0.288	0.303	0.253	0.022	.	0.32	0.167	0.117
	N	3	3	3	3	3	3	3	3	3	3
Pb	Pearson Correlation	0.913	0.845	.999(*)	0.557	0.994	0.858	0.876	1	0.721	-0.774
	Sig. (2-tailed)	0.268	0.359	0.033	0.624	0.067	0.343	0.32	.	0.488	0.437
	N	3	3	3	3	3	3	3	3	3	3
Cu	Pearson Correlation	0.941	0.238	-0.755	0.977	0.79	0.974	0.966	0.721	1	-0.997
	Sig. (2-tailed)	0.22	0.847	0.455	0.136	0.42	0.145	0.167	0.488	.	0.051
	N	3	3	3	3	3	3	3	3	3	3
Cd	Pearson Correlation	-0.965	-0.315	0.805	-0.96	-0.836	-0.989	-0.983	-0.774	-0.997	1
	Sig. (2-tailed)	0.169	0.796	0.404	0.187	0.369	0.094	0.117	0.437	0.051	.
	N	3	3	3	3	3	3	3	3	3	3

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

Correlations (Station 4)

		sand	silt	clay	Fe	Mn	Zn	Ni	Pb	Cu	Cd
sand	Pearson Correlation	1	1.000(**)	1.000(**)	-0.96	-0.983	0.996	0.931	0.424	0.2	0.983
	Sig. (2-tailed)	.	.	.	0.184	0.116	0.055	0.239	0.721	0.872	0.118
	N	3	3	3	3	3	3	3	3	3	3
silt	Pearson Correlation	-1.000(**)	1	1.000(**)	0.958	0.983	0.996	0.931	0.424	-0.2	0.983
	Sig. (2-tailed)	.	.	.	0.184	0.116	0.055	0.239	0.721	0.872	0.118
	N	3	3	3	3	3	3	3	3	3	3
clay	Pearson Correlation	1.000(**)	1.000(**)	1	-0.96	-0.983	0.996	0.931	0.424	0.2	0.983
	Sig. (2-tailed)	.	.	.	0.184	0.116	0.055	0.239	0.721	0.872	0.118
	N	3	3	3	3	3	3	3	3	3	3
Fe	Pearson Correlation	-0.958	0.958	-0.958	1	0.994	0.979	0.996	0.665	0.472	0.995
	Sig. (2-tailed)	0.184	0.184	0.184	.	0.068	0.129	0.055	0.537	0.687	0.066
	N	3	3	3	3	3	3	3	3	3	3
Mn	Pearson Correlation	-0.983	0.983	-0.983	0.994	1	0.995	0.982	0.582	0.375	1.000(**)
	Sig. (2-tailed)	0.116	0.116	0.116	0.068	.	0.061	0.122	0.605	0.755	0.002
	N	3	3	3	3	3	3	3	3	3	3
Zn	Pearson Correlation	-0.996	0.996	-0.996	0.979	0.995	1	0.959	0.501	0.284	0.995
	Sig. (2-tailed)	0.055	0.055	0.055	0.129	0.061	.	0.184	0.666	0.817	0.063
	N	3	3	3	3	3	3	3	3	3	3
Ni	Pearson Correlation	-0.931	0.931	-0.931	0.996	0.982	0.959	1	0.727	0.545	0.982
	Sig. (2-tailed)	0.239	0.239	0.239	0.055	0.122	0.184	.	0.482	0.633	0.12
	N	3	3	3	3	3	3	3	3	3	3
Pb	Pearson Correlation	0.424	0.424	0.424	-0.67	-0.582	0.501	0.727	1	0.972	0.584
	Sig. (2-tailed)	0.721	0.721	0.721	0.537	0.605	0.666	0.482	.	0.151	0.603
	N	3	3	3	3	3	3	3	3	3	3
Cu	Pearson Correlation	0.2	-0.2	0.2	-0.47	-0.375	0.284	0.545	0.972	1	0.378
	Sig. (2-tailed)	0.872	0.872	0.872	0.687	0.755	0.817	0.633	0.151	.	0.753
	N	3	3	3	3	3	3	3	3	3	3
Cd	Pearson Correlation	0.983	0.983	0.983	-1	1.000(**)	0.995	0.982	0.584	0.378	1
	Sig. (2-tailed)	0.118	0.118	0.118	0.066	0.002	0.063	0.12	0.603	0.753	.
	N	3	3	3	3	3	3	3	3	3	3

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

Correlations (Station 5)											
		sand	silt	clay	Fe	Mn	Zn	Ni	Pb	Cu	Cd
sand	Pearson Correlation	1	-0.923	0.089	-0.78	-0.991	0.633	-0.989	0.971	1.000(**)	0.046
	Sig. (2-tailed)	.	0.252	0.943	0.428	0.085	0.564	0.093	0.155	0.008	0.971
	N	3	3	3	3	3	3	3	3	3	3
silt	Pearson Correlation	-0.923	1	-0.466	0.482	0.864	0.286	0.857	0.988	0.928	-0.427
	Sig. (2-tailed)	0.252	.	0.692	0.68	0.336	0.816	0.344	0.097	0.244	0.719
	N	3	3	3	3	3	3	3	3	3	3
clay	Pearson Correlation	0.089	0.466	1	0.551	0.044	0.715	0.057	0.326	-0.102	.999(*)
	Sig. (2-tailed)	0.943	0.692	.	0.629	0.972	0.493	0.964	0.788	0.935	0.027
	N	3	3	3	3	3	3	3	3	3	3
Fe	Pearson Correlation	-0.783	0.482	0.551	1	0.858	0.977	0.865	0.609	0.774	0.586
	Sig. (2-tailed)	0.428	0.68	0.629	.	0.343	0.136	0.335	0.583	0.436	0.601
	N	3	3	3	3	3	3	3	3	3	3
Mn	Pearson Correlation	-0.991	0.864	0.044	0.858	1	0.73	1.000(**)	0.93	0.989	0.087
	Sig. (2-tailed)	0.085	0.336	0.972	0.343	.	0.479	0.008	0.24	0.093	0.945
	N	3	3	3	3	3	3	3	3	3	3
Zn	Pearson Correlation	-0.633	0.286	0.715	0.977	0.73	1	0.738	0.428	0.623	0.744
	Sig. (2-tailed)	0.564	0.816	0.493	0.136	0.479	.	0.471	0.719	0.572	0.465
	N	3	3	3	3	3	3	3	3	3	3
Ni	Pearson Correlation	-0.989	0.857	0.057	0.865	1.000(**)	0.738	1	0.925	0.987	0.099
	Sig. (2-tailed)	0.093	0.344	0.964	0.335	0.008	0.471	.	0.248	0.101	0.937
	N	3	3	3	3	3	3	3	3	3	3
Pb	Pearson Correlation	-0.971	0.988	-0.326	0.609	0.93	0.428	0.925	1	0.974	-0.285
	Sig. (2-tailed)	0.155	0.097	0.788	0.583	0.24	0.719	0.248	.	0.147	0.816
	N	3	3	3	3	3	3	3	3	3	3
Cu	Pearson Correlation	1.000(**)	0.928	-0.102	0.774	0.989	0.623	0.987	0.974	1	-0.059
	Sig. (2-tailed)	0.008	0.244	0.935	0.436	0.093	0.572	0.101	0.147	.	0.962
	N	3	3	3	3	3	3	3	3	3	3
Cd	Pearson Correlation	0.046	0.427	.999(*)	0.586	0.087	0.744	0.099	0.285	-0.059	1
	Sig. (2-tailed)	0.971	0.719	0.027	0.601	0.945	0.465	0.937	0.816	0.962	.
	N	3	3	3	3	3	3	3	3	3	3

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

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

Means of sediment parameters

Report (Seasonal)					
Season		Protein	Total Organic Carbon	Tannin and Lignin	Exchangeable ammonium
Pre Monsoon	Mean	8.29	1.04	3.41	2.2
	Std. Deviation	7.59	0.77	2.91	1.92
	CV	91.53	73.63	85.48	87.28
	Median	9.42	1.18	3.38	2.17
Monsoon	Mean	5.34	1.05	4.31	1.67
	Std. Deviation	5.37	0.75	4.08	1.77
	CV	100.52	72.16	94.83	106.04
	Median	4.37	1.34	3.17	0.82
Post Monsoon	Mean	5.27	1.12	4.28	1.6
	Std. Deviation	5.42	0.75	4.07	0.92
	CV	102.91	67.18	95.13	57.27
	Median	4.89	1.41	4.1	1.56
Total	Mean	6.3	1.08	4	1.82
	Std. Deviation	6.16	0.74	3.62	1.57
	CV	97.83	68.49	90.65	85.88
	Median	5.61	1.41	3.6	1.52

Report (Station wise)					
Station		Protein	Total Organic Carbon	Tannin and Lignin	Exchangeable ammonium
1	Mean	9.1	1.67	4.21	2.12
	Std. Deviation	5.97	0.23	1.55	1.16
	CV	65.57	13.68	36.76	54.95
	Median	7.75	1.61	4.25	2.08
2	Mean	12.51	1.45	5.72	2.41
	Std. Deviation	3.55	0.15	1.67	1.45
	CV	28.35	10.14	29.15	59.92
	Median	11.89	1.46	6.04	2.72
3	Mean	9.33	1.77	8.29	3.31
	Std. Deviation	4.27	0.57	4.6	1.9
	CV	45.79	32.26	55.45	57.37
	Median	8.66	1.8	5.91	3.26
4	Mean	0.44	0.26	1.08	0.76
	Std. Deviation	0.43	0.1	0.6	0.44
	CV	98.03	40.2	55.73	57.42
	Median	0.31	0.25	0.96	0.72
5	Mean	0.12	0.26	0.69	0.52
	Std. Deviation	0.12	0.06	0.62	0.66
	CV	98.17	22.7	90.2	127.27
	Median	0.09	0.25	0.49	0.19
Total	Mean	6.3	1.08	4	1.82
	Std. Deviation	6.16	0.74	3.62	1.57
	CV	97.83	68.49	90.65	85.88
	Median	5.61	1.41	3.6	1.52

Report (Seasonal)											
Season		sand	silt	clay	Fe	Mn	Zn	Ni	Pb	Cu	Cd
Pre Monsoon	Mean	30	19.6	50.4	234.4	0.7	0.74	0.36	225.88	262.84	11.72
	Std. Deviation	23.23	10.24	16.36	146.94	0.25	0.45	0.19	161.49	154.3	8.58
	CV	77.42	52.23	32.47	62.69	35.83	61.28	52.83	71.49	58.7	73.21
	Median	22	20	59	259	0.75	0.67	0.44	288.2	295.6	8.88
Monsoon	Mean	27.4	24.6	48	125.4	0.64	0.53	0.31	123.06	200.43	37.62
	Std. Deviation	29.64	10.9	20.84	118.96	0.42	0.26	0.23	103.69	92.24	40.15
	CV	108.19	44.31	43.43	94.86	65.86	49.68	73.91	84.26	46.02	106.8
	Median	11	22	55	75	0.5	0.44	0.25	113.4	204.5	20.8
Post Monsoon	Mean	31.4	28	40.6	216.8	1.04	0.77	0.38	273.8	314.18	9.56
	Std. Deviation	12.62	5.61	15.14	139.15	0.44	0.56	0.18	164.5	126.88	7.14
	CV	40.2	20.04	37.3	64.18	41.87	72.29	46.66	60.08	40.39	74.75
	Median	25	28	44	211	1.1	0.63	0.49	261.1	395.9	8.86
Total	Mean	29.6	24.07	46.33	192.2	0.8	0.68	0.35	207.58	259.15	19.63
	Std. Deviation	21.3	9.25	16.88	134.87	0.4	0.42	0.19	149.97	127.09	25.89
	CV	71.96	38.45	36.42	70.17	49.8	62.43	53.64	72.25	49.04	131.9
	Median	23	24	49	211	0.75	0.63	0.44	222.8	267.5	8.88

Report (Station wise)											
Station		sand	silt	clay	Fe	Mn	Zn	Ni	Pb	Cu	Cd
1	Mean	18.33	24	57.67	298.33	1.14	0.68	0.47	228	320.67	25.56
	Std. Deviation	9.07	10.82	4.73	79.76	0.2	0.06	0.03	63.3	69.19	28.9
	CV	49.49	45.07	8.2	26.73	17.16	8.19	5.63	27.76	21.58	113.1
	Median	22	21	56	311	1.05	0.67	0.48	233.8	295.6	8.88
2	Mean	20	28.33	51.67	354	1.16	0.82	0.57	241.07	378.67	12.96
	Std. Deviation	13.08	5.13	9.45	58.8	0.41	0.04	0.06	209.15	67.53	6.87
	CV	65.38	18.11	18.29	16.61	34.84	5.32	9.77	86.76	17.83	53.03
	Median	14	27	55	378	1.18	0.84	0.58	309.4	410.5	10.07
3	Mean	17.33	23.33	59.33	181.67	0.78	1.2	0.4	358.6	335.17	47.64
	Std. Deviation	6.66	4.16	9.61	95.44	0.3	0.67	0.14	157.19	113.25	43.44
	CV	38.41	17.84	16.19	52.54	38.48	55.91	33.76	43.84	33.79	91.19
	Median	19	22	61	211	0.75	1.46	0.45	322.2	395.9	24.28
4	Mean	25.33	29	45.67	59.33	0.51	0.26	0.14	95.53	145.67	3.29
	Std. Deviation	4.16	6.25	2.08	42.77	0.17	0.03	0.04	24.58	34.11	2.93
	CV	16.43	21.53	4.56	72.09	32.68	12.52	26.42	25.73	23.42	89.25
	Median	24	31	45	82	0.6	0.27	0.16	105.7	162.6	1.76
5	Mean	67	15.67	17.33	67.67	0.39	0.44	0.16	114.7	115.57	8.71
	Std. Deviation	13.45	15.14	5.86	22.37	0.18	0.05	0.05	126.81	60.9	6.18
	CV	20.08	96.66	33.8	33.06	46.93	11.3	32.12	110.56	52.69	70.93
	Median	71	9	15	78	0.36	0.46	0.15	44	96.58	6.54
Total	Mean	29.6	24.07	46.33	192.2	0.8	0.68	0.35	207.58	259.15	19.63
	Std. Deviation	21.3	9.25	16.88	134.87	0.4	0.42	0.19	149.97	127.09	25.89
	CV	71.96	38.45	36.42	70.17	49.8	62.43	53.64	72.25	49.04	131.9
	Median	23	24	49	211	0.75	0.63	0.44	222.8	267.5	8.88

Two way ANOVA

Protein

Source of Vari	DF	SS	MS	F	P
Season	2	59.379	29.689	3.148	0.072
Station	4	768.272	192.068	20.367	0.001
Season x Statio	8	132.382	16.548	1.755	0.166
Residual	15	141 453	9.43		
Total	29	1101.487	37.982		

Total Organic Carbon

Source of Vari	DF	SS	MS	F	P
Season	2	0.0254	0.0127	0.106	0.9
Station	4	13.818	3.454	28.958	0.001
Season x Statio	8	0.25	0.0313	0.262	0.969
Residual	15	1 789	0.119		
Total	29	15.883	0.548		

Tannin and Lignin

Source of Vari	DF	SS	MS	F	P
Season	2	5 236	2.618	0.359	0.704
Station	4	245 389	61.347	8.422	0.001
Season x Statio	8	20.721	2.59	0.356	0.928
Residual	15	109.264	7 284		
Total	29	380.609	13 124		

Exchangeable ammonium

Source of Vari	DF	SS	MS	F	P
Season	2	2.157	1.078	0.577	0.574
Station	4	32.77	8.192	4.383	0.015
Season x Statio	8	8.144	1.018	0.545	0.806
Residual	15	28.034	1.869		
Total	29	71 105	2.452		

Texture and Metals

sand

Source of Vari	DF	SS	MS	F	P
Season	2	41 2	20.6	0.173	0.844
Station	4	5359.6	1339.9	11.274	0.002
Residual	8	950.8	118.85		
Total	14	6351 6	453.686		

silt

Source of Vari	DF	SS	MS	F	P
Season	2	178.533	89.267	1.051	0.393
Station	4	340.933	85.233	1 004	0.459
Residual	8	679.467	84 933		
Total	14	1198.933	85.638		

clay

Source of Varia	DF	SS	MS	F	P
Season	2	260.933	130.467	4.651	0.046
Station	4	3502	875.5	31.212	<0.001
Residual	8	224.4	28.05		
Total	14	3987.333	284.81		

Fe

Source of Varia	DF	SS	MS	F	P
Season	2	34241.2	17120.6	16.555	0.001
Station	4	212149.733	53037.433	51.284	<0.001
Residual	8	8273.467	1034.183		
Total	14	254664.4	18190.314		

Mn

Source of Varia	DF	SS	MS	F	P
Season	2	0.467	0.234	7.751	0.013
Station	4	1.496	0.374	12.407	0.002
Residual	8	0.241	0.0301		
Total	14	2.204	0.157		

Zn

Source of Varia	DF	SS	MS	F	P
Season	2	0.178	0.0891	0.959	0.423
Station	4	1.596	0.399	4.29	0.038
Residual	8	0.744	0.093		
Total	14	2.518	0.18		

Ni

Source of Varia	DF	SS	MS	F	P
Season	2	0.0109	0.00545	1.045	0.395
Station	4	0.437	0.109	20.964	0.001
Residual	8	0.0417	0.00521		
Total	14	0.49	0.035		

Pb

Source of Varia	DF	SS	MS	F	P
Season	2	59318.044	29659.022	1.994	0.198
Station	4	136579.571	34144.893	2.296	0.147
Residual	8	118970.349	14871.294		
Total	14	314867.964	22490.569		

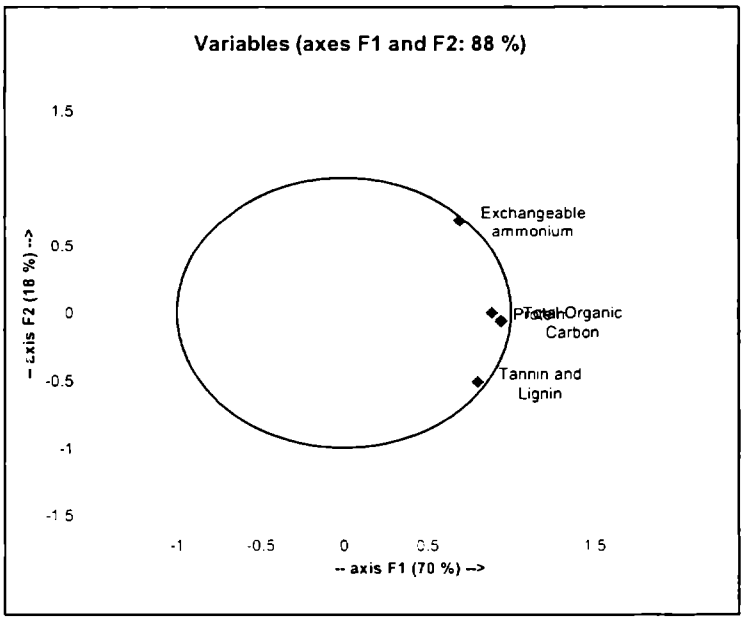
Cu

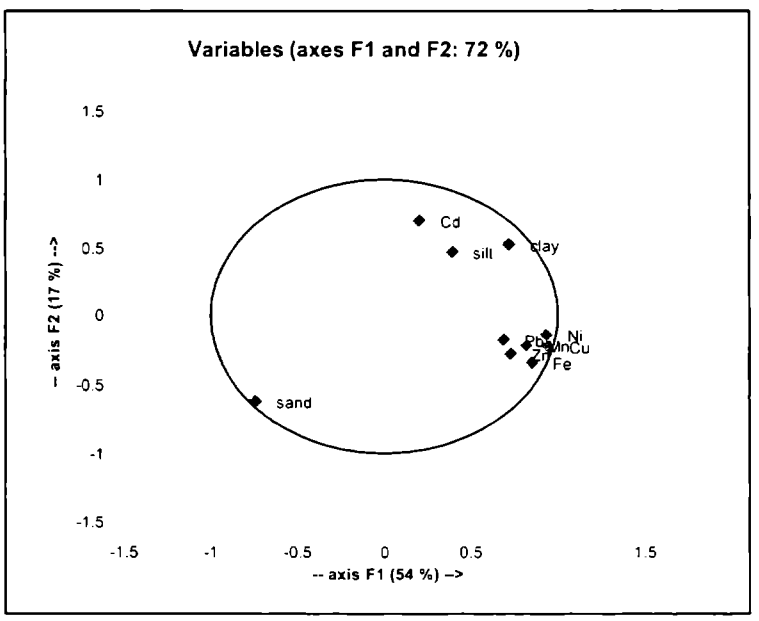
Source of Varia	DF	SS	MS	F	P
Season	2	32451.978	16225.989	5.998	0.026
Station	4	172022.252	43005.563	15.897	<0.001
Residual	8	21642.425	2705.303		
Total	14	226116.656	16151.19		

Cd

Source of Varia	DF	SS	MS	F	P
Season	2	2437.681	1218.841	3.051	0.104
Station	4	3752.237	938.059	2.348	0.141
Residual	8	3195.753	399.469		
Total	14	9385.671	670.405		

Cluster Analysis





Chapter V

Mangrove Plant Chemistry

5.1 Introduction

Mangroves are ecologically important and biologically diverse ecosystems wedged between the land and sea (Walters *et al.*, 2008). They are found along the coastline of tropical seas, in sheltered mud flats, lagoons and river mouths. Mangrove ecosystems are periodically flooded by tides and therefore are often subjected to pollution from industrial and other anthropogenic activities. Mangroves are highly productive ecosystems with high requirements for nutrients including trace elements (Alongi et al, 2004). These eco systems are auto tropic with excess carbon probably buried in the soils and stored in tree biomass. Though they are inhospitable and in many cases inaccessible, they are the habitat of many organisms. Moisture content of soil, salinity, pH, water temperature, soil redox potential, tidal inundation and nutrient availability are some of the parameters affecting their existence and propagation. Changes in mangrove vegetation may be used as a means to monitor changes in coastal environments arising out of pollution, global warming, sedimentation, climate changes etc. Mangroves can help to reduce global warming by acting as a sink for atmospheric carbon. They support estuarine food web and provide habitats for marine and terrestrial animals. Mangroves provide breeding, growing, refuge, and feeding zones for marine organisms that later migrate to adjacent coastal waters or to the ocean. Deforestation of mangrove communities is thought to be one of the major reasons for the decrease in the coastal fisheries of many tropical and subtropical countries. They mitigate erosion and stabilize coastal land forms. They support abundant benthic communities and high rates of organic matter turnover (Alongi et al, 2001). While mangrove ecosystems as a whole are net autotrophic, sediments and creek waters are largely net heterotrophic. Tree litter is usually considered the main source of carbon for decomposer food webs in mangrove sediments and creeks, but the contribution from algae and

allochthonous material such as phytoplankton may in certain areas be of considerable importance. In spite of its ecological and economical values, mangrove ecosystems still in many parts of the world have been considered as wasteland.

Mangrove soils can absorb and retain metals, which can be translocated to plants (Ravikumar et al, 2007). Generally metals accumulated in the roots are transported to aerial parts in a restricted manner. The heavy metals accumulated in the soil and mangrove plants can adversely affect many organisms including man (Hsu et al, 2006). The mangroves of Cochin are an endangered ecosystem. Industrialization and urbanization has lead to elevated pollution in almost all coastal areas of Kerala, including Cochin. Since mangroves have an impact on the food web of coastal areas it is essential to have firsthand information about the accumulation of metals in the mangrove soil and plants. Land reclamation activities including increasing industrialization, urban runoff effluent discharges from industries along the coastal areas have resulted into depletion of mangroves. The study was undertaken to find the extent of metal pollution in the mangrove ecosystems of Cochin, which can be used to gain information about the extent to which metal pollution can affect living organisms including man. In this chapter, rate of accumulation of some important parameters like moisture, tannins and lignin, proteins as well as the concentration of seven metals, which are of concern to the environment accumulated in mangrove plants are discussed. Mangroves find wide applications in folk medicine, as a food source and are put to various traditional uses (Loo et al, 2006). The concentration of the above mentioned parameters in the root, stem and leaf of the mangrove plants, *R. Apiculata A. Ilicifolius* and *A. marina*, were analysed. These plants are known to be used in traditional medicines. For example, the leaves of A. *Ilicifolius* have been used by local people to treat rheumatism, neuralgia and even for poisonous snakebites. This chapter contains details regarding mangrove plants at the research sites as well as the relevant graphs and statistical analysis results. Statistical analysis such as Pearson correlation, cluster analysis and anova are used to study the interdependence of various parameters. The abbreviations used are R for *Rhizopora*, Ac for *Acanthus* and

Av for *Avicennia*. The abbreviations r, l and s stand for root, stem and leaf respectively.

5.2 Moisture

Water is the matrix of life. Mangroves grow in water logged, often anaerobic soils. Soil moisture is maintained through the attractive forces between the soil particles and water. Water is stored in the void spaces in the soil mass and it plays an important role in determining a number of important physico chemical properties of the soil. Decomposition rate of organic matter, weathering rate of minerals in soil, rates of formation of secondary minerals, deposition of materials between different soil layers, amount of micro organisms etc are influenced by soil moisture. There are many soil microbes that depend on water to obtain nutrients, as well as for their mobility. In wet unsaturated soils, all types of microbes are active, but in drying soils, it may ultimately become confined to filamentous organisms such as fungi which can utilize water unavailable to bacteria through the growth of hyphae (Sim and Chrysikopoulos, 2000).The viruses get adsorbed onto the soil through the thin film of water surrounding the soil and may reach the surface water or ground water used by humans. Water logging causes the soil to be under predominantly reducing conditions (Olle Selinus, 2005). Rainfall or surface flow saturates the upper most layer of the soil. Water then advances down ward as a wetting front and a saturation level is reached in each layer (Stephen, 1999). Water that infiltrates the soil will surround soil particles, fill pore spaces and then move towards the water table. Anthropogenic activities modify the moisture bearing capacity of the soil. Soils that contain a high proportion of sand will transmit water rapidly. The clay soil holds water with more force and consequently water will migrate from a sandy layer to a clayey layer if both have the same initial moisture content. The availability of water is also controlled by the amount, size and interconnections between the interstices of the soil. This will influence the energy and nutrient flow through the soil. Bio turbation influences the interstitial water chemistry (Alongi, 1998).

In plants, water plays an important role in the folding of proteins and helps to stabilize proteins against heating. Enzymes activity is known to be proportional to water content. Nucleotide crystals are reported to contain about 50-75% of water which helps to stabilize the helical structure of nucleotides. The phase transitions of phospholipids are also known to be water dependent. Phase transition of lipid bi layer of cell membrane may result in cell fusion or leakage of chemical species from the cell due to dehydration (Felix, 2000).The presence of chemically active forms of the metal is also dependent on the moisture content, as the moisture content can affect the redox conditions of the soil. Redox conditions of the soil control the precipitation and dissolution of a number of elements. This in turn affects the bioavailability of elements. In the transportation of water, water always follows the movement of salts or other solutes. In mangrove swamps, since the external salt concentration and osmotic pressure is higher than those in the root cells, water tends to flow out of plants. But in mangroves, the leaf cells actively absorb salts instead of excluding them and wilting is avoided. The raised osmotic pressure caused by the salt, helps to draw water into the cells from the xylem, in effect increasing the suction pressure and drawing up water from the roots. Mangroves show decreasing growth rate as salinity rises, mainly due to lack of water, than due to the toxic effect of salt (Collin Little,2000).

Results and discussion

Mangrove species are known to vary in the water accumulation within their system in response to the hydrology of their environment (Bosire *et al.*, 2008). They are known to exhibit a decrease in osmotic potential of leaf tissues during the dry season when salinity levels increased in ground water. This osmotic adjustment was due to changes in the symplasmic water fraction, the osmotically active solutes in leaf cells, or both. Changes in cell wall elasticity have also been reported, with the cell walls becoming more rigid during the dry season in many mangrove species. *Rhizophora mangle* had more rigid cell walls. During pre monsoon the moisture content in *Rhizopora*, varied between 56.2 % and 87.4%. *Rhizopora* root showed more

water content than stem and leaf at all stations except at station 3 where the leaf had higher moisture content than root and stem. In *Acanthus*, the moisture varied between 60.4 % and 83.3 %. In *Acanthus,* the root and leaf showed higher water content than stem. This may be due to their greater succulent nature. Water stressed plants are also likely to invest in means of obtaining more water and of reducing transpiration. In *Avicennia* the moisture content varied between 54.7% and 87.3%. The order of water content was root> leaf > stem. Mangroves slow down the rate by which water is lost by decreasing transpiration even though this may lead to problems of over heating. Thick and waxy leaf cuticles and the stomata placed in deep groves also help to minimize water loss. Lower water content in plants under medium or high saline conditions may be considered as a sign of salt stress. A typical response to water stress observed in mangrove plants was that smaller leaves were produced in order to reduce transpirational losses (Parida and Das, 2005). During monsoon the water content varied between 55.2 % and 86.7% for Rhizopora, whereas it varied between 53.4% and 90.8% for *Acanthus* and between 66.5% and 84.9 % for *Avicennia.* In *Rhizopora,* the moisture content of the various plant parts did not show any characteristic pattern during monsoon, but for *Acanthus* the order was root> stem> leaf and for *Avicennia* it was root> leaf > stem. *Acanthus and Avicennia* showed increase in moisture content especially in leaves during monsoon. This may due to enhanced transpiration during monsoon. Mangrove species, particularly those that are less tolerant of high saline conditions such as *Acanthus*, could be opportunistically absorbing and storing more water when they are exposed to low saline conditions (Kathiresan and Bingham, 2001). During post monsoon, the water content in various parts of *Rhizopora* did not seem to vary much at stations 1, 2, and 3, a trend not seen during pre-monsoon and monsoon. The lowest water content in *Rhizopora* during post-monsoon was 59.4% recorded in *Rhizopora* stem at station 3 and the highest was 78.5%, observed again in its stem at station 3. *Acanthus* root and stem did not show much variation in water content during post- monsoon at stations 2, 3 and 4. The water content in leaf was quite lower than that in stem and root. In *Avicennia*, the various plant parts showed clear variation in moisture content during post monsoon with the general trend being root>

leaf>stem. Thus the moisture content of *Avicennia* during all the 3 seasons was root> leaf>stem. Also *Rhizopora* leaves did not show much difference in moisture content during pre monsoon and post monsoon. The order of moisture content in the three plants was monsoon > post monsoon > pre monsoon. Irfan et al (2005) has reported that water and osmotic potentials were higher in plants during the monsoon period in July and August when plants faced high tides and became lower during the drier, more saline period in December and January. In this work also, higher percentage of water contents were recorded under low saline conditions. This is because mangroves are more active in their uptake of water and nutrients, during periods of freshwater input. Moisture showed significant correlation only with Kjeldhal nitrogen, that too only at station 1. The mean and standard deviation of moisture for *Rhizopora* was 72.50 and 8.08, while for *Acanthus* it was 79.03 and 7.81, and for *Avicennia* it was 72.44 and 8.75. The mean deviation for root, stem and leaves were 79.53, 71.85 and 72.58, while the corresponding standard deviations were 6.68, 9.95 and 7.19 respectively. Considering the various seasons, for pre-monsoon, monsoon and post-monsoon the means for moisture was 71.35, 77.17 and 75.45 where as the standard deviations were 8.75, 9.21 and 7.24 respectively. For stations 1 to 4 the mean values of moisture was 75. 91, 73.92, 74.03 and 74.76 % while the corresponding standard deviations were 8.29, 9.50, 8.62 and 8.75. Anova showed significant variations of moisture in plants with $P < 0.001$.

5.3 Organic Carbon

Mangroves are among the most productive ecosystems of the world. They are more productive than salt marshes. Mangroves sequester carbon from the atmosphere through photosynthesis. It is estimated that mangroves sequester large amounts of carbon approx 25.5 million tones of C every year. Since mangroves fix store a large amounts of C, loss of mangroves will lead to a huge loss of stored carbon (Cebrian, 2002). Degradation of mangroves will disturb their anaerobic environment and lead to higher rates of decomposition of organic matter stored in their soils and augment the green house gas emissions. Though mangroves may act as a sink for organic

carbon, they will also release CO_2 when the fauna breathes or when microbial oxidation of organic matter takes place. Crustaceans such as sesarmid crabs ingest twice as much as detritus than they can ingest. The organic matter ingested will become available as faecal matter to the decomposers. The burrowing activity of the crabs will enhance the hydraulic conductivity of mangrove sediments which increases the pore water mediated export of nutrients and organic matter to the aquatic environment(Mazda & Ikeda, 2006).Though mangrove ecosystems also trap carbon rich sediments (Dittamer et al, 2006), the organic carbon hidden away in soil mostly originates from plants. It is a fundamental component of soil's organic matter, integral to the health of the soil and an important sequester of carbon that contributes to global warming. The efficiency of mangrove ecosystems in trapping suspended material from water column depends on a range of factors such as particle size, salinity, tidal pumping and the aerial content of the intertidal zone(Kitheka et al., 2002).Other than mangrove litter, benthic microalgae also make significant contributions to the autochthonous carbon source in mangrove sediments. Phytoplankton and sea grasses can also make a significant contribution to the sedimentary organic carbon (Marchand, 2005).

Mangroves can sequester carbon faster than terrestrial plants (Suratman, 2008). The soil carbon is estimated to be lower than the biomass stocks. Numerous classes of compounds have been characterised from mangrove tissues. These include carbohydrates, amino acids, lignin derived compounds, tannins, fatty acids, triterpenoids and n-alkanes. Marchand et al (2005) showed that mangrove leaves have lesser concentrations of carbohydrates than wood. Glucose, arabinose, galactose, rhamnose and xylose are the various carbohydrates identified from mangrove different species. Carbohydrates such as xylose can be used to discriminate the debris derived from mangrove roots from those of derived from algae, which contain a large quantity of rhamnose. Another class of organic compounds identified in abundance in mangrove plants are tannins. Mangrove leaves recorded higher tannin content than many other dicotyledonous plants (Hernes et al, 2001). Typical lignin signature of vascular plants is shown by mangrove plants. This

signature varies greatly between leaves and wood. Lignin is more refractive than other organic molecules. It is lost at a lower rate during decomposition than neutral sugars or bulk organic carbon (Marchand et al, 2005). Fatty acid profile can be used to differentiate mangrove species. Saturated fatty acids dominate the leaves with palmitate as the most abundant saturated fatty acid in leaves (Hall et al, 2006). Since the concentration of saturated fatty acids decline constantly with age, they can be used as an indicator of degradation state. But long chain fatty acid content of leaves remains rather constant and can be used as biomarkers (Mflinge et al, 2003). Tri terpenoids such as taraxerol is found in high concentration in Rhizopora leaves (Versteegh et al, 2004). Taraxerol appears to withstand microbial degradation and can be used as a resource for paleo environmental studies (Koch et al, 2005). Similarly betulin can be used as a tracer for *Avicennia*. The organic carbon fixed in the mangroves has an important impact on the dissolved organic matter. Carbon that is present in the mangrove sediments is exported to adjacent waterways as dissolved organic carbon (Bouillon et al, 2007a). The majority of this is re - cycled in the photic zone and enhance microbial growth that forms the basis of food chain. The organic carbon derived from mangroves forms the basis of a dependent tropic chain of bacteria, fungi, cellular algae, and other detritus feeding organisms such as sesarmid crabs (Cannicci et al., 2008). The organic matter in the mangrove ecosystems may be remineralised microbially and bound organically in the mangroves itself by primary and secondary producers, thus becoming sedimented in mangroves. The degradation of organic matter in sediments is mediated by both aerobic and anaerobic processes using a variety of electron acceptors. The organic carbon in plant is made up of different source materials which have different degradability. These can be used as signatures for mangrove derived organic matter in sediments (Hernes et al, 2001).

Results and discussion

Carbon storage has increased in past decades due to higher concentration of CO_2 in the atmosphere. Plants sequester organic carbon through photosynthesis. The climate of the tropics results in rapid plant growth and

most of the carbon stored can be found in the vegetation (Lewis et al, 2009). Mangroves are autotrophic, producing more fixed carbon than they consume. Out of the C produced, 9% is exported, 10% is stored in sediments, and 40% is decomposed and recycled and 9% is consumed by herbivores. The excess carbon is stored in the ecosystem is about 40% of the net primary production. Mature forests have a long term capacity to store C in the wood (Chambers et al, 2001). Losses of carbon from mangroves probably reflects greater anthropogenic activity, lower efficiency of carbon processing, as well as greater loss of carbon due to respiration. The carbon sequestering and release processes are complex and change with time. Organic carbon in *Rhizopora* parts varied between77.7% and 95% while in *Acanthus* it varied between 83.2% and 91.4% and in *Avicennia* it varied between 76.6% and 90% during pre-monsoon. During monsoon it varied between 72.95% and 95.6% in *Rhizopora*, between 79.8 and 88.2% in *Acanthus* and between 68.9% and 94.4% in *Avicennia.* The variation in organic carbon during post monsoon was as follows – in *Rhizopora* it varied between 71.9% and 90%, while in *Acanthus* the variation was between 51.2% and 90.4% and for *Avicennia* it varied between 60.3% and 91%. The organic carbon percentage was high in roots during monsoon. In post -monsoon the organic carbon content showed a decrease. During post monsoon the bacterial activity increases. Hence the mangrove substrate acted on by bacteria is generally much more depleted in carbon. Organic carbon did not show correlation with any parameters for plant data. The mean value of organic carbon for *Rhizopora, Acanthus and Avicennia* was 84.30, 81.48 and 83.75 respectively, while the corresponding standard deviation was 6.06, 9.88 and 7.62. The means for organic carbon in plants was 86.23, 86.06 and 77.24 while the standard deviations were 3.82, 5.55 and 9.86 respectively for pre-monsoon, monsoon and post –monsoon. For the various plant parts the mean values were 83.59 for roots, 83.82 for stem and 82.32 for leaves. The corresponding standard deviations were 8.08, 8.50 and 7.63. The roots and stem appeared to have greater organic carbon storage facility than leaves. For the different mangrove stations, the mean value of organic carbon in plants was 85.32 for station 1, 85.27 for station 2, 81.51 for station 3 and 80.60 % for station 4. The standard deviations were 5.72, 4.34, 9.74 and

10.02 for stations 1 to 4. The lowest mean value of organic carbon was found in station 4 which also had high salinity for the aqueous medium. Salinity is a key determinant of mangrove growth and zonation (Krauss *et al.*, 2008), affecting the organic carbon content in plants. Three way anova showed significant variations in organic carbon seasonally and for stations with $P < 0.001$.

5.4 Proteins

Proteins in mangroves play many important roles. They are synthesized in the plant body to regulate a number of important metabolic processes. Proteins regulate water fluxes and oxygen scavenging radicals. These proteins are secreted in response to salinity conditions of the environment. A large number of proteins are known to have chaperone activity. They are responsible for protein folding, assembling, translocation and degradation in an array of metabolic processes. Proteins are known to be expressed in response to a number of environmental factors such as water stress, salinity etc. Similarly the heat shock proteins prevent a large number of processes such as aggregation which are deleterious to cells under stress. Soluble protein content of leaves get reduced in response to salinity (Parida et al, 2005). The decrease in total protein content of leaves depends on salinity and well as the duration of sanity conditions. The total amino acid increases as the total protein content decreases in mangrove species such as B. Parvoflora (Behera et al, 2009). The detritus of mangroves is rich in proteins. Mangroves are highly productive marine ecosystems where bacteria actively participate in bio mineralisation of organic matter and bio transformations of minerals. Soil organic matter decomposition will cause an increase in microbial products including proteins (Ferreira, 2009). Sugars and proteins are generally believed to be susceptible to microbial degradation and thus can be quickly incorporated into food webs. In sediments a large portion of organic matter available for microbial decomposition occurs as polymers including proteins. The origin of proteins can be due to massive macrophytic production, the micro floral community through lysis, as well as extra cellular enzymatic activity, proteinaceous releases by macrophytic rooting tissues,

and epipelic algal populations. The contributions of each of these may vary seasonally. Mangrove leaves and wood are degraded primarily by a large variety of microorganisms and later by higher organisms (Holguin et al, 2001). The protein in plants reaching sediments through litter decomposition can also represent a significant source of nitrogen for micro flora. The utilization of protein by the micro flora represents a recycling of nitrogen by exploitation of nitrogen sources not directly available to the plant community. The protein degradation is light dependent and also related to algal mat on the sediment surface. Proteolytic activity is reported to support the amino acid degrading population not directly involved in the proteolytic processes. Enzymatic activity is a key step in the degradation of high molecular weight organic matter. Most these activities are believed to be carried out by bacteria, thereby playing a crucial role in the nutrient dynamics and energy flow of the ecosystem. Tree exudates can fuel the bacterial activity and soil particle size influence the bacterial biomass and structure of the bacterial community. Soils composed mainly of clay and fine silt particles showed a greater diversity of bacteria than those with larger particles (Sessitsch et al, 2001). Nutrients in sediments also contributed to the variability and distribution of bacteria. Bacterial concentration is known to increase in the wet season than in the dry season perhaps due to the increase in dissolved oxygen. But oxygen production by algae and microalgae in waters might increase the bacterial population in warm season. The heterotrophic community of mangroves contains a large population of nitrogen fixing bacteria which might be suppressed because of oxygen produced. Another group of organisms called protists which are known to be present in mangrove environment also play an important role in the decomposition of organic matter. They pervade various solid substrates and have been isolated from mangrove leaves and aid in the decomposition process by secreting many extra cellular enzymes. Peptide degrading enzymes leucine and valine aryl amidase were isolated from many strains of these organisms and the exo enzymatic activities of amino peptidase accounted for more than 30% of the total enzymatic activity(Raghu Kumar,2002).

The long term survival of labile proteins in mangrove sediments may result from their interaction with refractory organic matter present in sediments. Interaction of proteinaceous materials with humic substances via physical adsorption on its surface, entrapment within its 3-D structure and chemical bonding can help preserve proteins in sediments for long periods of time (Zang et al,2 000). The highly branched structure of humic acids will help the proteinaceous material encapsulated in its structure to be resistant to chemical hydrolysis (Riboulleau et al., 2002). Polymers such as tannin which are mostly water-soluble and highly reactive, exhibit protein-binding ability, influencing nitrogen dynamics in ecosystems. Tannins form microbially recalcitrant complexes with proteins (Kraus et al. 2003). However, Maie et al. (2008) showed that the molecular structure of tannins was modified during degradation of foliage, accompanied by a decrease in the protein binding capacity. For this reason, it could be expected that bio labile proteins can be re-released into the water column through the diagenetic alteration of insoluble tannin–protein complexes. Proteins were released gradually from tannin–protein complexes incubated under light conditions but not under dark conditions, indicating a potentially buffering role of tannin–protein complexes on dissolved organic nitrogen (DON) recycling in mangrove estuaries. Thus the protein content of mangrove plants have significant impact on the ecosystem and its dependants.

Results and discussion

During pre-monsoon the protein content of *Rhizopora* root varied between 5.45 and 6.46 mg/g, in *Acanthus* root between 5.68 and 13.17 mg/g and in *Avicennia* root between 4.34 and 14.30 mg/g. In *Rhizopora* stem it varied between 4.95 and 9.13mg/g, in *Acanthus* stem between 10.46 and 14.40mg/g and in Avicennia between 7.47 and 13.90mg/g. In *Rhizopora* leaves the variation was between 9.97 and 14.88mg/g, in *Acanthus* leaves *b*etween 10.49 and 15.71mg/g and in *Avicennia* between 6.40 and 16.75mg/g. In *Rhizopora* the lowest concentration of protein was 4.95mg/g during pre- monsoon, found in its stem at station 3 and the highest concentration of 14.88 mg/g in its leaves, also at station 3. In *Acanthus,* the

lowest concentration of protein 5.86mg/g was in roots at station 4 and the highest concentration of 15.71mg/g was in the leaves at station 3. In *Avicennia*, the lowest protein content 4.34mg/g was in its roots at station 4 and the highest was in its leaves at station 2 (16.75mg/g). Among the roots of the three plants, the lowest protein concentration was in *Avicennia* (4.34mg/g), among stems in *Rhizopora (*4.95mg/g), and among leaves in *Avicenna* (6.40mg/g). Similarly among roots the highest concentration of protein was in *Avicenna (*14.30mg/g), among stems in *Acanthus* (14.40 mg/g) and among leaves in *Avicennia* (16.75 mg/g). During pre monsoon, *Avicennia* leaves had lower protein content than *Rhizopora* or *Acanthus*. This may be due to the fact that *Avicennia* has a higher salt accumulating tendency than the other two which decreases the soluble protein content of leaves (Parinda et al, 2002). During monsoon the protein content of *Rhizopora* root varied between 1.54 and 5.86 mg/g, in *Acanthus* root between 3.03 and 14.03 mg/g and in *Avicennia* root between 2.30 and 12.94 mg/g. In *Rhizopora* stem it varied between 3.16 and 7.87 mg/g, in *Acanthus* stem between 3.45 and 12.96 mg/g and in *Avicennia* between 5.24 to 8.17 mg/g. In *Rhizopora* leaves the variation was between 4.27 and 13.83 mg/g, in *Acanthus* leaves *b*etween 7.84 and 19.53 mg/g and in *Avicennia* between 5.41 and 12.55 mg/g. During monsoon in *Rhizopora* the protein concentration varied between 1.54 and 13.83 mg/g, in *Acanthus* it varied between 3.03 and 19.53mg/g and in *Avicennia* it varied between 2.30 and 12.94mg/g. Among the roots the lowest concentration was 1.54 mg/g found in *Rhizopora* at station 1 and highest of 14.03mg/g was shown by in Ac at station3. Among stems the lowest concentration was 3.16 mg/g found in *Acanthus* stem at station 1 and highest was 12.96mg/g found in *Avicennia* stem at station 3. Among leaves the lowest concentration of 4.27mg/g was found in *Rhizopora* leaves at station 1 and highest was 19.53mg/g found in *Acanthus* leaves at station 3. There was a lowering of protein content in all plants during monsoon. This is accompanied by the lowering of organic carbon in mangrove plants during monsoon. In monsoon, among the plant parts, greater protein is concentrated in leaves. This is because as salinity deceases, there is an increase in soluble proteins (Agastiana et al., 2000) which can be trans located to leaves effectively in monsoon due to the higher moisture content in plants. During

post monsoon, the protein content of *Rhizopora* root varied between 3.52 and 5.77 mg/g, in *Acanthus* root between 2.78 and 13.39 mg/g and in *Avicennia* root between 1.61 and 4.86 mg/g. In *Rhizopora* stem it varied between 3.35 and 11.47 mg/g, in *Acanthus* stem between 5.43 and 11.90 mg/g and in *Avicennia* between 6.44 and 13.18 mg/g. In *Rhizopora* leaves the variation was between 6.39 and 13.30 mg/g, in *Acanthus* leaves *b*etween 5.48 and 12.79 mg/g and in *Avicennia* between 4.42 and 16.33 mg/g. During post monsoon, protein content in *Rhizopora* varied between 3.35 and 13.30mg/g; in *Acanthus* it varied between 2.78 and 13.39mg/g and in *Avicennia* it varied between 1.61 and 16.33mg/g. Among roots the lowest protein concentration was 1.61 and highest was 13.39mg/g, among stems the corresponding values were 3.35 and 13.18mg/g and among leaves it was 4.42 and 16.63mg/g. During post monsoon there is a lowering of protein in roots. The decrease in protein content can be an adaptation to high salinity conditions by mangroves, involving the hydrolysis of some proteins. It may be due to increase in proteolytic activity of acid and alkaline protease (Behera et al, 2009).

Statistical analysis showed that protein correlated negatively with Fe in post-monsoon. In post monsoon, the clay content decreased which will reduce the amount of organic matter present in sediments and impact the biogeochemical processes. In station wise correlation protein showed negative correlation with moisture at station 1 and positive correlation with Mn at station 2. The correlation between Mn and protein may be due to the uptake of Mn for the biosynthesis of Mn active enzyme induced under anaerobic conditions to protect cell wall against oxygen toxicity. The enzyme is biosynthesized in response to a variety of environmental stresses including exposure to oxygen, iron chelation and presence of oxidants (Hassan and Laura, 2006). The mean value of protein for *Rhizopora* was 7.24mg/g, for *Acanthus* it was 9.57mg/g and for *Avicennia* it was 8.06 mg/g. The mean value of protein for root is 5.70mg/g, for stem it is 8.49 mg/g and for leaves it is 10.68mg/g respectively. This shows that leaves accumulated more protein than stem or root. During pre-monsoon the mean value of protein was 9.88mg/g, in monsoon it was 7.67mg/g and for post monsoon it

was 7.31mg/g. In pre-monsoon there exists salt stress on plants, which are complex, but largely it imposes a water deficit because of osmotic effects on a wide variety of metabolic activities. Mangroves synthesize osmotically active metabolites, specific salt inducible proteins and regulate water fluxes and support scavenging oxygen radicals and chaperons to avoid s adverse condition (Jithesh et al., 2006), which is evident from the high value of protein concentration during pre-monsoon. At station 1 the mean value of protein was 7.57, at station 2 it was 7.49 at station 3 it was 10.12 and at station 4 it was 7.97 mg/g. Three way anova did not show any significant variations for protein.

5.5 Metals in mangrove plants

Mangroves are a unique ecosystem which despite its ecological and economical values is still considered as a waste land (Akshayya Saete, 2009). But the truth is that they provide valuable resources and provide physical protection against catastrophic natural phenomena (Along, 2007). Mangroves are increasingly affected by urban and industrial development (Cuong, et al, 2005). Mangrove ecosystems although possessing enormous ecological and commercial importance are often subject to effluent discharges, urban and agricultural run off and solid waste dumping due to their proximity to urban development. Among the main anthropogenic impacts in mangrove ecosystems from these sources are heavy metals, due to their affinity and immobilization within anaerobic sediments (Mac Farlane, 2002). Natural weathering, human activities and suspended particulate matter are the three main sources of metal pollution. High levels of metals is a reflection of anthropogenic activity (Edwards et al, 2009). Metals are found to be strongly associated with particulates that enter the marine environment through atmospheric transport of dust and through sediment movement in overland flows and in waterways. In the pH range 5 –8.5, concentration of the cationic trace elements normally does not exceed 0.25mg/litre. Mangrove sediment can act as sink for heavy metals and pollutants because the sediments effectively sequester heavy metals and often immobilize them as sulphides, due to high organic content, low pH and prevailing anaerobic conditions.

Though mangrove sediments act as a sink for trace metals the bio- availability of metals is found to be less. This may be due to the immobilization of metals by various chelating agents present in the sediments. Trace metals may also be bound in organic complexes that show low bio availability. Metals will also independently form inorganic precipitates, for instance as oxides and chlorides. Generally these precipitates are relatively stable. Mangrove forests thus act as traps for sediment nutrients and anthropogenic chemical contaminants before they enter adjacent waters. Metals in mangrove soils are associated with a number of different phases. Variations in pH, temperature, DO etc are the other environmental factors which determine the solublisation of metals. The differences in seasonal flood and ebb tidal condition could also affect the availability of heavy metals for plant uptake (Sarangi et al, 2002). Disturbances in the form of prolonged dry periods, changes in the frequency and duration of tidal flooding, or changes in salinity, may cause mangrove soils to loose their metal –binding capacity, resulting in the mobilization of metals. Coarser, organic matter poor, sandy sediments have better percolation of water, allowing higher pH, lower salinity and oxidizing conditions. But in mangrove sediments, the low diffusion of water and gases through fine particles and large amounts of organic matter favour reducing conditions for suphate reducing bacterial activity. Despite this mangroves possess a great tolerance to heavy metal pollution.

There exists a sediment bio availability threshold for metals. If the concentration is below this, mangroves avoid uptake of metals (Mac Farlane at al 2003). Mangrove trees are effective at sequestering toxic heavy metals and immobilizing them as sulphides in sediments and accumulating them within their leaves, which are then exported as detritus. Most mangrove plants have developed strategies to reduce uptake of metals by rhizosphere oxidation and fixation of metals at root level. The mangrove forests store elements below ground level mostly in soil and roots (Alongi, 2003), but restricted transport occurs to aerial parts. Plants living in water logged areas transport air from aboveground to belowground organs, thereby oxidizing rhizosphere sediments. This in turn will cause partial precipitation of trace metals in rhizosphere sediments. This together with co precipitation of various

metals on root surface, root induced formation of oxy – hydroxides, extensive pyrite and iron plaque formation will act as act as protective mechanism against the up take of toxic solutes such as sulphides and decrease metal uptake by plants and transfer via detritus of above ground plants tissues (Alongi, 2004). Plant tolerance to heavy metals is also thought to include cell wall immobilization, sequestering, and peroxidase induction. The low availability of metals in mangroves may also be due to exclusion of metals by the mangroves at root epidermis level (Machado et al, 2002). Most heavy metals are accumulated in the root and stem tissue (Macfarlane and Burchett, 2003). The fact that mangrove trees appear to have tolerance or some internal mechanisms to overcome the effects of metal toxicity is evident from the fact that the mangrove forests are highly productive despite the high metal concentration in mangrove sediments. The trace elements entrapped in the mangrove sediments are remobilized and re-suspended back to the water column under favourable conditions and hence become a secondary source of pollution. The concentration of metal in mangrove plants may be used to evaluate the potential of metal loss from the forest through detritus export.

Metal uptake by mangrove plants is known to be species dependent, varying with the saline environment that may affect the uptake and distribution of metals in the plants. Uptake of metals may initiate a variety of sub cellular responses or metabolic reactions, which may cause damage at cellular level or possibly lead to wider phytotoxic effects and thus act as potential biological markers of metal stress. The formation of free radical species (all forms of active oxygen) initiated directly or indirectly by metals can cause severe damage to different cell components, particularly biological membranes. Cytoplasmoic streaming is a very good indication of metal toxicity. Concentration of Peroxidase enzyme is found to increase in metal stress condition. Peroxidase catalyses quenching reactions of toxic free radical intermediates. The total phyto toxic effect arises from combined metal stress of accumulated metals in an additive fashion at the biochemical level. Mangrove forests may retain their sediment metal load predominantly under forms with a low potential for remobilization and biotic uptake.

Remobilization of the metals most commonly occurs under the following circumstances: redox changes, complexing with organic acids, increased temperature and microbial activity. All three result in the metals moving from the sediment back into the water column. All are the direct or indirect result of bacterial action in nature.

The levels of trace metal which accumulate in mangroves differ seasonally and spatially. Variations in pH, temperature, DO etc are the other environmental factors which determine the solubulisation of metals. The differences in seasonal flood and ebb tidal condition could also affect the availability of heavy metals for plant uptake (Sarangi et al, 2002). The concentration of metal in mangrove plants may be used to evaluate the potential of metal loss from the forest through detritus export. A relatively low metal allocation in leaves appear to effectively reduce the metal export, as well as the metal availability to enter in food chains based on leaf consumption (Machado & Silva,2002). This is possibly true for many mangrove areas, since mangrove plants commonly induce changes in the sediment chemistry due to processes such as oxygen release, which will help to prevent a potentially deleterious metal uptake and tend to show a low transfer of metals from below ground to above ground tissues. Toxicity and environmental behaviour of heavy metals is highly dependant on their physicochemical speciation which is metal and environment specific. Toxicity bio assay can be a valuable tool for determining bioavailability and can also be cost effective for screening and monitoring metal contamination (Susane Dal Jensen, 2000). Bioaccumulation of metals in mangrove plants poses health risks. The mangrove detritus are used as food source by fishes, oysters etc present in the mangrove environment. Bio available metals accumulate in fauna of mangroves. Following solubilisation in the acidic juices of the feeder's gut, the sediment bound metals can thus accumulate in an organism. For eg: the mollusks in mangrove areas are reported to have high Zn and Cd levels crustaceans had high levels of copper (Kathiresan and Bingham, 2001). The exchange of toxins between trophic levels can sometimes result in greater concentrations in the higher trophic organism. Two classic examples of bio magnification of a toxic substance through serial

accumulation are the outbreak of Minamata disease in Japan as a result of mercury entering the food chain, and Itai-Itai disease where cadmium from a smelting company entered a river supplying water to rice paddies. Biota which accumulates trace metals can be used to assess spatial and temporal variations in the bio available concentration s of contaminants in estuarine and coastal waters (Judith Dobson, 2000). For eg: Algae collected from polluted and unpolluted sites show large difference in the heavy metal content(Ivorra, 2000) and can be used as environmental health monitors.

Internal salt control mechanism has reported to affect metallic contents of mangrove plants and cause differences among species. The order of abundance in concentration of heavy metals falls as Fe, Mn, Cu, Zn (Sarangi & Kathiresan, 2002). *A. Officianalis* is found to be more effective in accumulating the trace elements under the same environmental conditions as these plants have salt excreting property. A. *marina* is a mangrove species known for its tolerance to environmental stresses, particularly to temperature extremes and salinity. *Avicennia* species are considered to be especially robust to heavy metals and accumulates metals to greater quantities than other mangrove species.. It grows luxuriantly even in polluted sites. *A. marina* translocates air absorbed through lenticles in pnuematophores from underground roots. This creates oxidized rhizospheres within the anaerobic soil environment leading to a reduction in complexing sulphides, a lowered stability of iron plaques and a consequent higher trace metal concentration in exchangeable form (Akshayya Saete, 2007). Elevated concentration of non essential metals in tissue does suggest a function of sequestering toxic metals, especially with respect to lead. *Rhizophoreaceae* family exhibit relatively low concentration of metals due to salt exclusion mechanism. In *Rhizopora* iron plaque formation by metal precipitation in rhizosphere and co-precipitation of different metals on root surfaces act as physical barriers to metal uptake (Machado et al, 2005). Higher concentration of metals in the roots of *R. mangle* compared to stem and leaves may be due to the large amount of tannins present in them, which renders the metal inactive by binding and thereby delaying their entry into the plant system. Many researchers have measured high concentration of

metals in mangrove plant species with no apparent impact on plant health. When plants absorbed and accumulated heavy metals the vessels became constricted due to blockage of vascular system and retarded the water transport system. Heavy metal concentration significantly reduced leaf number and stem basal diameter in *Gymnorrizha*. Most of the absorbed heavy metals accumulated in the stem and root tissues and very little amount accumulated in the leaf tissue. Hence the root tissue can be used as a more potential environmental bio indicator than leaves. Phytochelatins (PCs) play an important role in heavy metal resistance and accumulation in plants (Jiang et al, 2007).

5.5.1 Iron

Mangroves are unique ecosystems which require specific conditions to grow, thus restricting their geographic range (Agoramoorthy et al, 2008). Mangroves are found in water logged areas and are often exposed to anoxic conditions. They are known to tolerate extreme environmental conditions such as salinity and metal pollution. Human activities related to industry and technology is bringing about a decline in the world's mangrove ecosystem at an alarming rate (Ives and Cardinale, 2004). The impact of human interference can be gathered by measuring the accumulation of metals in the biota. Heavy metal accumulation in mangrove sediments and plants are known to cause a decline in mangrove areas and cause adverse effects in all the organisms including man, which depend on them for various purposes. Mangroves are reported to have a remarkable capacity to retain heavy metals and their metal retention capacity depends on a number of physico chemical parameters (Amusan and Adeniyi, 2005). Clays have high specific area and can directly trap metals. Clays present in sediments also act as a substrate for organic matter flocculation which in turn leads to adsorbtion of metals (Roulet, 2000). The mangrove plants though growing in anaerobic conditions are able to perform oxygen transport to belowground organs and change the sediment chemistry (Marchand et al., 2004). This is true in the case of plants with aerial roots. The oxygen transport may induce precipitation of trace metals in the oxidized forms. Excessive precipitation of metals such as iron on

root will kill the root hairs (Machado et al, 2005). Mangrove plants require certain metals as essential nutrients. Fe is an essential but potentially toxic metal for plants. It interacts with the expressed toxicity of heavy metals through competition for chelators. Fixation and oxidation of sulphides in carbon rich sediments is controlled to a large extent by reactive iron species. Suphate reducing bacteria present in mangrove soils will produce sulphide, which is usually in the form of H_2S. The H_2S formed will convert the Fe present to black ferrous sulphide. The formation of FeS will make the soil acidic. FeS formation is observed in mangroves with high organic matter content, which will have higher sulphate reduction and sulphide concentration. This process is an important sink for trace metals, since many trace metals are incorporated into it during its formation (Aragon and Miguens, 2001). The oxidation of sulphides leads to very low pH and releases Fe into the soluble phase (Marchand et al., 2006). Fe bacteria cause precipitation of Fe in water. Ferrous/ferric form insoluble hydroxides and have short residence times in media with high oxygen levels. It is thus difficult to keep iron in solution (Susanne, 2000).

Results and discussion

In the mangrove plants, Fe showed greater concentration in the roots than in leaf. Creation of Fe rich root coatings called plaques due to oxygen release by roots may be the reason for the elevated iron concentration. Fe plaque formation plays an important role in the biological uptake of metals by plants. Iron accumulation in root tissue will partially suppress its translocation to leaves (Machado et al., 2005). Greater Fe accumulation in root tissues was observed in pre-monsoon than in monsoon or post monsoon. This is because greater sediment concentration of Fe was also observed during pre-monsoon. In pre- monsoon the concentration of Fe varied between 0.62 to 27.52ppm in *Rhizopora* roots, between 0.62-2.40ppm in *Acanthus roots* and between 0.55 to 8.34 ppm in *Avicennia* roots at various stations. *Rhizopora* roots showed a higher tendency to accumulate Fe than *Acanthus* and *Avicennia* roots. The variations in Fe concentrations in the stem of the above plants were between 0.08-0.51ppm in *Rhizopora,* between 0.10 and

0.43ppm in Acanthus and between 0.16 and 0.47ppm for *Avicennia*. Among the plant leaves, the variations were between 0.37-1.62ppm for *Rhizopora*, between 0.42-0.67ppm for *Acanthus* and between 0.14 to 0.82ppm for *Avicennia*. The maximum and minimum concentrations of Fe in various plant parts was between 0.08 and 27.52ppm respectively for *Rhizopora*, 0.10 and 2.40ppm for *Acanthus* and 0.14 and 8.34 for *Avicennia*. The above observations show that the tendency to accumulate Fe in plants was *Rhizopora* > *Avicennia* > *Acanthus* during pre-monsoon. The bio-concentration factor (BCF)) of Fe for *Rhizopora* root was lowest at station 3(0.0030ppm) and highest at station 1 (0.0742ppm) , for *Rhizopora* stem it varied between 0.0003ppm(at station 3) and 0.0060ppm(at station4) and in *Rhizopora* leaves it varied between 0.0010ppm(at station1) and 0.0088ppm (at station 4) respectively. In *Acanthus* root the bio concentration of Fe varied between 0.0019ppm(at station2) and 0.0093ppm(at station 3), in stem it varied between 0.0003ppm(at station 1) and 0.0050ppm(at station 4) and in *Acanthus* leaves it varied between 0.0016ppm (at station 3) and 0.0063ppm(at station 4) respectively. In *Avicennia* root the lowest bio concentration of 0.0021ppm was seen in station 3and the highest of 0.0221ppm in station 1, in *Avicennia* stem it varied between 0.005ppm(station 2) and 0.0019ppm(Station4) and in *Avicennia* leaves it varied between 0.0005ppm (station 3)and 0.0095ppm(Station 4).

Similarly in monsoon the Fe concentration in *Rhizopora* roots varied between 0.155ppm and 1.847ppm, in *Acanthus* roots it varied between 0.849and 8.138ppm and in *Avicennia* roots it varied between 0.433 and 2.182ppm respectively. For the stems of the different mangrove plants, in *Rhizopora* stem the variations were between 0.077 and 0.571ppm, in *Acanthus stem* it was between 0.125 and 0.260ppm, while in *Avicennia* stem it was between 0.288 and 0.393ppm respectively. In *Rhizopora* leaves the variations of Fe concentrations were between 0.108 and 0.828, in *Acanthus* leaves between 0.189 and 0.520 ppm and in *Avicennia* leaves it varied between 0.141 and 0.506ppm respectively. The Fe accumulation capacity of *Rhizopora* leaves was shown to be higher than *Acanthus* leaves and *Avicennia* leaves. Among the different plants the variations in Fe concentrations for *Rhizopora* were

between 0.077 and 1.847ppm, in *Acanthus* between 0.125 and 8.138ppm and in *Avicennia* between 0.141 and 2.182ppm during monsoon. During monsoon the maximum concentration of Fe of 8.138ppm was observed in *Acanthus* root at station 2 and the minimum Fe concentration of 0.077ppm in plants was observed in *Rhizopora* stem at station 4. During monsoon, Fe concentration in roots was found to follow the order *Acanthus>Avicennia> Rhizopora.* Dissolved organic carbon in soils forming soluble organic metallic complexes can increase the availability of metal to plants (Antoniadis and Alloway, 2002), whereas precipitation of metal sulphides under anoxic conditions lowers availability. During monsoon the concentration of Fe in *Rhizopora* followed the order r > l >s at stations 1 and 4, l>r>s at station 2 and l>s>r at station 3. For *Acanthus* at all the stations the order was found to be r>l>s. For *Avicennia* at stations 1, 2 and 4, r>s>l was the order for the concentration of Fe, while at station 3 it was r>l>s. The bio-concentration factor (BCF)) of Fe for *Rhizopora* root varied between 0.0009 and 0.0630, for *Rhizopora* stem it varied between 0.0006 and 0.0077 and in *Rhizopora* leaves it varied between 0.0014 and 0.0108 respectively. In Acanthus root the bio concentration of Fe varied between 0.0040 and 0.5753, in stem it varied between 0.0009 and 0.0125 and in *Acanthus* leaves it varied between 0.0018 and 0.0189 respectively. In *Avicennia* root the variations were 0.0015 and 0.1601, in *Avicennia* stem it varied between 0.0011 and 0.0228 and in *Avicennia* leaves it varied between 0.0005 and 0.0212.

In post- monsoon the Fe concentration in *Rhizopora* root was found to be between 0.320 and 1.236ppm, in *Acanthus* root it was shown to be between 0.077 and 3.274ppm and in *Avicennia* root it varied between 1.540 and 6.498ppm. The Fe concentration varied between 0.150 and 1.389ppm in *Rhizopora* stem, between 0.098 and 0.206ppm in *Acanthus* stem and between 0.116 and 1.279ppm in *Avicennia* stem. In leaves the Fe concentration varied between 0.377 and 1.343ppm in *Rhizopora* leaves, between 0.428 and 0.805ppm in *Acanthus* leaves and between 0.139 and 1.041ppm in *Avicennia* leaves. Among the plants at the four stations, *Rhizopora* had Fe concentration between 0.237 and 1.343ppm, *Acanthus* had Fe concentration between 0.077 and 3.274ppm and *Avicennia* had Fe

concentration between 0.116 and 6.498ppm respectively in their different parts. Among all the plants, the lowest Fe concentration was recorded in *Acanthus* root at station 3 and the highest was found in *Avicennia* root at station 1. During post monsoon, at station 1 the Fe concentration in *Rhizopora* followed the order r>l>s at station1, l>r>s at stations 2 and 3, and s>r>l at station 4. Temporal and spatial loading patterns in trace metals and nutrients can strongly influence the abundance and production of sensitive phytoplankton species (Bundy et al,2003), thus affecting the entire food chain. The bio-concentration factor (BCF) of Fe for *Rhizopora* root varied between 0.0015 and 0.0151ppm, for *Rhizopora* stem it varied between and 0.005 and 0.0169ppm and in *Rhizopora* leaves it varied between 0.0016 and 0.0046ppm respectively. In *Acanthus* root, the bio concentration of Fe varied between 0.0004 and 0.0205ppm, in the stem it varied between 0.0004 and 0.0012ppm and in *Acanthus* leaves it varied between 0.0014 and 0.0081ppm respectively. In *Avicennia* root the lowest bio concentration was 0.0039 and the highest was 0.0364ppm, in *Avicennia* stem it varied between 0.0004 and 0.0156ppm and in *Avicennia* leaves it varied between 0.0006 and 0.0049ppm respectively.

Statistical analysis showed that Fe correlates positively with Pb during monsoon and with Kjeldhal nitrogen during post monsoon. Considering station wise correlation, at stations 2 and 3, Fe correlates with Cd. The mean of Fe for different plants are as follows.1.73ppm (*Rhizopora*), 1.02ppm (*Acanthus*) and 1.07ppm (*Avicennia*). The means for different plant parts are 2.98ppm (root), 0.31ppm (stem), and 0.53ppm (leaf). For stations 1 to 4 the means of Fe concentrations are 1.86ppm, 1.75ppm, 0.57ppm, and 0.91ppm respectively. This indicates that among the three plants *Rhizopora* has better Fe accumulation capacity, among plant parts root is far more efficient than stem and leaf in Fe storage. Also plants at station 1 have greater bioaccumulation of Fe. Three way anova for Fe did not show any significant P values.

5. 5. 2 Manganese

Manganese is an essential micronutrient for all organisms including man. Manganese is the second most prevalent trace metal after Fe in the earth's crust. It finds use in dry cell batteries as depolarizer, in non ferrous alloys as a hardener for Al, Mg, Cu, Ni, and Zn alloys, for rust proofing and in the manufacture of inks, varnishes, dyes, and ceramics. Anthropogenic sources of such as emissions from iron and steel industry, combustion of fossil fuels etc pollute the air with Mn. River discharge, leachate from land fills and soils release Mn into water. Mn has alternating red-ox states which can easily transform under natural conditions. One of the reasons for the natural abundance of Mn is due to its role in electron exchange reactions of plants. Mn (II) is soluble the form of Mn found in nature. Increasing pH will enhance Mn oxidation and precipitation, especially in the presence of catalytic surfaces such as MnO_2 (Scott et al, 2002). Mn (II) is more bio available than Mn (IV) with decreasing pH and redox potential (Heal 2001). The lower Mn (II) predominates in reducing environments and higher Mn concentration is observed in flooded soils and results in higher bioavailability. Mn toxicity is widespread in plants growing in waterlogged soils. This is due to the fact that Mn becomes more bio available at low pH and in reducing environments. Manganese toxicity is a major problem for plants growing in acidic soils. Micro organisms also play an important role in Mn cycling in aquatic environment (Stein et al, 2001). Though Mn(IV) is also found, it is easily reduced to Mn(II) by cyano bacteria. Being easily bio available Mn in the reduced form can accumulate in the fauna such as lobsters and its eggs (Erikson, 2000). Uptake of Mn by aquatic organisms increase with temperature, decreases with pH and increases with decreasing salinity. Redox conditions, pH, oxygen content and of the soil and overlying water as well as benthic organic carbon supply are factors controlling Mn cycle in sediments. Mn concentrations at depth may partly reflect the original nature of sediments before mangrove forests were formed. Under suboxic conditions Pb, Ni, and Co can be easily adsorbed on Mn oxides (Dong et al, 2000).

Mn toxicity in plants is manifested in chlorosis, brown speck formation, deformed leaves and necrosis. These symptoms arise when Mn toxicity leads to inhibition of chlorophyll synthesis. Mn accumulation in cell walls is also another factor for the above conditions. Excess of Mn interferes with the Ca^{2+} homeostasis. Plants over come Mn excess by accumulating it in vacuoles. They also exhibit distinct compartmentalization patterns such as accumulation in the epidermal layer and desorption in trichomes to over come the negative effects of accumulated Mn. Manganese transporter enzymes helps to delocalize excess Mn from a point. Mn deficiency is known to produce phototropic inhibition in plants. Mn content was found to be higher in older leaves than in younger leaves and was preferentially accumulated in the leaf marginal tissue. Organically bound fractions and Fe and Mn oxide fractions were more significant for mangroves. Mn oxides along with Fe oxides are known to play an important role in the trace metal retention in mangrove soils (Amusan et al., 2005). Mn in mangrove plants are known to have a higher concentration in monsoon and post monsoon. During these seasons there was a lowering of pH making Mn more bio available. Manganese under anaerobic conditions and high salinity will be existing as carbonates (Marchand, 2004). Carbonate is a rather stable phase of Mn. When aeration rates are high, Mn in the dissolved phase decreases and consequently there is an increase in the solid phase presumably due to precipitation as oxi-hydroxides leading low bio accumulation of Mn observed in pre-monsoon. Mn was mobile only in xylem. Golgi based Mn accumulation therefore results in Mn tolerance through vehicular trafficking and exo cytosis. Transpiration also controls the rate of distribution of Mn in plants (Edgar Peiter, 2007).

Results and discussion

In pre- monsoon the concentration of Mn varied between 0.030 and 0.132ppm in *Rhizopora* roots, between 0.003 and 0.057ppm in *Acanthus* roots and between 0.025 to 0.048ppm in *Avicennia* roots at various stations. *Rhizopora* roots showed a higher tendency to accumulate Mn than *Acanthus or Avicennia roots.* The variations in Mn concentrations in the stem of the above plants were between 0.012 and 0.049ppm in *Rhizopora,* between

0.020 and 0.048ppm in Acanthus and between 0.019 to 0.054ppm for *Avicennia*. Among the plant leaves, the variations were between 0.009 to 0.122ppm for *Rhizopora*, between 0.054 and 0.099ppm for *Acanthus* and between 0.021 and 0.224ppm for *Avicennia*. This shows that Mn tended to accumulate more in leaves than root. Mn content decreased quickly in root and increased simultaneously in leaf. The maximum and minimum concentrations of Mn in various plant parts was between 0.009 and 0.132ppm respectively for *Rhizopora*, 0.003 and 0.099ppm for *Acanthus* and 0.019 and 0.224ppm for *Avicennia*. The above observations show that the tendency to accumulate Mn in plants was *Av >R >Ac* during pre-monsoon. The bio-concentration factor (BCF)) of Mn in pre-monsoon for *Rhizopora* root varied between 0.045 and 0.1261ppm, for *Rhizopora* stem it varied between 0.0113 and 0.0745ppm and in *Rhizopora* leaves it varied between 0.0126 and 0.2026ppm respectively. In *Acanthus* root the bio concentration of Mn varied between 0.0044 and 0.0776, in the stem it varied between 0.0216 and 0.0795 and in *Acanthus* leaves it varied between 0.0511 and 0.1325 respectively. In *Avicennia* root the lowest bio concentration was 0.0421ppm and the highest was 0.0646ppm, in *Avicennia* stem it varied between 0.0249ppm and 0.0747ppm and in *Avicennia* leaves it varied between 0.0284 and 0.2454 respectively.

Similarly in monsoon the Mn concentration in *Rhizopora* roots varied between 0.003 and 0.055ppm, in *Acanthus* roots it varied between 0.027 and 0.69 ppm and in *Avicennia* roots it varied between 0.026 and 0.092ppm respectively. For the stems of the different mangrove plants, in *Rhizopora* stem the variations were between 0.017 and 0.064 ppm, in *Acanthus* stem it was between 0.013 and 0.027ppm, while in *Avicennia* stem it was between 0.021 and 0.047ppm respectively. In *Rhizopora* leaves the variations of Mn concentrations were between 0.022 and 0.094ppm, in *Acanthus* leaves between 0.024 and 0.181ppm and in *Avicennia* leaves it varied between 0.032 and 0.207ppm respectively. The Mn accumulation capacity of *Avicennia* leaves was shown to be higher than *Acanthus* leaves and *Avicennia* leaves. Among the different plants the variations in Mn concentrations for *Rhizopora* were between 0.003 and 0.094ppm, in *Acanthus*

between 0.013 and 0.181ppm and in *Avicennia* between 0.021 and 0.207ppm during monsoon. The maximum concentration of Mn 0.207ppm was observed in *Avicennia* leaves at station 1 during monsoon and the minimum Mn concentration of 0.003ppm in plants was observed in *Rhizopora* roots *at station 3.* During monsoon the concentration of Mn in Rhizopora followed the order l >s >r at stations 1 and3, l> s =r at station 2 and r >s >l at station 4. For *Acanthus* at all the stations except station 1, the order was found to be r>l>s. For station 1 it was l>s>r. For *Avicennia* at stations 2, 3 and 4, l > r> s was the order for the concentration of Cd while at station 1 it was l>s r>. There was a greater tendency for accumulation of Mn in leaves during monsoon. This was especially true in the case of *Rhizopora* and *Avicennia.* The bio-concentration factor (BCF)) of Mn in monsoon for *Rhizopora* root varied between 0.0064 and 0.1708, for *Rhizopora* stem it varied between 0.0160 and 0.1401 and in *Rhizopora* leaves it varied between 0.0678 and 0.1878 respectively. In *Acanthus* root the bio concentration of Mn varied between 0.0275 and 0.2118, in the stem it varied between 0.015 and 0.0852 and in *Acanthus* leaves it varied between 0.0202 and 0.1814 respectively. In *Avicennia* root the lowest bio concentration was 0.0224 and the highest was 0.2876, in *Avicennia* stem it varied between 0.0177 and 0.1407 and in *Avicennia* leaves it varied between 0.2073 and 0.4617 respectively. In post-monsoon the Mn concentration in *Rhizopora* roots was found to be between 0.009 and 0.027ppm, in *Acanthus* root it was shown to be between 0.011 and 0.234ppm and in *Avicennia* root it varied between 0.034 and 0.160ppm. The Mn concentration varied between 0.013 and 0.115ppm in *Rhizopora* stem, between 0.020 and 0.037 ppm in *Acanthus* stem and between 0.024 and 0.129ppm in *Avicennia* stem. In leaves the Mn concentration varied between 0.042 and 0.184ppm in *Rhizopora* leaves, between 0.034 and 0.061ppm in *Acanthus* leaves and between 0.053 and 0.329ppm in *Avicennia* leaves. Among the different plants at the four stations, *Rhizopora* had Mn concentration between 0.099 and 0.102ppm, Acanthus had Mn concentration between 0.011 and 0.234ppm and *Avicennia* had Mn concentration between 0.024 and 0.329 ppm respectively in their different parts. Among all the plants the lowest Mn concentration of 0.009 was recorded in *Rhizopora* root at station 1, and the highest of 0.329ppm

was found in *Avicennia* leaves at station 2. During post monsoon at stations 1, 2 and 4, the Mn concentration in Rhizopora followed the order l>s>r and at station 3, it was s>l>r. For Acanthus the variations were r>l>s at stations 1 and 4, l>s>r at station 2 and s>l>r at station 3. The bio-concentration factor (BCF)) of Mn in post-monsoon for *Rhizopora* root varied between 0.0069 and 0.0434, for *Rhizopora* stem it varied between 0.0095 and 0.1856 and in *Rhizopora* leaves it varied between 0.0383 and 0.2975 respectively. In *Acanthus* root the bio concentration of Mn varied between 0.0104 and 0.3781, in the stem it varied between 0.0218 and 0.0372 and in *Acanthus* leaves it varied between 0.0308 and 0.0710 respectively. In *Avicennia* root the lowest bio concentration was 0.0248 and the highest was 0.2575, in *Avicennia* stem it varied between 0.0216 and 0.1250 and in *Avicennia* leaves it varied between 0.2107 and 0.2808 respectively.

Statistical analysis showed that Mn correlates positively with Kjeldhal nitrogen and protein at station 2. No other significant correlation exists between Mn and any other parameters. The mean of Mn for different plants are as follows: 0.05 ppm (*Rhizopora*), 0.05ppm (*Acanthus*) and 0.09ppm (*Avicennia*). This indicates that among the three plants *Avicennia* has better Mn accumulation capacity. The means for different plant parts are 0.05 ppm (root), 0.04 ppm (stem) and 0.10 ppm (leaf). Hence among plant parts leaf is far more efficient than root and stem in Mn storage. For stations 1 to 4 the means of Mn concentrations are 0.07 ppm, 0.05ppm, 0.05ppm and 0.08ppm respectively. Therefore plants at station 4 have greater bioaccumulation of Mn. Three way anova did not show any significant variations for Mn concentrations between plants or between stations.

5. 5. 3 Zinc

Most of the metals are cumulative poisons and the toxicity of a metal depends on its inherent capacity to interfere adversely in the metabolic processes of an organism. Pesticides, brass manufacturing, galvanizing iron and steel industry, petrochemicals, combustion of coal, organic chemicals etc are the prominent contributors to elevated concentration of Zn in the environment.

Zn is an essential plant micronutrient and due to its mobility, it gets bio accumulated in plant parts (Akshayya et al, 2007). In anaerobic conditions enhanced sulphide co precipitation actively removes Zn from the dissolved phase. Zn is a metal that is more concentrated in mangrove sediments (Marchand, 2006). Metals in general are not detoxified and bio accumulates in organisms which are exposed to them. The salinity plays a dominant role in the toxicity of metals. Adsorption rate of zinc per unit mass and time has been shown to decrease with increasing salinity. Zn is more bio available to invertebrates at lower salinities. The moulting of crustaceans temporarily increases the rate of uptake of metals into the body, with temporary increase in body surface permeability prior to formation of new cuticle. Algae such as *Cladophora* showed high levels of Zn. Concentration of Zn also impacted the concentration of other elements such as Cd, Fe and Pb. The concentration of Zn in marine fishes from Cochin area showed increased concentration in gills and alimentary canal (Nair et al, 1997). *Rhizopora* is known to be a storehouse of poly phenols. Higher concentration of metals is found in roots of *Rhizopora* compared to stem and leaves. Large amounts of tannins present in them render metals inactive by binding them and thereby delaying their re - entry into the system and slowing down their cycling. Zn accumulation in root tissue was found to increase with increase in NaCl (Chiu et al, 1995). This observation was found in the present study too in the case of *Rhizopora*. Zn was the most mobile of all metals and was accumulated to the greatest quantity in leaf tissue of mangrove plants such as *A. marina* (Macfarlane 2002).

Results and discussion

Zn concentrations varied between 1.020 and 0.023ppm during pre monsoon; In monsoon it varied between 0.181ppm and 0.017ppm and in post monsoon it varied between 0.278 and 0.010ppm in various plant parts. The Zn concentration was high in *Rhizopora* stem in stations 1and 2, while in stations 3 and 4 root had greater concentration during pre monsoon. This indicates that *Rhizopora* at stations 3and 4 must be having sufficiently high concentrations of complexing compounds to prevent their translocation. In

pre- monsoon the concentration of Zn varied between 0.037 and 1.020ppm in *Rhizopora* roots, between 0.043 and 0.092ppm in *Acanthus* roots and 0.046 and 0.133ppm in *Avicennia* roots at various stations. *Rhizopora* roots showed a higher tendency to accumulate Zn than *Avicennia and Acanthus roots*. The variations in Zn concentrations in the stem of the above plants were between 0.026 and 0.097ppm *in Rhizopora* between 0.062 and 0.312ppm in Acanthus and between 0.040 and 0.112ppm for *Avicennia*. Among the plant leaves, the variations were between 0.023 and 0.037ppm for *Rhizopora*, between 0.068 and 0.258ppm for *Acanthus* and between 0.032 and 0.103ppm for *Avicennia*. The maximum and minimum concentrations of Fe in various plant parts was between 0.023 and 1.020ppm respectively for *Rhizopora*, 0.043 and 0.312ppm for *Acanthus* and 0.032 and 0.133ppm for *Avicennia*. The above observations show that the tendency to accumulate Fe in plants was *Rhizopora> Acanthus> Avicennia,* during pre-monsoon. The Zn accumulation tendency for *Rhizopora* plant parts at various stations were s>r>l at stations 1 and 2, r>l>s at station 3 and r>s>l at station 4. For *Acanthus* it was s>l>r at station 1, l>s>r at stations 2 and 3, and r>s>l at station 4. For *Avicennia* the order was l>r>s at stations 1and 4 and r>s>l at stations 2 and 3. The bio-concentration factor (BCF) of Zn for Rhizopora root varied between 0.0301 and 3.778, for *Rhizopora* stem it varied between 0.0181 and 0.3604 and in *Rhizopora* leaves it varied between 0.0195 and 0.0849 respectively. In *Acanthus* root the bio concentration of Mn varied between 0.0398 and 0.3407, in the stem it varied between 0.0742 and 0.2956 and in *Acanthus* leaves it varied between 0.0977 and 0.2868 respectively. In *Avicennia* root the lowest bio concentration was 0.0648 and the highest was 0.1815, in *Avicennia* stem it varied between 0.0571 and 0.1480 and in *Avicennia* leaves it varied between 0.0381 and 0.1885 respectively.

Similarly in monsoon the Zn concentration in *Rhizopora* roots varied between 0.019 and 0.029, in *Acanthus* roots it varied between 0.026 and 0.137ppm and in *Avicennia* roots it varied between 0.041 and 0.112ppm respectively. Among the stems of the different mangrove plants, in *Rhizopora* stem the variations were between 0.018 and 0.055ppm, in *Acanthus* stem it was between 0.028 and 0.113ppm, while in *Avicennia* stem it was between 0.034

and 0.116 ppm respectively. In *Rhizopora* leaf the variations of Zn concentrations were between 0.017 and 0.050ppm, in *Acanthus* leaf between 0.039 and 0.103ppm and in *Avicennia* leaf it varied between 0.024 and 0.181ppm respectively. The Zn accumulation capacity of Av leaf was shown to be higher than *Acanthus* leaf and *Rhizopora* leaf. During monsoon the concentration of Zn in *Rhizopora* followed the order l > s >r at stations 1, while it was s>l>r at station 2 and s>r>l at station 3 and l>r>s at station 4. For *Acanthus* at stations 1 and 4 the order was found to be l>s>r, while at stations 2 it was r>l>s and at station 3 it was r>s>l. For *Avicennia* at station1, it followed the sequence l>r>s, at station 2, l>s>r, at station 3, r>s>l while at station 4, it was r>l>s. Among the plants *Rhizopora* had higher Zn in stem and leaf while in *Acanthus* and *Avicennia* more Zn was found in root and leaves. Among the three plants the concentration of Zn was *Avicennia* > *Acanthus* > *Rhizopora*. The bio-concentration factor (BCF)) of Zn during monsoon for *Rhizopora* root varied between 0.0304 and 0.0866ppm for *Rhizopora* stem it varied between 0.0444 and 0.1251ppm and in *Rhizopora* leaves it varied between 0.0393 and 0.0986ppm respectively. In *Acanthus* root the bio concentration of Mn varied between 0.0351 and 0.3107ppm, in the stem it varied between 0.0325 and 0.2570ppm and in *Acanthus* leaves it varied between 0.0479 and 0.4698ppm respectively. In *Avicennia* root the lowest bio concentration was 0.0548ppm and the highest was 0.2924ppm, in *Avicennia* stem it varied between 0.0531ppm and 0.1526ppm and in *Avicennia* leaves it varied between 0.0552ppm and 0.2524ppm respectively.

In post- monsoon, the Zn concentration in *Rhizopora* root was found to be between 0.010 and 0.170ppm, in *Acanthus* root it was shown to be between 0.032 and 0.114ppm and in *Avicennia* root it varied between 0.038 and 0.127ppm. The Zn concentration varied between 0.021 and 0.074ppm in *Rhizopora* stem, between 0.022 and 0.074ppm in *Acanthus* stem and between 0.027 and 0.073ppm in *Avicennia* stem. In leaves the Zn concentration varied between 0.017 and 0.105ppm in *Rhizopora* leaves between 0.071 and 0.278ppm in *Acanthus* leaves and between 0.042 and 0.094ppm in *Avicennia* leaves. Among all the plants the lowest Zn concentration of 0.10ppm was recorded in *Rhizopora* root at station 1 and the

highest of 0.278ppm was found in *Acanthus* leaves at station 2. The Zn accumulation tendency for Rhizopora plant parts at various stations were l>s>r at station 1, l>r>s at station 2, r>l>s at station 3 and s>r >l at station 4. For *Acanthus* it was l>r >s at station 1, l>s>r at stations 2 and 3, and r> l > s at station 4. For Avicennia the order was l>r>s at station 1, r> l > s, at stations 2 and 3 and s>l>r at station 4. From this we can see that in *Rhizopora* and *Acanthus* more Zn accumulated in leaves, while in *Avicennia* more Zn concentrated in root. Heavily polluted mangrove is reported to have zinc at 14.3ppm in leaf. Higher sediment pH, organic content and pH promoted leaf Zn accumulation. The additive effect of Pb and Zn in increasing *A. Marina* leaf Zn accumulation was observed. *Peroxidase* activity is a good biochemical indicator of Zn accumulation (Macfarlane, 2002). Zn is an essential requirement for chloroplast reactions enzyme systems protein synthesis carbohydrate and growth hormone productions. Perhaps its importance in light related reactions explains its greater translocations to leaf. The bio-concentration factor (BCF)) of Zn in post monsoon for *Rhizopora* root varied between 0.159 and 0.0996, for *Rhizopora* stem it varied between 0.0277 and 0.1293 and in *Rhizopora* leaves it varied between 0.0614 and 0.1169 respectively. In *Acanthus* root the bio concentration of Mn varied between 0.0188 and 0.4081, in the stem it varied between 0.0431 and 0.0834 and in *Acanthus* leaves it varied between 0.0513 and 0.3611 respectively. In *Avicennia* root the lowest bio concentration was 0.0605 and the highest was 0.1350, in *Avicennia* stem it varied between 0.0433 and 0.1740 and in *Avicennia* leaves it varied between 0.0552 and 0.1496 respectively.

Statistical analysis showed that Zn correlates positively with Ni during monsoon and post monsoon. The mean of Zn for different plants are as follows.0.07ppm (*Rhizopora*), 0.08ppm (*Acanthus*) and 0.06 ppm (*Avicennia*). This indicates that among the three plants *Acanthus* has better Zn accumulation capacity. The means for different plant parts are 0.09ppm (root), 0.06ppm (stem) and 0.07ppm (leaf). For stations 1to 4 the means of Zn concentrations are 0.05ppm, 0.06ppm, 0.09ppm and 0.09ppm respectively. Among plant parts, root is more efficient than leaf and stem in Zn storage.

Also plants at stations 3 and 4 show greater uptake of Zn. Three way anova for Zn did not show any significant variation.

5.5.4 Nickel

Ni has been found in a variety of plants and animal tissues. Ni essentiality to plants is indicated by increase in plant height and improved growth and yield. Ni poisoning on the other hand produced dwarfing and at advanced stages produced chlorosis, followed by necrosis and death of plant. Nickel is consistently present in RNA. It is bound to several biological substrates such as proteins (keratin and insulin) amino acids and serum albumin. It also activates enzymes such as acetyl coenzyme a, carboxylase and synthetase. Among the different mangrove plant parts, pnuematophores are known to accumulate the highest concentration followed by bark. The leaves had the lowest concentration (Lacerda, 1997). Ni was found to be in highest concentration in pnuematophores because they are perennial parts of the plant and accumulates the elements with time. Leaves showed a low concentration probably because they are deciduous. The concentration of Nickel in mangrove sediments is reported to vary between 90.32 and 152.03ppm with an average value of 115.49ppm (Saifullah, Khan and Ismail, 2002). Great proportion of Ni was deposited in mangrove sediments than in plants. The geochemical processes occurring beneath the mangrove forest floor exert an important influence on the storage and availability of soil elements (Alongi et al, 2004). Ni was higher at surfacial sediments due to recent impacts from anthropogenic sources. The sediments release the metals only on strong oxidation.

Results and discussion

In the mangrove plants, Ni showed slightly higher concentration in the roots and stem than in leaves. In pre- monsoon the concentration of Ni varied between 0.005 to 0.014ppm in *Rhizopora* roots, between 0.009and 0.026ppm in *Acanthus* roots and between 0.005 and 0.030ppm in *Avicennia* roots at various stations. *Acanthus* and *Avicennia* roots showed a higher tendency to

accumulate Ni than Rhizopora roots. The variations in Ni concentrations in the stem of the above plants were between 0.005 and 0.014ppm in *Rhizopora*, between 0.006 and 0. 026ppm in Acanthus and between 0.005 and 0.028ppm in Avicennia. Among the plant leaves, the variations were between 0.006 and 0.013ppm for *Rhizopora*, between 0.006 and 0.022ppm for *Acanthus* and between 0.004 and 0.011ppm for *Avicennia*. The above observations show that the tendency to accumulate Ni was *Rhizopora<Avicennia< Acanthus* during pre-monsoon. The maximum and minimum concentrations of Ni in various plant parts were between 0. 005 and 0.014ppm respectively for *Rhizopora*, 0.006 and 0.026ppm for *Acanthus* and 0.004 and 0.030ppm for *Avicennia*. Among the roots of the three mangrove plants the maximum Ni concentration of 0.030ppm was shown by *Avicennia* root at station 2, among the stem, the maximum concentration of 0.028ppm was shown by *Avicennia* stem at station 2 and among the leaves the highest concentration 0.022ppm was shown by *Acanthus* at station 2, indicating that station2 had a higher Ni accumulating capacity. The bio-concentration factor (BCF) of Ni in pre monsoon for *Rhizopora* root varied between 0.0133 and 0.0314ppm, for *Rhizopora* stem it varied between 0.0380 and 0.124ppm and in *Rhizopora* leaves it varied between 0.0158 and 0.0381ppm respectively. In *Acanthus* root the bio concentration of Ni varied between 0.0203 and 0.0588ppm, in the stem it varied between 0.0134 and 0.0581ppm and in *Acanthus* leaves it varied between 0.0143 and 0.0470ppm respectively. In *Avicennia* root the lowest bio concentration was 0.0120 and the highest was 0.0647ppm, in *Avicennia* stem it varied between 0.0111 and 0.0576ppm and in *Avicennia* leaves it varied between 0.0094 and 0.0436ppm respectively.

Similarly in monsoon, the Ni concentration in *Rhizopora* roots varied between 0.007 and 0.015ppm and *Acanthus* root it varied between 0.008 and 0.019ppm and in *Avicennia* root it varied between 0.010 and 0.036ppm respectively. For the stems of the different mangrove plants, in *Rhizopora* stem the variations were between 0.010 and 0.026ppm in *Acanthus* stem it was between 0.010 and 0.026ppm, while in *Avicennia* stem it was between 0.008 and 0.022ppm respectively. In *Rhizopora* leaves, the variations of Ni

concentrations were between 0.006 and 0.022ppm, in *Acanthus* leaves between 0.007 and 0.032ppm and in *Avicennia* leaves it varied between 0.005 and 0.028ppm respectively. The Ni accumulation capacity of *the* 3 plants was shown to be almost similar during monsoon with Acanthus showing slightly higher tendency for Ni accumulation. The minimum Ni concentration of 0.005ppm was observed in *Avicennia* root at station 3 in monsoon and the maximum Ni concentration of 0.036ppm among various plants was observed in *Avicennia* root at station 2 and The Ni concentration during monsoon in each plant varied as follows: in *Rhizopora* between 0.006 and 0.022ppm, in *Acanthus* between 0.077 and 0.032ppm and in *Avicennia* between 0.005 and 0.036ppm. During monsoon Ni concentration of Ni in roots was found to follow the order *Av> Ac>R*, in stem and leaves Ac> Av>R. During monsoon the concentration of Ni in *Rhizopora* followed the order l> s>r at station1, s>l>r at stations 2 and 3 and s>r>l at station 4. For *Acanthus* at station1, the order of Ni accumulation in various parts of the plant was found to be l>s>r, l=s>r at station 2 and r>s>l at station 3 and r=s>l at station 4. For *Avicennia* at station1, Ni concentration varies as s > r = l, at station 2, r > l > s, at stations 3 and 4 the accumulation order for Ni was r>s>l. The bio-concentration factor (BCF)) of Ni in monsoon for *Rhizopora* root varied between 0.0192 and 0.0746ppm, for *Rhizopora* stem it varied between 0.0281 and 0.1060ppm and in *Rhizopora* leaves it varied between 0.0225 and 0.0641ppm respectively. In *Acanthus* root the bio concentration of Mn varied between 0.0177and 0.1025ppm, in the stem it varied between 0.0218 and 0.0963ppm and in *Acanthus* leaves it varied between 0.0298 and 0.0795ppm respectively. In *Avicennia* root the lowest bio concentration was 0.0206ppm and the highest was 0.1221ppm, in *Avicennia* stem it varied between 0.0259 and 0.0982ppm and in *Avicennia* leaves it varied between 0.0198and 0.0744ppm respectively

In post- monsoon the Ni concentration in *Rhizopora* roots was found to be between 0.004 and 0.009ppm, in *Acanthus* root it was shown to be between 0.004 and 0.024ppm and in *Avicennia* roots it varied between 0.009 and 0.016ppm. The Ni concentration varied between 0.005 and 0.010ppm in *Rhizopora* stem, between 0.004 and 0.008ppm in *Acanthus* stem and

between 0.003 and 0.005ppm in *Avicennia* stem. In leaves the Ni concentration varied between 0.006 to 0.015 ppm in *Rhizopora* leaves, between 0.010 to 0.018ppm in *Acanthus* leaves and between 0.004 to 0.009ppm in *Avicennia* leaves. Among the plant roots, *Avicennia* roots showed the highest value for Ni concentration, while among stems *Acanthus* stem had the highest value and among the leaves, *Acanthus* leaves contained the highest Ni content. Among the different plants at the four stations, *Rhizopora* had Ni concentration between 0.004 and 0.015ppm, *Acanthus* had Ni concentration between 0.004and 0.024ppm and *Avicennia* had Ni concentration between 0.003 and 0.016ppm respectively. Among all the plants parts the lowest Ni concentration of 0.003ppm was found in *Avicennia* stem was recorded at station 3 and the highest Ni concentration of 0.024 was found in *Acanthus* root at station 4. The bio-concentration factor(BCF) of Ni in post monsoon for *Rhizopora* root varied between 0.0091 and 0.0467, for *Rhizopora* stem it varied between 0.0097 and 0.0620 and in *Rhizopora* leaves it varied between 0.0146and 0.0373 respectively. In *Acanthus* root the bio concentration of Mn varied between 0.0078 and 0.1512, in the stem it varied between 0.0098 and 0.0246 and in *Acanthus* leaves it varied between 0.0205 and 0.0618 respectively. In *Avicennia* root the lowest bio concentration was 0.0174 and the highest was 0.0622, in *Avicennia* stem it varied between 0.0068and 0.518 and in *Avicennia* leaves it varied between 0.0137 and 0.0249 respectively. During post monsoon the Ni concentration in *Rhizopora* followed the order l>s>r at station 1, l>r>s at station 2, and s > r = l at stations 3 and 4. In *Acanthus* the variations in plant parts at the different stations followed the order l>r>s at station 1, r>l>s at stations 2 and 4 and l>s>r at station 3. Statistical analysis results showed that Ni correlates positively with Zn during monsoon and with Cu during post monsoon. In station wise correlation Ni correlates with Cu at station 3. In cluster analysis, Ni forms a cluster with Cu and Cd. Three way anova showed that seasonal and station wise variations of Ni are significant with $P<0.001$.

5.5.5 Lead

Marine ecosystems close to urban development and sources of metal contamination accumulate more trace elements. Pb and Cd are typical constituents of heavy metal pollution. Pb is a non essential element, which will cause toxicity at higher concentrations. Lead toxicity is of concern even in less polluted areas. Pb appears to be more toxic than Cd for all tested phytoplankton strains. This is in accordance with the general observation that toxicity of heavy metals tends to increase with electro positivity (Susanne dal Jenson, 2000). Lead produces low growth in plants (Adam and Duncun, 2001). Leaded petrol, ship breaking industry, oil refineries, fertilizers, dredging of harbour, batteries, photography pulp and paper industry are some of the sources which brings about lead pollution. Oxygen poor water at the water sediment interface will cause chalcophilic metals such as lead to precipitate from water and settling in sediments. Lead is found to present in the reducible, and to a lesser extent in the oxidisable and carbonate fractions. Lead bound to these fractions will behave differently in different sedimentary and diagenetic environments and have different potential for remobilization. Arsenic has an antagonistic impact on lead accumulation (Luan et al, 2008). Lead readily complexes and binds strongly to dissolved and particulate organic matter. As the amount of organic matter decreases, lead associated with this fraction decreases by oxidation from the organic matter during early diagenesis. Contrary to Cd, Pb is present mainly in the free form and only a minor portion of lead in water is present as free dissolved ion. It has the ability to form soluble sulphide species and remain in solution once solubilised. Under anaerobic conditions active sulphide co precipitation removes lead from the dissolved phase (Schlieker et al, 2001). Lead binds strongly to organic material. Lead toxicity can be expected to vary considerably, being influenced by binding to organic matter, by inorganic complexing and by pH sensitive complex heterogeneous co-precipitation or flocculation reactions. Low pH and low organic matter contribute to greater amount of Pb in the labile form. Lead is bound to be present in the more labile phase throughout early diagenesis or be lost from sediments. Metals

bound to the residual phases are generally unlikely to be reactive during sedimentation and diagenesis and have little potential for bioavailability. Under suboxic conditions lead can be easily adsorbed onto Mn oxides (Dong et al, 2000). Rapid chemical changes will induce elevated lead concentration in the solid phase. Precipitation as metal sulphides under anoxic conditions will reduce bioavailability. Low concentration of metals is found in the sulphide oxidation zones due to the release of metal in the dissolved phase (Marchand et al., 2006).

Higher the concentration of lead to which fishes are exposed, the more it accumulates, showing no regulation. Lead has an affinity for metabolic ligands especially metallothionein. Lead is known to be concentrated in bony organs such as gills, backbone and tail of fishes. Fishes during the process of feeding suck up the surface layer of mud and transfer the mineral particles into their system. The detritus feeders are exposed to greater metal pollution than pelagic feeders. Inorganic granules containing greater concentration of calcium is also a location were lead deposits are found. In the gills and the intestine of fishes, lead is reported to complex with the mucous (Senthilnathan and Balasubramanian, 1998). Shellfish found in polluted areas can easily imbibe lead, thus increasing potential toxicity on its consumers, including man. In humans lead accumulation will lead to anaemia, as it interferes with oxygen transport by haemoglobin. Thus it inhibits the most important process of energy production and utilization in the body. Pb exhibits limited uptake, minimal mobility and less toxic effects in terms of growth responses up to 800 ug/g (Mc Farlane, 2002). As Pb in leaf tissue increases peroxidase activity increases. So measurement of peroxidase activity also gives an indication about lead toxicity. Cells are known to possess very rapid and effective detoxification methods for lead. Endoplasmic reticulum R is the site of lead accumulation. Lead enters the cell to a greater extent than Cd. Thiol s such as glutamic acid and glutathione complexes with lead. Low concentration of lead in the soil leads to low mobility in the soil.

Lead is a toxic non –essential metal for plants. Different plants have different rates of accumulation for same metal due to physiological differences and

variations that exists in metal accumulation strategies in different plant species (Lindsey et al, 2005). Earlier studies on metal accumulation in mangrove plants of Kerala have shown that seasonal variations in lead content were not prominent among different mangrove species. Pb concentration in mangrove plants is reported to vary from 75-225 µg/g in *A. Officianalis* and from 25-125 µg/g in *A. ilicifolius* (Thomas and Fernandez 1997). In the polluted Punta mala bay Pb leaf concentration was as high as 6.14 ppm. This is an elevated concentration. In the mangrove plants studied lead showed low concentration and tend to accumulate in the roots. The concentration of lead in the samples analysed varied between 22.13ppb to undetectable levels in various mangrove plant parts. Elevated concentration of non -essential metals in root tissue does suggest function of sequestering toxic metals especially with respect to lead. Increase in salinity may result in less effective blocking of metal uptake due to imbalance of salt uptake control mechanism. In *A. marina* Pb is excluded at the root epidermis (Macfarlane and Burchett, 2000). Various studies have indicated that lead accumulation showed variations among plants and stations as well as among seasons. The pre monsoon concentrations were higher. The leaves of *Avicennia* followed by *Acanthus* showed a higher accumulation of lead than *Rhizopora* leaves. Pb is known to show a significant relation between sediment and Pb in leaves, with Pb reaching only ug/g at the most contaminated site. Also Pb concentration is reported to be significantly different among sites and accumulation of Pb in leaf tissue is found to be very low (0.01 to 3.9 ug/g). Lead continues to be a significant public health problem in developing countries in Asia, not only among humans, but also among various species of terrestrial organisms (Hsu et al., 2006).

Results and discussion

The pre- monsoon concentration of Pb varied between 0 to 11.67 ppb in *Rhizopora* roots, 0 to 22.13ppb in *Acanthus* roots and between 0.06 to 29.21ppb in *Avicennia* roots at various stations. *Avicennia* roots showed a higher tendency to accumulate Pb than *Rhizopora* and *Acanthus* roots. The

variations in Pb concentrations in the stem of the above plants were between 0 and 6.69 *ppb in Rhizopora,* between 0 and 12.11ppb in *Acanthus* and between 0 and 37.89ppb for *Avicennia*. Among the plant leaves, the variations were between 0 and 3.96ppb for *Rhizopora*, between 0.17 and 18.97ppb for *Acanthus* and between 0 to 12.61ppb for *Avicennia*. The maximum and minimum concentrations of Pb in various plant parts was between 0 and 11.67 ppb respectively for *Rhizopora*, 0 and 22.13 ppb for *Acanthus* and 0 and 37.89 for *Avicennia*. The above observations show that the tendency to accumulate Pb in plants was *Avicennia* > *Acanthus* > *Rhizopora during* pre-monsoon. The concentration of Pb at various stations during pre-monsoon followed the sequence r>l>s at station 1, l>r>s at station 2, l>s>r at station 3 and r>s>l at station 4. Thus in *Rhizopora* greater Pb concentration was seen in root and leaf. But in *Acanthus* and *Avicennia* more Pb accumulated in the root. The bio-concentration factor (BCF)) of Pb in pre monsoon for *Rhizopora* root varied between 0000 and 0.1079, for *Rhizopora* stem varied between 0.00 and 0.0992 and in *Rhizopora* leaves varied between 0.0000 and 0.0123 respectively. In *Acanthus* root the bio concentration of Pb varied between 0.0000and 0.0687, in the stem it varied between 0000 and 0.0376 and in *Acanthus* leaves it varied between 0.0004 and 0.0589 respectively. In *Avicennia* root, the lowest bio concentration was 0.0001 and the highest was 0.4327, in *Avicennia* stem it varied between 0.0000 and 0.3895 and in *Avicennia* leaves it varied between 0.0000 and 0.0391 respectively.

Similarly in monsoon the Pb concentration in *Rhizopora* root varied between 4.14 and 14.73 ppb in *Acanthus* roots it varied between 3.53 and 18.23 ppb and in *Avicennia* roots it varied between 7.80 and 11.62ppb respectively. For the stems of the different mangrove plants, in *Rhizopora* stem the variations were between 3.40 and 9.48ppb, in *Acanthus* stem it was between 0.42 and 9.76ppb, while in *Avicennia* stem it was between 3.85 and 11.48ppb respectively. In *Rhizopora* leaves the variations of Pb concentrations were between 0.46 and 5.32ppb, in *Acanthus* leaves between 2.48 and 7.49ppb and in *Avicennia* leaves it varied between 0.82 and 5.23 ppb respectively. Among the different plants the variations in Pb concentrations for *Rhizopora* were between 0.46 and 14.73ppb, in *Acanthus* between 0.42 and 18.23ppb

and in *Avicennia* between 0.82 and 11.62ppb during monsoon. The maximum concentration of Pb was observed in *Acanthus* roots during monsoon. And the minimum Pb concentration of 0.42ppb in plants was observed in *Acanthus* stem. During monsoon higher Pb concentration in roots was found to follow the order *Acanthus* >*Rhizopora*> *Avicennia*. During monsoon the concentration of Pb in *Rhizopora* followed the order r > s > l at all stations. For *Acanthus,* at stations 1 and 2 the order was found to be l>r>s, at station 3, r>s>l and at station 4, the order was found to be r >l>s. For *Avicennia* at stations 1, 2 and 4, the order was r>s>l and at station 3, s > r >l. The bio-concentration factor (BCF) of Pb in monsoon for *Rhizopora* root varied between 0.0485 and 0.6577, for *Rhizopora* stem it varied between 0.0259 and 0.0593 and in *Rhizopora* leaves it varied between 0.0020and 0.2334 respectively. In *Acanthus* root the bio concentration of Pb varied between 0.0151 and 1.7518, in the stem it varied between 0.0018 and 0.9770 and in *Acanthus* leaves it varied between 0.0112 and 1.777 respectively. In *Avicennia* root the lowest bio concentration was 0.0334 and the highest was 1.5, in *Avicennia* stem it varied between 0.0165and 1.0048 and in *Avicennia* leaves it varied between 0.0151 and 0.1300 respectively.

In post- monsoon the Pb concentration in *Rhizopora* root was found to be between 0.04 and 5.84ppb, in *Acanthus* root it was shown to be between 0 and 13.58ppb and in *Avicennia* root it varied between 0 and 13.83ppb. The Pb concentration varied between 0 and 7.90 ppb in *Rhizopora* stem, between 0 and 9.42 ppb in *Acanthus* stem and between 0.53 and 3.58ppb in *Avicenna* stem. In leaves the Pb concentration varied between 0 and 5.96 ppb in *Rhizopora* leaves, between 3.10 and 9.39 ppb in *Acanthus* leaves and between 1.04 and 4.16ppb in *Avicennia* leaves. Among the different plants at the four stations, *Rhizopora* had Pb concentration between 0.04 and 7.90ppb, *Acanthus* had Pb concentration between 0.55 and 13.58ppb and *Avicennia* had Pb concentration between 1.04 and 13.83 ppb respectively in their different parts. Among the plants, the lead concentration in post monsoon followed the order *Avicennia*> *Acanthus*> *Rhizopora*. During post monsoon Pb concentration in *Rhizopora* followed the order s>r>l at station 1, l>r>s at station2, r>l>s at station 3 and at stations 4, only root showed lead

accumulation. In *Acanthus* the order was s>r>l at station 1, r > l at station2, s >l, at station 3 and station 4, l>r>s. In *Avicennia* Pb concentration followed the order r>l >s at stations 1 and 2, r> s >l, at station 3 and station 4, l> s. The bio-concentration factor (BCF) of Pb in post monsoon in *Rhizopora* root varied between 0.004 and 0.0125, in *Rhizopora* stem it varied between 0.000and 0.0488 and in *Rhizopora* leaves it varied between 0.0000 and 0.0220. In *Acanthus* root the bio concentration of Pb varied between 0.0000 and 0. 0504, in the stem it varied between 0.0000 and 0.0582 and in *Acanthus* leaves it varied between 0.0072 and 0.0889 respectively. In *Avicennia* root the lowest bio concentration was 0.000 and the highest was 0.0477, in *Avicennia* stem it varied between 0.0050 and 0.0182 and in *Avicennia* leaves it varied between 0.0020 and 0.0256 respectively.

Statistical analysis showed that Pb correlated positively with Cd in pre monsoon, with Fe in monsoon and with Ni in post-monsoon. The mean of Pb for different plants are as follows: 3.94ppb (*Rhizopora*), 6.35ppb (*Acanthus*) and 7 12 ppb(*Avicennia*). The means for the three seasons are 6.53 for pre-monsoon, 6.97 for monsoon and 3.90 for post monsoon. The means for different plant parts are 7.76 ppb (root), 5.68 ppb (stem) and 3.97 ppb (leaf). For stations 1to 4 the means of Pb concentrations are 6.31 ppb, 3.92 ppb, 6.60 ppb and 6.39 ppb respectively. This indicates that among the three plants *Avicennia* has better Pb accumulation capacity, among plant parts root is far more efficient than stem and leaf and in Pb storage. Also plants at stations 1, 3 and 4 have almost similar lead accumulation tendency which is quite higher than that at station 2. Anova did not show any significant variations.

5.5.6 Copper

Cu is an essential micro nutrient element required for normal growth & development of plants. The existence of copper as Cu^{2+} and Cu^{+} is responsilble for both its essentiality and toxicity (I.Yruela, 2005). Cu fungisides, fertilizers, antifouling paints, corrosion of copper pipes and wires,

petroleum refining etc are some of the anthropogenic sources of copper. Petroleum and ballast waters are potential pollutants affecting mangroves (Lindsay, 2005) which are located in close proximity of their transportation route. Land reclamation and construction activities points to high pollution input. Dissolved organic ligands may keep Cu in the dissolved phase (Allison et al, 2007). Cu plays an important part in the electron transport of photo synthesis, mitochondrial respiration as well as hormone signaling in addition to being an important cofactor for many enzymes. It is also essential for iron mobilization of plants. Cu is also an essential component of haemocyanin, the respiratory pigment of certain mollusks and crustaceans. Cu deficiency leads to changes in gene expression and malformation of leaves. Plants avoid accumulation of toxic metals at sensitive cell sites by various cellular mechanisms such as chelation by organic acids or phyto chelations, reduction of metal acquisition at root level by complex formation with molecule such as citrate outside the root. Excess metal is stored in special cellular parts like vacuole or trichomes. Toxicity of a metal is determined by its solubility, stability and biological activity. Cu excess in plants induces oxidative stress and changes antioxidant pathways of plants (Wang et al., 2004). Excess of Copper caused chlorosis, stunting of plants, leaf discoloration and inhibition of root growth. Cu enhances the adverse effects of light. The photosynthetic activity decreases when oxygenic organisms are exposed to prolonged illumination with high light intensities. Plants growing under high levels of Cu showed lower chlorophyll content (Shakya et al., 2008). Reduced chlorophyll content observed in the presence of high copper concentrations made leaves more susceptible to photo inhibition as a consequence of copper induced Fe deficiency (Patsikka et al (2002). Copper is an effective catalyst in the formation of reactive oxygen species. Photo inhibition by copper may also arise due to the production of hydroxyl radicals. A family of cytosolic, soluble, low molecular weight, metal receptor proteins called metallo chaperons are involved in the intercellular movement of metal ions. The Cu chaperons bind and deliver Cu to inter cellular compartments and insert copper to active sites of copper dependent enzymes (I.Yruela, 2005).

Temporal and spatial loading patterns in trace metals and nutrients can strongly influence the abundance and production of sensitive phytoplankton species. Variations in phytoplankton biomass and composition arising out of interaction between trace metals and phytoplankton brings about changes in speciation and concentration of phytoplankton community which may impinge on higher trophic levels (Hagy and Boynton, 2000). Addition of Cu caused a decline of 31% in primary productivity. Higher nutrient loadings may mask the effect of trace metals on sensitive species and their predators. Mangroves are predominantly under reducing conditions. Fe^{2+} and Mn^{2+} increased significantly under reducing conditions, while Cu^{2+} appeared to increase in an oxidizing environment. Copper shows limited accumulation in leaf tissue. Regulation of copper translocation is due to endodermal casparian strip (MacFarlane and Burchett, 2000). Cu accumulation in leaf tissues increases with increase in sedimentary copper and salinity. Decrease in sediment pH and concentration of Zn were also found to contribute to the accumulation of Cu in leaf tissue. In general toxicity of trace metals is found to be inversely related to salinity. Decrease in pH mobilizes exchangeable copper species thus enhancing its uptake (MacFarlane, 2002). Cu being an essential nutrient its accumulation in plant tissue is triggered by metabolic requirements. Temporal and spatial loading patterns in trace metals and nutrients can strongly influence the abundance and production of sensitive phytoplankton species (Bundy et al, 2003) thus affecting the entire food chain.

Results and discussion

The concentration of Cu in post monsoon was lower than that in pre-monsoon and monsoon. In pre- monsoon the concentration of Cu varied between 8.83 and 21.6 ppm in *Rhizopora* roots, between 11.36 and 27.34ppm in *Acanthus* roots and between 0.89 to 19.0 ppm in *Avicennia* roots at various stations. Acanthus roots showed a higher tendency to accumulate Cu than *Rhizopora* and *Avicennia* roots. The variations in Cu concentrations in the stem of the above plants were between 5.73 to 18.12ppm in *Rhizopora,* between 15.18 and 32.20ppm in Acanthus and between 0.30 and 19.89ppm for *Avicennia*. Among the plant leaves, the variations were between 6.66 and

17.77ppm for *Rhizopora*, between 10.47 and 17.75 ppm for *Acanthus* and between 0.28 and 18.32 ppm for *Avicennia*. The maximum and minimum concentrations of Cu in various plant parts was between 5.73 and 21.65 ppm respectively for *Rhizopora*, 10.47 and 32.20ppm for *Acanthus* and between 0.28 and 19.89 ppm for *Avicennia*. The above observations show that the tendency to accumulate Cu in plants was *Acanthus* > *Rhizopora* > *Avicennia* during pre-monsoon. The bio-concentration factor (BCF)) of Cu in pre-monsoon for *Rhizopora* root varied between 0.0247 and 0.0830ppm, for *Rhizopora* stem it varied between 0.0142 and 0.0797ppm and in *Rhizopora* leaves it varied between 0.0386and 0.0626ppm respectively. In *Acanthus* root the bio concentration of Cu varied between 0.0384 and 0.1402ppm, in the stem it varied between 0.0375 and 0.2282ppm and in *Acanthus* leaves it varied between 0.0351 and 0.1115ppm respectively. In *Avicennia* root the lowest bio concentration was 0.0022 and the highest was 0.1124ppm, in *Avicennia* stem it varied between 0.0007and 0.1869ppm and in *Avicennia* leaves it varied between 0.0007 and 0.0763ppm respectively.

Similarly in monsoon the Cu concentration in *Rhizopora* root varied between 26.17 and 108.24ppm, in *Acanthus* root it varied between 12.20 and 112.69ppm and in *Avicennia* root it varied between 0 and 30.15ppm respectively. During monsoon, higher Cu concentration in roots was found to follow the order *Acanthus* root > *Rhizopora* root > *Avicennia* root. The concentration of protein in Acanthus roots was high during monsoon, facilitating greater accumulation of copper in *Acanthus* root through complexation. For the stems of the different mangrove plants, in *Rhizopora* stem the variations in Cu were between 16.90 and 32.25ppm, in *Acanthus* stem it was between 16.29 and 59.92ppm, while in *Avicennia* stem it was between 0 and 32.14ppm respectively. In *Rhizopora* leaves the variations of Cu concentrations were between 5.11 to 26.05ppm, in *Acanthus* leaves between 8.13 to 17.01ppm and in *Avicennia* leaves it varied between 8.13to 28.79ppm respectively. The Cu accumulation capacity of *Avicennia* leaves was thus higher than *Rhizopora* leaves and *Acanthus* leaves. Among the different plants the variations in Cu concentrations for *Rhizopora* were between 5.11 and 108.24ppm, in *Acanthus* between 8.13 and 112.69ppm and

in *Avicennia* between 0 and 32.14 ppm. The maximum concentration of Cu 112.69 ppm was observed in Acanthus root at station 3, during monsoon. And the minimum Cu concentration of 0.00 ppm in plants was observed in *Avicennia root* and stem at station 2. During monsoon the concentration of Cu in *Rhizopora* followed the order r > l >s at all stations. For *Acanthus* at station 1, the order was s>l>r. At stations 2 and 3 the order was found to be r> s > l and at station 4 it was r>l>s. For *Avicennia* at station 1, r> l > s was the order for the concentration of Cu, while at station 3 it was s> l > r while at station 4 it was l > r > s. The bio-concentration factor (BCF) of Cu in monsoon for Rhizopora root varied between 0.0896 and 0.1664 for *Rhizopora* stem it varied between 0.0608and 0.1730 and in *Rhizopora* leaves it varied between 0.0250 and 0.1046 respectively. In *Acanthus* root the bio concentration of Cu varied between 0.0456 and 0.5511, in the stem it varied between 0.0541 and 0.2240 and in *Acanthus* leaves it varied between 0.0398 and 0.1046 respectively. In *Avicennia* root the lowest bio concentration was 0.0000 and the highest was 0.1615, in *Avicennia* stem it varied between 0.0000and 0.1571 and in *Avicennia* leaves it varied between 0.0397 and 0.1632 respectively.

In post- monsoon, the Cu concentration in *Rhizopora root* was found to be between 9.65 and 11.84ppm, in *Acanthus* root it was shown to be between 9.73 and 26.26ppm and in *Avicennia* root it varied between 8.12 and 20.79ppm. The Cu concentration varied between 7.60 to 10.19 ppm in *Rhizopora* stem, between 6.28 and 18.56ppm in *Acanthus* stem and between 7 16 and 16.59ppm in *Avicennia* stem. In leaves the Cu concentration varied between 4.88 and 37.08ppm in *Rhizopora* leaves, between 9.49 and 24.90ppm in *Acanthus* leaves and between 6.97 and 12.96ppm in *Avicennia* leaves. Among the different plants at the four stations, *Rhizopora* had Cu concentration between 4.88 and 37.08ppm, *Acanthus* had Cu concentration between 6.28 and 26.26ppm and *Avicennia* had Cu concentration between 6.97 and 20.79ppm respectively in their different parts. Among all the plants, the lowest Cu concentration of 4.88ppm was recorded in *Rhizopora* leaves at station 4 and the highest Cu concentration of 37.08 was also found in *Rhizopora* leaves, at station 2. During post monsoon at stations 1 and 2,

the Cu concentration in *Rhizopora* followed the order l>r>s, at station3 it followed the order r>l>s, while at station 4 the variation was r>s>l. In Acanthus the corresponding observations were l>r>s at station 1, l>s>r at stations 2 and 3 and r>l>s at station 4. For Avicennia it was s>l>r at station 1, r>l>s at stations 2 and 3, while at station 4 it was r>s>l. Cu concentrations in leaves were found to be generally higher than in root and stem during post monsoon. This shows that there is greater translocation of Cu to the leaves. The bio-concentration factor (BCF)) of Cu in post-monsoon for Rhizopora root varied between 0.0251 and 0.0638, for *Rhizopora* stem it varied between 0.0221and 0.0452 and in *Rhizopora* leaves it varied between 0.0244 and 0.0874 respectively. In *Acanthus* root the bio concentration of Cu varied between 0.0246 and 0.1563, in the stem it varied between 0.0318 and 0.0437 and in *Acanthus* leaves it varied between 0.0383 and 0.0624 respectively. In *Avicennia* root the lowest bio concentration was 0.0004 and the highest was 0.0525, in *Avicennia* stem it varied between 0.0182and 0.0426 and in *Avicennia* leaves it varied between 0.0199 and 0.0415 respectively.

In pre-monsoon and post monsoon the highest concentration of Cu in leaves was shown by *Avicennia*, while in post monsoon *Rhizopora* leaves at station 2 showed the maximum Cu accumulation. During post monsoon station 2 had higher sand content (35%) and lower pH than all the other stations, enabling better Cu dissolution and mobilization. The low Fe concentration in *Rhizopora* roots during post monsoon has provided an additive effect on the better uptake of Cu by *Rhizopora* during pre-monsoon because Fe and Mn oxides can trap other metals such as Cu and change their distribution and remobilization (Naylor et al, 2006). Statistical analysis showed that Cu correlates positively with Ni during post monsoon, considering the season wise correlation. Cu also showed significant correlation with Ni at station 3, when station wise correlations were considered. The mean of Cu for different plants are as follows: 18.38ppm (*Rhizopora*), 21.40ppm (*Acanthus*) and 12.78ppm (*Avicennia*). This indicates that among the three plants *Acanthus* has better Cu accumulation capacity. The means for different plant parts are 21.76ppm (root), 16.44ppm (stem) and 14.36ppm (leaf). For stations 1 to 4

the means of Cu concentrations are 17.58ppm for station 1, 15.80ppm for station 2, 19.22ppm for station 3, and 17.48ppm for station 4 respectively showing that plants at station 3 have greater bioaccumulation of Cu. Three way anova showed significant seasonal variations for Cu with $P<0.001$.

5.5.7 Cadmium

Cadmium is a non nutritive element which is highly toxic. It is prevalent in the environment due to industrial applications. In plants Cd absorbed from the soil is translocated by xylem and phloem. Transpiration plays an important role in the translocation of Cd (Takayuki et al, 2009). Cd is present in the free form in the cell walls. The cell wall is the main site of metal accumulation. Their presence in plasmodesmata indicates that they transported between cells. Phytochelatins which are metal complexing peptides play a key role in Cd tolerance. Histidine also acts as a complexing agent for Cd and lead in epidermal cells. Cd interferes with the uptake of nutrients, decrease root respiration and inhibit root production. Diatoms and flagellates under high concentration of nitrates, accumulated higher Cd concentration (Riedel and Sanders, 2003). Cd, is normally recognized as a redox sensitive metal and its concentration in sediments is influenced by the hypoxic conditions (Russell and Morford,2001). Cd and Ni showed the highest concentration in the most DO depleted zone (Valdes, 2004). Cd in natural sediments are strongly bound to organic substances (sulphides) but that with anthropogenic origin are bound very weakly (Lekov and Kristic, 2002). It is more bio available to invertebrates at lower salinities. Inorganic chloride can form complexes with Cd which increases the bioavailability of Cd to the plant. Cd is not significantly incorporated into pyrite (Billon at al, 2001), because of its ability to form soluble sulphide species and thus remain in solution once solubilized.

Cd is mostly unavailable to plants and its uptake is inhibited by the presence of large amounts of other metals present in the soil especially Zn. Ingestion of even trace quantities of cadmium can influence the physiology, health, reproduction and survival of organisms. Cadmium is easily taken up by people depending on mangrove ecosystems because the mangrove plants

are used in folk medicine (Ravindran et al., 2005). Cd accumulates in the first few centimeters of the soil and its concentration decreased with depth, indicating that Cd moved downwards only when the top layers became saturated. Cd binds mainly to organic matter and clay and if only loosely bound to these materials and may re-enter the aqueous phase. Hence the adsorbed Cd can act as a secondary source of pollution (Amusan and Adeneyi, 2005). Cd interferes with the uptake of nutrients; decreases root respiration and inhibit root production. Cadmium forms a precipitate with carbonate in alkaline conditions. Gerringa et al., (2001), reported increased dissolution of Cd compared to Zn upon oxidative dissolution of Cd at higher salinities. This was attributed to a combination of the lower solubility of CdS compared to ZnS and the formation of stable $CdCl_2$ complexes with increasing salinities. The formation and re-oxidation of small amounts of sulphides might be dominant in determining the total metal concentration of Cd in different profile layers in sediments and the mobility of Cd in sediments (Du Liang et al, 2007 b). Following sulphide oxidation the released Mn and Fe oxides can be re-precipitated and deposited as insoluble oxides and hydroxides to which newly released metals such as Cd can be adsorbed at varying rates and extents (Eggleton and Thomas, 2004).

The concentration of Cd in leaves was very small compared to that in roots and in many instances it was un-detectable in leaves during pre monsoon and post monsoon. Cd being a non essential metal will show reduced transfer through roots though it revealed phyto availability comparable to copper (Overesch et al, 2007). Microbial species can increase the adsorption surface area of root hairs. They can assimilate toxic metals thus restricting its uptake by plants. Cd is found to be located in cell walls(56%) complexed with organic acids such as citric and malic acid which plays an important role in the detoxification of the metal (Hall, 2002). During monsoon the concentration of Cd in leaves increased probably due to insufficient complexation at root level. Also during monsoon sediment oxidation conditions may prevail. Cd changes from strongly bound oxidisable fractions to weakly bound carbonate fractions during sediment oxidation, which significantly increased the dissolved Cd concentration (Stephans, 2001) enhancing bioavailability.

Results and discussion

In the mangrove plants, Cd showed greater concentration in the roots than in stem and leaf during pre- monsoon. The pre-monsoon concentration of Cd varied between 0 to 1.23ppm in *Rhizopora* roots, between 0 to 3.05ppm in *Acanthus* roots and between 0 to 1.09ppm in *Avicennia* roots, at various stations. *Acanthus* roots showed a higher tendency to accumulate Cd than *Rhizopora* and *Avicennia* roots. The variations in Cd concentrations in the stem of the above plants was between 0 and 2.25ppm *in Rhizopora,* between 0 and 0.85ppm in Acanthus and between 0and 5.78ppm for *Avicennia*. Among the plants, the variations were between 0 and 1.03ppm for *Rhizopora*, between 0 and 0.89ppm for *Acanthus* and 0.05 and 2.78ppm for *Avicennia*. The minimum and maximum concentrations of Cd were 0ppm and 2.25ppm in various plant parts respectively for *Rhizopora*, 0 and 3.05ppm for *Acanthus* and 0 and 5.78ppm for *Avicennia*. The above observations show that the tendency to accumulate Cd in plants was *Avicennia* > *Acanthus* > *Rhizopora* during pre-monsoon. The variation of Cd in the plant parts at the different stations were as follows: For *Rhizopora*, at station 1, l>s>r, at station 2, r>s>l, at and station 3, s>r>l. At station 4, no Cd concentration was recorded. For Acanthus, at station 1, Cd was observed in the root level only. At station 2, r >s with nil concentration in leaves. At station 3, r>l>s and nil Cd concentration was observed at station 4. In *Avicennia*, the order of accumulation was s>r>l at station 1, r>s>l at station 2, l>s>r at station 3. Only and the leaves of *Avicennia* showed Cd concentration at station 4.The bio-concentration factor (BCF)) of Cd in pre-monsoon for *Rhizopora* root varied between 0.0000 and 0.1534 for *Rhizopora* stem it varied between 0.0000 and 0.0926 and in *Rhizopora* leaves it varied between 0.0000 and 0.1165 respectively. In *Acanthus* root the bio concentration of Cd varied between 0.0000 and 0.1258, in the stem it varied between 0.0000 and 0.0352 and in *Acanthus* leaves it varied between 0.0000 and 0.0532 respectively. In *Avicennia* root the lowest bio concentration was 0.0000 and the highest was 0.0137, in *Avicennia* stem it varied between 0.0000and

0.6515 and in *Avicennia* leaves it varied between 0.0055 and 1.5773 respectively.

Similarly in monsoon the Cd concentration in *Rhizopora* roots varied between 0.02 and 23.70ppm, in *Acanthus* roots it varied between 0.72 and 22.68ppm and in *Avicennia* roots it varied between 0 and 26.26ppm respectively. For the stems of the different mangrove plants, in *Rhizopora* stem the variations were between 1.31 and 28.13ppm in *Acanthus* stem it was between 0. 60 and 16.52ppm while in *Avicennia* stem it was between 0 and 15.15ppm respectively. In *Rhizopora* leaves the variations of Cd concentrations were between 0.04 and 17.01ppm, in *Acanthus* leaves between 0.64 and 17.01ppm and in *Avicennia* leaves it varied between 0.16 and 26.54ppm respectively. The Cd accumulation capacity of *Rhizopora* leaves was shown to be higher than *Acanthus* leaves and *Avicennia* leaves. Among the different plants the variations in Cd concentrations for *Rhizopora* were between 0.02 and 28.13ppm, in *Acanthus* between 0.60 and 22.68ppm and in *Avicennia* between 0 and 26.54ppm during monsoon. The maximum concentration of Cd 26.54 ppm was observed in *Avicennia* leaves at station 4, during monsoon. During monsoon Cd concentration in roots was found to follow the order, *Avicennia* > *Rhizopora* > *Acanthus*. During monsoon the concentration of Cd in *Rhizopora* followed the order s>l>r at stations 1, 2 and 4 and the order s>r>l at station 3. For *Acanthus* at all the stations the order was found to be r>l>s. For *Avicennia* at stations1, 2 and 4, leaves showed the highest concentration of Cd, while at station 3 it was the root. From this it was shown that the leaves showed greater translocation for Cd in Avicennia. During monsoon root and stem accumulated more Cd than leaves. The bio-concentration factor (BCF) of Cd in monsoon for *Rhizopora* root varied between 0.0027 and 0.4022, for *Rhizopora* stem it varied between 0.0140and 4.2183 and in *Rhizopora* leaves it varied between 0.0004 and 2.5503 respectively. In *Acanthus* root the bio concentration of Cd varied between 0.0074 and 3.4010, in the stem it varied between 0.0062 and 2.477 and in *Acanthus* leaves it varied between 0.0065 and 2.551 respectively. In *Avicennia* root the lowest bio concentration was 0.0000 and the highest

was 3.938, in *Avicennia* stem it varied between 0.0000and 2.271 and in *Avicennia* leaves it varied between 0.0032 and 3.979 respectively.

In post- monsoon, the Cd concentration in *Rhizopora* roots was found to be between 0.206 and 0.804ppm, in *Acanthus* roots it was shown to be between 0.271 and 1.517ppm and in *Avicennia* roots it varied between 0.344 and 1.795ppm. The Cd concentration varied between 0.033 and 0.958ppm in *Rhizopora* stem, between 0.003 and 0.602ppm in *Acanthus* stem and between 0.212 and 1.025ppm in *Avicennia* stem. In leaves the Cd concentration varied between 0 and 1.109ppm in *Rhizopora* leaves, between 0.081 and 0.594ppm in *Acanthus* leaves and between 0 and 0.891ppm in *Avicennia* leaves. Among the different plants at the four stations, *Rhizopora* had Cd concentration between 0 and 1.109, *Acanthus* had Cd concentration between 0.003 and 1.517ppm and *Avicennia* had Cd concentration between 0 and 1.795ppm respectively in their different parts. Among all the plants the highest was found in *Avicennia* roots at station 3. During post monsoon at station 1, the Cd concentration in *Rhizopora* followed the order l>s>r, at station 2 it followed the sequence s>r>l at station 3 it was l>r>s and at stations 4, r>l>s. For Acanthus the tendency for Cd accumulation was r>s>l and l>r>s at stations 1 and 2 respectively while at stations 3 and 4 it was shown to be s > r >l and r>l>s. In Avicennia, the sequence was s>r>l and r>s>l at stations 1 and 2 respectively while at stations 3 and 4 it was r>s>l. The bio-concentration factor (BCF) of Cd in post- monsoon for Rhizopora root varied between 0.0232 and 0.2238 for *Rhizopora* stem it varied between 0.005 and 0.095 and in *Rhizopora* leaves it varied between 0.0000 and 0.0671 respectively. In *Acanthus* root the bio concentration of Cd varied between 0.0120 and 0.7333, in the stem it varied between 0.002 and 0.068 and in *Acanthus* leaves it varied between 0.0058 and 0.0590 respectively. In *Avicennia* root the lowest bio concentration was 0.0342 and the highest was 0.9863, in *Avicennia* stem it varied between 0.021and 0.213 and in *Avicennia* leaves it varied between 0.0000 and 0.1727 respectively.

Statistical analysis showed that Cd has significant positive correlation with Pb(at 0.01 level) during pre-monsoon.. At station 1, Cd correlates with Cu (at 0.05level) and with Fe (0.01 level) at stations 2 and 3. The mean of Cd for different plants are as follows: 2.67ppm (*Rhizopora*), 2.21ppm (*Acanthus*) and 2.57ppm (*Avicennia*). The means for different plant parts are 2.69 ppm (root), 2.36 ppm (stem) and 2.41 ppm(leaf). For stations 1 to 4 the means of Cd concentrations in all the 3 plants taken together are 2.12ppm, 0.59ppm, 0.72ppm and 6.50ppm respectively. For the various seasons the means are 0.65ppm, 6.29ppm and 0.51ppm respectively for pre-monsoon, monsoon and post-monsoon seasons. The means indicate that among the three plants, *Rhizopora* has better Cd accumulation capacity. Also plants at station 4 have greater bioaccumulation of Cd and plants at station2 had the least. Among the seasons, monsoon had the highest mean for Cd and posts monsoon the least. In cluster analysis Cd formed its own group which indicates that Cd has a different distribution process compared to other metals (Lekov and Kristic, 2002).Three way anova for Cd showed significant variations in Cd concentrations among season, station and season x station.

5.6 Tannin and Lignin in leaves

Tannins are water soluble poly hydroxy aromatic compounds. They are made up of aromatic acids such as gallic or ellagic acid. They show the ability to precipitate proteins, such as gelatin from solution- a property called astringency by which they differ from most other natural phenolic compounds. Tannins are common in plant material but not in animal tissue. They make the plants less palatable to herbivores and micro organisms and are one of the important defence strategies developed by plants (Stephen and Vanessa, 2005). Their molecular weight varies between 500-3000. Tannins are diverse compounds with great variation in structure and concentration within and among plant species. Based on their structures, tannins in vascular plants are divided into two groups- the proanthocyanidins or condensed tannins which show biological activities such as antibacterial, anti herpetic, anthelmintic as well as cytotoxic and antineoplastic tendency. Their anti bacterial property is made use of in wood preservation and to prevent dental

caries. The other group of tannins is called hydrolysable tannin (Hernes et al., 2001). Proanthocyanidins, are linked to proteins and polysaccharides. They are water soluble (Zhang and Lin, 2008).

Contribution of mangrove leaves to the sedimentary organic matter in mangroves is quite significant (Marchand et al., 2003).Higher plant materials make an important contribution to organic matter. Tannins form a major component of leaf tissue and bark, and therefore can have a significant impact on the bulk properties of organic mixtures, such as aromaticity, organic carbon:nitrogen ratios, phenolic OH, color, and reactivity. Unlike carbohydrates, lipids, amino acids, and pigments—which are ubiquitous in organic matter and have both marine and terrestrial sources—tannins (along with lignin and cutin) are uniquely terrestrial. Thus, in addition to bulk importance, tannins have potential to provide source information that is complementary to lignin and cutin. The ability to complex with proteins and amino acids leads to another geochemically significant trait of tannin mentioned previously—inhibition of organic matter degradation. Tannins have long been suspected as precursors to humic materials via "autoxidation" when neutral to alkaline pH conditions prevail. Again, this is due to the ease of formation of quinones and subsequent condensation reactions. Because so little is known about molecular-level tannins in natural samples, the role of tannins in humification is still largely theoretical. Molecular-level tannin analyses of natural samples coupled with isolation of humics and bulk characterization by NMR is used to provide a first look at the empirical relationship of tannins to humification. In addition to complexing bacterial exo enzymes and directly slowing degradation, tannin may also bind up the nitrogen source used by degraders for growth. Despite the challenges of measuring tannins, there may be a gold-mine of information to be coaxed from them specifically because of their highly reactive nature. Because of tannin's redox and photochemical sensitivity, it may be possible to use tannins as an indicator of the environmental history of associated organic matter. For instance, tannins present in anoxic sediments may be able to tell us whether the sediments have been under constant or intermittent anoxia.

Lignin is a biopolymer found abundantly in cell walls where it is associated with hemicelluloses. Lignin is a unique tracer for vascular plants and can be used as tracers for terrestrial material and to distinguish between different types of vegetation. Lignin has along half life which is found to be 150 years (Dittamar and Lara, 2001). It forms a net work around cellulose fibers in maturing xylem. Coumaryl, coniferyl and sinapsyl alcohol which are biosynthesized enzymztically from glucose will under go condensation to produce poly phenolic lignin compounds. Lignin is next to cellulose in abundance - about 20-30% as compared to 40-60% of cellulose (Stephen and Vanessa, 2005). Mangroves are store houses of lignin and considerable amounts of lignin phenols leach out from mangrove leaves during early diagenesis. It can also be used to identify the transport and fate of organic matter as well as to give a chemical signature to organic matter present in mangrove area (Benner, 2004). Litter fall plays a crucial role in the tannin and lignin cycling of mangrove systems due to the large amount of organic mater returned to the aquatic system through leaf senescence.

Results and Discussion

Indian mangroves have high tannin content. *Rhizopora* is known for its high tannin content which also accounts for its for its high resistance to rot and borers comparable to that of tropical palms (Bandarnayake,1998), whereas lower tannins in *Avicennia* leaves makes it decompose faster. The analysis of tannin and lignin content of mangrove leaves at various stations showed the following results. The pre-monsoon concentration of tannin and lignin in *Rhizopora* leaves varied between 0.64-1.08mg/g, for *Acanthus* leaves between0.50 and 3.39mg/g and for *Avicennia* it varied between 0.59 and 3.0608mg/g. Generally, when salinity increased, the chloride content of leaves increased, while the tannin and lignin decreased. Soluble sugar content in leaves increased with salt concentration in mangrove species (Yan and Guizhu, 2007). Complexation between sugars and tannins will increase with salinity, rendering tannins less available in the extractable form. Maie et al (2008) have reported that the dissolved tannin concentration decreased with the increase in salinity and at salinities above 15%, about 75% of mixed

tannins were eliminated from the aqueous phase. This may be the reason for the lower concentration of tannin and lignins in the extract. In pre monsoon the tannin and lignin content of the stations followed the order station 2>station 4>station 1>station3 for *Rhizopora* and *Acanthus* leaves while for *Avicennia* it was station 4>station 2>station 1>station3. Among all the stations, the leaves of mangrove plants of station 3 had the least tannin and lignin concentration during pre monsoon. The periodic tidal flushing and urban discharge must have washed out the soluble tannin and lignin thus making available lower tannin and lignin for uptake by plants. During monsoon the corresponding variations were between 0.56 and 1.4508mg/g in *Rhizopora*, 0.87 and 1.0608mg/g in *Acanthus* and between 0.74 and 1.4108mg/g in *Avicennia* respectively. In monsoon there is an increase in tannin and lignin content for *Rhizopora* but decrease in tannin and lignin content for *Acanthus* and *Avicennia*. There was a general decrease in the protein content of plants during monsoon and hence secondary metabolites such as tannin and lignins will be more bio-available to plants which must have the enhanced bio-concentration of tannin and lignin in *Rhizopora*. The concentration pattern of tannin and lignin in the various stations for the 3 plant leaves were station 2>station 1>station 3>station4 for *Rhizopora* and *Acanthus* and station 2>station 4>station 1>station3 *for Avicennia*.

Post-monsoon variations were between 0.87-1.4108mg/g for *Rhizopora,* 0.88-1.1308mg/g *Acanthus* and 1.15-1.3108mg/g for *Avicennia.* Both Physical and chemical processes control the fate of tannins and lignins. Tannins undergo self aggregation, absorption on to sediments and photochemical alterations in aquatic environments. Elimination in aquatic environment occurs noticeably through self aggregation as salinity increases. Mycorrhizae present on mangrove roots can sometimes produce exo enzymes that degrade tannin–protein complexes (Wu et al. 2003), thus controlling the concentration of tannins and lignins. The mangrove canopy and disturbances of the natural environment can determine the amount of sunlight reaching the mangrove waters and sediments. Tannins undergo chemical modifications based on the availability of sunlight, which may affect its sequestration with organic molecules and impact its bio-availability in plants. Tannin and lignin of

plants at station 2 showed increased tannin and lignin content during all seasons probably due to less complexation with bio-chelates. Hydrochemistry also impacts the biogeochemistry of tannins in mangrove environments. The variation in tannin and lignin concentration at the various stations during post monsoon were station 4>station 2>station 3=station4 for *Rhizopora*, station 1>station 2>station 3>station4 for *Acanthus* and station 1>station 2>station 4>station3 *for Avicennia.* Among the station wise correlations, strongest negative correlation exists between tannin and lignin and chloride at station 1, followed by station 4, station 3 and the least at station 2. Negative correlation exists between tannin and lignin and chloride content of leaves when total correlation, seasonal correlation as well as station wise correlations was considered. Tannin and lignin content in plants impacts the mobility of ions through the plant body by complexing them at appropriate sites which explains the negative correlation existing between tannin and lignin and chloride. Two -way anova showed that variations of tannin and lignin in the leaves were significant with $P<0.001$.

5.7 Chloride content of leaves

Mangrove plants have various mechanisms for salinity tolerance. Mangroves are divided into two distinct groups on the basis of their salt management strategies. One is "secretors" having salt glands or salt hairs for excretion of excess salt and the other is "non-secretors" lacking such morphological features. Mangrove species incorporate salts from substrate and transport them to the leaves via the transpiration stream. The uptake helps to maintain osmotic pressure under high salinity. Under high salinity, salt regulation mechanism is the key factor that helps in the survival of the plant. Some mangrove plants exclude salts during uptake of water while others excrete salt through salt glands mostly as NaCl, succulence and relocation of salts through to other organs (Subrado, 2001). Salt regulation mechanism helps in the maintenance of K^+/Na^+ ratio, which is required for proper metabolic activities in the leaf cell. Many plants store their Na^+ ions in vacuole and maintain high ratio of K^+/Na^+ Low K^+/Na^+ ratios in plant tissue is one of the key elements in salinity tolerance. Halophytes vary in their ability to transport

and accumulate Na^+ and K^+ under salinity. Many halophytes maintain a high ratio of K^+/Na^+ under high salinity because of their ability to use K^+ instead of Na^+ for metabolic processes (Wang et al, 2004). K^+ plays an important role in many metabolic reactions such as osmo regulation, protein synthesis, and enzyme activation. The capability of *A. germinans* to take up K^+ efficiently even in high-salinity environments may be regulated by the K^+ transporter family (Gierth and Mäser, 2007). The main ions accumulated in the leaf tissues are Na^+ and Cl^- and they represent 76-96% and 76-84 % of all cations and anions present. Both Na^+ and Cl^- concentration increased with salinity. But on increasing salinity, Na^+ reached a constant value, while Cl^- concentration markedly increased with increasing salinity in plants like A. Germinans (Suárez and Medina, 2005 and 2006). Salt excretion also increased with salinity due to increased activity of salt secreting glands, with night excretion showing a higher rate than day. Cl^- was found to be excreted at a greater level than Na^+ Leaf sap concentration of Cl^- was lower than Na^+ but excretion of Cl^- was higher. This shows that there is high selectivity in the secretion mechanism.

Salt concentration has a profound impact on the bio chemistry of plants. Salt secretions takes place with the preservation of essential nutrients like phosphate, nitrate and oxalate (Barhoumi et al, 2007). High levels of Na and Cl^- inhibits the enzyme activity of microbes (Roache et al, 2005). As NaCl salt stress increased in plants, uptake of nitrate and activity of nitrate reductase enzyme declined. Total nitrogen level and phosphate levels also decreased in leaves (Parida et al., 2004). There was also a decrease in stem length with high salinity (Carter et al, 2005). Net photosynthesis rate, stomata conductance and transpiration rate of leaves decreased with salt concentration in mangrove species. Salt may enter into the transpiration stream and eventually injure cells in the transpiring leaves, further reducing growth due to the salt-specific or ion-excess effect of salinity inside the plant (Yan and Chen, 2007). The salt taken up by the plant concentrates in old leaves. Continued transport into transpiring leaves over a long period eventually results in high Na^+ and Cl^- concentrations and the leaves die. The

salt load exceeding the ability of the cells might concentrate in vacuoles resulting in rapid salt build up in the cytoplasm and inhibition of enzyme activity. Alternatively, they might build up in the cell walls and dehydrate the cell. If the rate of production of new leaves is greater than the rate at which old leaves die, there will be enough photosynthesizing leaves of the plant to produce flowers and seeds, although reduced in numbers. However, if the reverse phenomenon is seen, the plant may not survive to produce seeds. Internal salt control mechanism has reported to affect metallic contents of mangrove plants and cause differences among species (Sarangi and Kathiresan, 2002). A. *Officianalis* is found to be more effective in accumulating the trace elements under the same environmental conditions as these plants have salt excreting property.

Results and discussion

Plants vary in their response to salinity and water stress (Munns, 2002). The research work showed that, in general all plant leaves showed highest Cl^- accumulation during pre-monsoon, when salinity was high. During pre monsoon the chloride content of Rhizopora varied between 38.91 and 61.68 mg/g, in acanthus the variation was between 24.09 and 61.68mg/g and in *Avicennia* it was between 12.70 and 39.98 mg/g respectively. The station wise concentration of chloride in *Rhizopora* leaves was station 2>station 3> station 1> station 4. In *Acanthus* leaves it was station 1> station 3> station 2> station 4. In Avicennia leaves it was station 2> station 3> station 1> station 4. These variations may be due to plants regulating shoot ion concentration and reducing salt concentration in leaf tissue by means such as salt secretion through leaf glands, succulence, and relocation of salt to other organs (Sobrado, 2001). During pre monsoon the leaves of plants at station 4 had the least chloride content. The activity of salt glands is associated with the salinity of the surrounding solution. Salt secretion is known to increase with salinity and there is greater tendency for secretion at night. The survival of plants in saline conditions depends on the maintenance of cell turgor mainly by decreasing osmotic potential thorough osmotic adjustments (Mulholland and Otte, 2002).

decreasing osmotic potential thorough osmotic adjustments (Mulholland and Otte, 2002).

During monsoon the chloride content of *Rhizopora* varied between 46.34 and 56.33mg/g, in *Acanthus* the variation was between 29.67 and 47.83mg/g and in *Avicennia* it was between 22.58 and 41.95mg/g respectively. The station wise concentration of chloride in *Rhizopora* leaves was station 1>station 3> station 2> station 4. In *Acanthus* leaves it was station 4> station 1> station3>station 2. In Avicennia leaves it was station 3> station 1> station 4> station 2. During monsoon the leaves of plants at station 2 had the lower chloride content. In monsoon, reduction in salinity produces a lowering of Cl^- in *Rhizopora* and *Acanthus*. The above observations related to similar studies done elsewhere (Suárez and Medina, 2005 & 2006). During post monsoon the chloride content of *Rhizopora* varied between 37.59 and 54.33 mg/g, in *Acanthus* the variation was between 43.14 and 52.40mg/g and in *Avicennia* it was between 19.66 and 35.47mg/g respectively. The increased salt content in Acanthus shows that succulence did not operate as a mechanism to dilute salt concentration in leaf tissues. The station wise concentration of chloride in *Rhizopora* leaves was station 1>station 2> station 3> station 4. In *Acanthus* leaves, it was station 4> station 1> station 3> station 2. In Avicennia leaves it was station 2> station 1> station 3> station 4. During post-monsoon the leaves of plants at station 4 had the lower chloride content. Av(I) showed low Cl^- than R(I) and Ac(I) due to its salt secretory glands. Secretion is carried out to build up ionic ratio favorable for metabolic processes of plants. It is a selective phenomenon to protect plants tissues against the toxic effects of ions without losing essential nutrients (Barhoumi, 2007). The tendency to accumulate salt in Rhizopora during different seasons followed the sequence pre monsoon > monsoon > post monsoon. In Acanthus it followed the order pre monsoon>post monsoon>monsoon. Avicennia had higher chloride content in monsoon probably due to reduced salt excretion. The increase in chloride content of leaves was followed by a decrease in tannin and lignin content and vice versa. Tannin and lignin content in plants impacts the mobility of ions through the plant body by complexing them at appropriate sites. Significant negative correlation exists between chloride content of

leaves and tannin and lignin content of leaves. This is due to decrease in tannins and lignins with increasing salinity due to enhancement of complexation with bio molecules such as sugars and proteins which increase with salinity (Yan and Guizhu,2007; Zhang and Lin,2008).

Conclusion

Mangrove plants of Cochin exhibited bioaccumulation of metals. The common anthropogenic metals such as Fe, Mn, and Cu had a higher concentration in the mangrove plants studied. The bio accumulation is seen to be related to the sediment concentration in many cases. Metal accumulation in plants is controlled by other parameters of the mangrove environment such as organic matter content and complexing bio polymers such as tannin and lignin as well as protein. Plants appeared to limit the uptake of non essential, toxic metals such as Pb and Cd, probably by excluding them at root level or by keeping them in sediments, in chemical forms of low bioavailability. Metals such as Fe and Mn showed positive correlations with each other, pointing a mutual impact on their bio accumulation. Metal accumulation varied seasonally and spatially. *Avicennia* a salt secreting plant had higher salt content in its leaves than non salt excreting plants such as *Rhizopora* or *Avicennia*. Cochin being a progressive metropolitan city is booming with anthropogenic and industrial activities. The impact on development activities will hit the mangroves also. The mangrove greenery of Cochin is shrinking day by day. The pollution index of mangroves will definitely shoot up and bioaccumulation of metals will also rise. The impact heavy metals on all organisms on the food chain loom large in Cochin. Hence corrective measures must be taken to save the mangroves and the population depending directly or indirectly on it from the impending threat of metal pollution. This will be possible only with the active participation of not just environmentalist but with the cooperation of people from all strata of society.

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Data of Plant Parts

(Seasonal Average)

Pre Monsoon

	Name of Plant Part	Moisture (%)	Organic carbon (%)	Kjeldhal nitrogen (mg/g)	Protein (mg/g)
Stn 1	R (r)	79.8	85.5	1.03	6.46
	R (s)	87.4	88.0	1.07	6.66
	R (l)	77.5	87.6	2.01	12.53
	Ac (r)	81.5	88.3	1.18	7.35
	Ac (s)	67.1	88.4	1.74	10.90
	Ac (l)	71.8	84.8	2.08	13.02
	Av (r)	78.8	89.0	0.88	5.49
	Av (s)	58.1	88.8	2.16	13.53
	Av (l)	61.2	87.3	1.80	11.25
Stn2	R (r)	74.3	84.1	0.87	5.45
	R (s)	63.6	83.0	1.46	9.13
	R (l)	73.5	83.3	1.60	9.97
	Ac (r)	80.5	91.4	0.99	6.19
	Ac (s)	71.1	87.8	1.61	10.06
	Ac (l)	74.0	84.4	1.68	10.49
	Av (r)	87.3	83.3	0.74	4.64
	Av (s)	59.6	87.5	1.20	7.47
	Av (l)	63.7	87.4	2.68	16.75
Stn3	R (r)	64.4	88.5	1.02	6.38
	R (s)	64.8	95.0	0.79	4.95
	R (l)	68.9	77.7	2.38	14.88
	Ac (r)	83.3	88.8	2.11	13.17
	Ac (s)	73.6	83.2	2.30	14.40
	Ac (l)	60.4	84.2	2.16	13.52
	Av (r)	67.7	88.1	2.29	14.30
	Av (s)	63.2	76.6	1.58	9.88
	Av (l)	68.1	90.0	1.02	6.40
Stn4	R (r)	82.6	82.2	1.00	6.28
	R (s)	56.2	88.8	1.35	8.46
	R (l)	72.3	87.2	2.11	13.16
	Ac(r)	77.2	84.2	0.91	5.68
	Ac (s)	71.1	91.2	1.85	11.58
	Ac (l)	80.3	85.8	2.51	15.71
	Av (r)	77.6	87.2	0.69	4.34
	Av (s)	54.7	77.9	2.22	13.90
	Av (l)	71.2	87.8	1.82	11.35

Monsoon

	Name of Plant Part	Moisture (%)	Organic carbon (%)	Kjeldhal nitrogen (mg/g)	Protein (mg/g)
Stn 1	R (r)	75.4	91.900	0.25	1.54
	R (s)	78.0	81.6	0.51	3.16
	R (l)	78.6	72.95	0.68	4.27
	Ac (r)	89.2	88.2	0.49	3.03
	Ac (s)	79.2	88.1	0.55	3.45
	Ac (l)	53.4	85.6	1.93	12.04
	Av (r)	84.9	68.9	0.37	2.30
	Av (s)	79.6	89.8	1.04	6.51
	Av (l)	76.8	86.6	2.01	12.55
Stn2	R (r)	59.8	92.8	0.78	4.86
	R (s)	72.9	86.9	1.26	7.87
	R (l)	55.2	77.2	1.07	6.71
	Ac (r)	87.7	81.4	0.87	5.46
	Ac (s)	90.8	84.8	1.21	7.54
	Ac (l)	78.3	85.7	1.25	7.84
	Av (r)	73.9	94.4	0.65	4.03
	Av (s)	66.5	90.5	0.84	5.24
	Av (l)	74.7	87.3	1.23	7.66
Stn3	R (r)	86.7	95.6	0.94	5.86
	R (s)	70.6	86.8	0.92	5.75
	R (l)	75.5	88.9	2.21	13.83
	Ac (r)	84.8	88.0	2.25	14.03
	Ac (s)	89.7	79.9	2.07	12.96
	Ac (l)	85.9	85.5	3.13	19.53
	Av (r)	80.1	88.0	2.07	12.94
	Av (s)	71.4	91.5	1.31	8.17
	Av (l)	78.3	86.0	0.87	5.41
Stn4	R (r)	82.5	93.0	0.40	2.52
	R (s)	62.9	88.3	1.18	7.37
	R (l)	68.6	83.0	1.74	10.88
	Ac(r)	85.7	83.9	0.74	4.63
	Ac (s)	80.2	79.8	1.72	10.76
	Ac (l)	79.5	84.5	2.43	15.18
	Av (r)	82.0	85.4	0.52	3.26
	Av (s)	84.7	86.7	1.22	7.66
	Av (l)	73.9	89.1	1.47	9.21

Post Monsoon

	Name of Plant Part	Moisture (%)	Organic carbon (%)	Kjeldhal nitrogen (mg/g)	Protein (mg/g)
Stn 1	R (r)	75.3	79.9	0.62	3.87
	R (s)	75.5	85.3	1.84	11.47
	R (l)	75.3	84.8	2.13	13.30
	Ac (r)	81.1	86.8	0.58	3.62
	Ac (s)	76.0	90.4	1.73	10.84
	Ac (l)	75.9	86.8	1.01	6.30
	Av (r)	85.9	71.9	0.26	1.61
	Av (s)	69.1	91.0	1.04	6.47
	Av (l)	77.2	85.5	1.74	10.87
Stn2	R (r)	77.8	90.0	0.56	3.52
	R (s)	78.5	84.1	0.54	3.35
	R (l)	77.5	81.3	1.54	9.62
	Ac (r)	84.0	75.8	0.44	2.78
	Ac (s)	85.3	84.7	1.49	9.33
	Ac (l)	77.0	83.1	1.54	9.61
	Av (r)	82.2	82.3	0.60	3.75
	Av (s)	64.5	87.3	1.03	6.44
	Av (l)	61.6	80.6	2.61	16.33
Stn3	R (r)	77.6	80.7	0.66	4.15
	R (s)	59.4	78.7	0.90	5.64
	R (l)	73.1	78.5	2.15	10.11
	Ac (r)	82.9	67.2	2.14	13.39
	Ac (s)	82.4	62.6	1.90	11.90
	Ac (l)	79.1	63.3	2.05	12.79
	Av (r)	67.7	71.6	0.78	4.86
	Av (s)	64.8	75.8	1.56	9.74
	Av (l)	74.5	60.3	0.71	4.42
Stn4	R (r)	74.3	76.6	0.92	5.77
	R (s)	61.5	73.1	0.70	4.38
	R (l)	72.2	71.9	1.02	6.39
	Ac(r)	81.7	63.1	0.70	4.35
	Ac (s)	85.4	51.2	0.87	5.43
	Ac (l)	77.9	60.6	0.88	5.48
	Av (r)	85.1	71.6	0.51	3.18
	Av (s)	66.8	75.4	2.11	13.18
	Av (l)	70.2	86.7	0.81	5.08

Tannin and lignin of leaves (Seasonal Average)

R(l)	Pre-mon	Monsoon	Post-mon
Stn 1	0.65	1.07	1.31
Stn2	1.48	1.41	1.20
Stn 3	0.59	0.74	1.15
Stn4	3.06	1.14	1.29

Ac(l)	Pre-mon	Monsoon	Post-mon
Stn 1	0.60	1.00	1.13
Stn2	3.39	1.06	0.99
Stn 3	0.50	0.97	0.93
Stn4	0.80	0.87	0.88

Av(l)	Pre-Mon	Monsoon	Post-mon
Stn 1	0.73	1.11	0.87
Stn2	1.08	1.45	1.10
Stn 3	0.64	0.68	0.87
Stn4	0.84	0.56	1.41

Chloride of leaves (Seasonal Average)

R(l)	Pre-mon	Monsoon	Post-Mon
Stn 1	39.41	56.33	54.33
Stn2	61.68	47.21	52.46
Stn 3	52.67	50.74	46.87
Stn4	38.91	46.34	37.59

Ac(l)	Pre-Mon	Monsoon	Post-Mon
Stn 1	61.68	47.57	50.15
Stn2	47.23	29.67	43.14
Stn 3	59.66	34.83	49.35
Stn4	24.09	47.83	52.40

Av(l)	Pre-Mon	Monsoon	Post-Mon
Stn 1	31.10	27.53	30.72
Stn2	39.98	22.58	35.47
Stn 3	31.43	41.95	26.88
Stn4	12.70	24.61	19.66

Metals in Plant Parts

Pre Monsoon

	Name of Plant Part	Fe (ppm)	Mn (ppm)	Zn (ppm)	Ni (ppm)	Pb (ppb)	Cu (ppm)	Cd (ppm)
Stn 1	R (r)	27.52	0.132	0.043	0.014	11.67	21.65	0.29
	R (s)	0.22	0.012	0.048	0.005	0.52	7.32	0.67
	R (l)	0.37	0.026	0.034	0.007	1.96	17.77	1.03
	Ac (r)	1.94	0.015	0.043	0.009	4.47	11.36	0.18
	Ac (s)	0.10	0.023	0.097	0.006	1.78	32.20	0.00
	Ac (l)	0.67	0.054	0.068	0.008	4.35	10.47	0.00
	Av (r)	0.78	0.044	0.046	0.007	0.45	7.90	0.64
	Av (s)	0.32	0.054	0.045	0.007	37.89	8.62	5.78
	Av (l)	0.60	0.224	0.062	0.011	6.42	8.72	0.05
Stn2	R (r)	15.05	0.030	0.037	0.012	0.09	12.83	1.23
	R (s)	0.43	0.028	0.047	0.014	0.00	18.12	0.21
	R (l)	1.62	0.076	0.037	0.013	0.28	16.53	0.00
	Ac (r)	0.71	0.057	0.049	0.026	0.00	27.34	0.73
	Ac (s)	0.24	0.039	0.062	0.026	0.00	31.85	0.20
	Ac (l)	0.65	0.099	0.082	0.022	0.17	17.75	0.00
	Av (r)	8.34	0.048	0.054	0.030	0.06	0.89	1.09
	Av (s)	0.17	0.019	0.048	0.028	0.00	0.30	0.79
	Av (l)	0.36	0.021	0.032	0.005	0.00	0.28	0.06
Stn3	R (r)	0.77	0.075	0.044	0.006	0.00	10.01	0.00
	R (s)	0.08	0.049	0.026	0.009	1.95	5.73	2.25
	R (l)	1.25	0.009	0.028	0.011	3.96	15.65	0.00
	Ac (r)	2.40	0.003	0.058	0.011	22.13	26.12	3.05
	Ac (s)	0.32	0.020	0.312	0.012	12.11	15.18	0.85
	Ac (l)	0.42	0.067	0.258	0.006	18.97	14.24	0.89
	Av (r)	0.55	0.048	0.133	0.005	11.81	19.07	0.03
	Av (s)	0.47	0.044	0.112	0.005	4.25	15.78	0.17
	Av (l)	0.14	0.096	0.103	0.004	12.61	18.32	0.54
Stn4	R (r)	0.62	0.052	1.020	0.005	7.28	8.83	0.00
	R (s)	0.51	0.045	0.097	0.006	6.69	8.48	0.00
	R (l)	0.75	0.122	0.023	0.006	0.00	6.66	0.00
	Ac(r)	0.62	0.047	0.092	0.010	4.11	14.92	0.00
	Ac (s)	0.43	0.048	0.080	0.010	2.01	24.28	0.00
	Ac (l)	0.54	0.072	0.077	0.008	1.71	11.87	0.00
	Av (r)	1.44	0.025	0.049	0.011	29.21	11.96	0.00
	Av (s)	0.16	0.045	0.040	0.010	26.29	19.89	0.00
	Av (l)	0.82	0.147	0.051	0.007	0.00	8.12	2.78

Monsoon

	Name of Plant Part	Fe (ppm)	Mn (ppm)	Zn (ppm)	Ni (ppm)	Pb (ppb)	Cu (ppm)	Cd (ppm)
Stn 1	R (r)	1.847	0.012	0.022	0.015	14.73	44.51	23.70
	R (s)	0.571	0.017	0.039	0.013	9.48	32.25	2.61
	R (l)	0.828	0.074	0.050	0.022	0.46	24.09	10.36
	Ac (r)	0.849	0.027	0.026	0.008	3.53	12.20	1.57
	Ac (s)	0.217	0.015	0.038	0.010	0.42	59.92	1.15
	Ac (l)	0.440	0.181	0.101	0.032	6.32	13.05	1.25
	Av (r)	2.182	0.041	0.041	0.010	7.80	15.63	0.42
	Av (s)	0.393	0.047	0.039	0.012	3.85	11.80	0.80
	Av (l)	0.154	0.207	0.042	0.010	3.53	12.05	2.00
Stn2	R (r)	0.248	0.015	0.028	0.012	4.14	26.96	0.11
	R (s)	0.159	0.019	0.038	0.020	3.40	18.32	1.31
	R (l)	0.399	0.087	0.033	0.014	1.47	26.05	0.79
	Ac (r)	8.138	0.069	0.062	0.013	11.04	26.54	3.99
	Ac (s)	0.260	0.013	0.028	0.026	6.16	16.29	1.02
	Ac (l)	0.520	0.024	0.041	0.026	1.20	12.40	0.88
	Av (r)	0.433	0.026	0.112	0.036	9.45	0.00	0.00
	Av (s)	0.325	0.021	0.116	0.022	6.33	0.00	0.00
	Av (l)	0.141	0.032	0.181	0.028	0.82	28.79	0.16
Stn3	R (r)	0.155	0.003	0.029	0.009	10.81	26.17	0.26
	R (s)	0.169	0.064	0.055	0.010	5.78	16.90	1.36
	R (l)	0.178	0.094	0.017	0.009	2.77	5.11	0.04
	Ac (r)	1.211	0.049	0.137	0.019	13.06	112.69	0.72
	Ac (s)	0.152	0.018	0.113	0.011	9.76	27.75	0.60
	Ac (l)	0.233	0.025	0.039	0.007	2.48	8.13	0.64
	Av (r)	1.058	0.036	0.101	0.011	9.78	30.15	0.65
	Av (s)	0.372	0.022	0.042	0.008	11.48	32.14	0.54
	Av (l)	0.506	0.179	0.024	0.005	5.23	8.13	0.31
Stn4	R (r)	0.630	0.055	0.019	0.007	9.80	108.24	0.02
	R (s)	0.077	0.045	0.018	0.011	5.30	28.13	28.13
	R (l)	0.108	0.022	0.022	0.006	5.32	17.01	17.01
	Ac(r)	5.753	0.068	0.032	0.010	18.23	22.68	22.68
	Ac (s)	0.125	0.027	0.045	0.010	3.11	16.52	16.52
	Ac (l)	0.189	0.030	0.103	0.008	7.49	17.01	17.01
	Av (r)	1.601	0.092	0.064	0.012	11.62	26.26	26.26
	Av (s)	0.228	0.045	0.034	0.010	11.03	15.15	15.15
	Av (l)	0.212	0.148	0.056	0.007	3.92	26.54	26.54

Monsoon

	Name of Plant Part	Fe (ppm)	Mn (ppm)	Zn (ppm)	Ni (ppm)	Pb (ppb)	Cu (ppm)	Cd (ppm)
Stn 1	R (r)	1.847	0.012	0.022	0.015	14.73	44.51	23.70
	R (s)	0.571	0.017	0.039	0.013	9.48	32.25	2.61
	R (l)	0.828	0.074	0.050	0.022	0.46	24.09	10.36
	Ac (r)	0.849	0.027	0.026	0.008	3.53	12.20	1.57
	Ac (s)	0.217	0.015	0.038	0.010	0.42	59.92	1.15
	Ac (l)	0.440	0.181	0.101	0.032	6.32	13.05	1.25
	Av (r)	2.182	0.041	0.041	0.010	7.80	15.63	0.42
	Av (s)	0.393	0.047	0.039	0.012	3.85	11.80	0.80
	Av (l)	0.154	0.207	0.042	0.010	3.53	12.05	2.00
Stn2	R (r)	0.248	0.015	0.028	0.012	4.14	26.96	0.11
	R (s)	0.159	0.019	0.038	0.020	3.40	18.32	1.31
	R (l)	0.399	0.087	0.033	0.014	1.47	26.05	0.79
	Ac (r)	8.138	0.069	0.062	0.013	11.04	26.54	3.99
	Ac (s)	0.260	0.013	0.028	0.026	6.16	16.29	1.02
	Ac (l)	0.520	0.024	0.041	0.026	1.20	12.40	0.88
	Av (r)	0.433	0.026	0.112	0.036	9.45	0.00	0.00
	Av (s)	0.325	0.021	0.116	0.022	6.33	0.00	0.00
	Av (l)	0.141	0.032	0.181	0.028	0.82	28.79	0.16
Stn3	R (r)	0.155	0.003	0.029	0.009	10.81	26.17	0.26
	R (s)	0.169	0.064	0.055	0.010	5.78	16.90	1.36
	R (l)	0.178	0.094	0.017	0.009	2.77	5.11	0.04
	Ac (r)	1.211	0.049	0.137	0.019	13.06	112.69	0.72
	Ac (s)	0.152	0.018	0.113	0.011	9.76	27.75	0.60
	Ac (l)	0.233	0.025	0.039	0.007	2.48	8.13	0.64
	Av (r)	1.058	0.036	0.101	0.011	9.78	30.15	0.65
	Av (s)	0.372	0.022	0.042	0.008	11.48	32.14	0.54
	Av (l)	0.506	0.179	0.024	0.005	5.23	8.13	0.31
Stn4	R (r)	0.630	0.055	0.019	0.007	9.80	108.24	0.02
	R (s)	0.077	0.045	0.018	0.011	5.30	28.13	28.13
	R (l)	0.108	0.022	0.022	0.006	5.32	17.01	17.01
	Ac(r)	5.753	0.068	0.032	0.010	18.23	22.68	22.68
	Ac (s)	0.125	0.027	0.045	0.010	3.11	16.52	16.52
	Ac (l)	0.189	0.030	0.103	0.008	7.49	17.01	17.01
	Av (r)	1.601	0.092	0.064	0.012	11.62	26.26	26.26
	Av (s)	0.228	0.045	0.034	0.010	11.03	15.15	15.15
	Av (l)	0.212	0.148	0.056	0.007	3.92	26.54	26.54

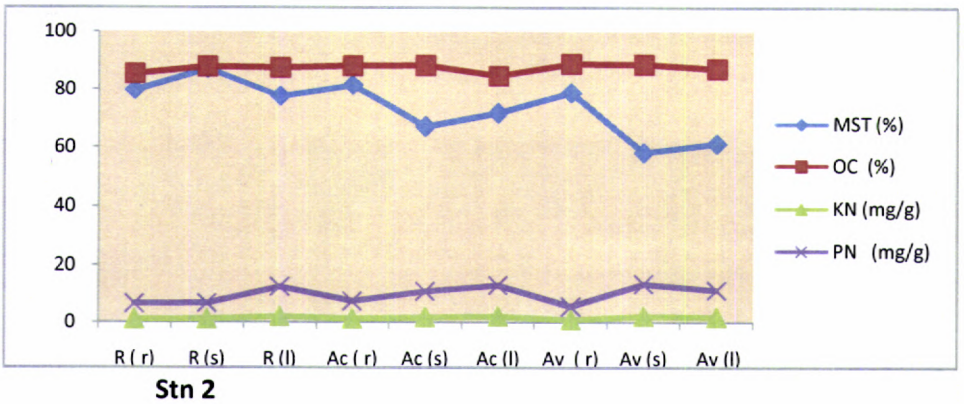
Post Monsoon

	Name of Plant Part	Fe (ppm)	Mn (ppm)	Zn (ppm)	Ni (ppm)	Pb (ppb)	Cu (ppm)	Cd (ppm)
Stn 1	R (r)	0.696	0.009	0.010	0.004	5.84	9.65	0.206
	R (s)	0.150	0.013	0.023	0.005	7.90	8.81	0.229
	R (l)	0.490	0.056	0.050	0.015	3.56	9.74	0.595
	Ac (r)	1.488	0.058	0.063	0.011	8.16	16.47	1.517
	Ac (s)	0.114	0.022	0.037	0.005	9.42	12.70	0.602
	Ac (l)	0.448	0.045	0.106	0.014	3.85	24.90	0.461
	Av (r)	6.498	0.034	0.052	0.009	4.84	11.41	0.488
	Av (s)	0.116	0.056	0.027	0.003	2.95	16.59	0.756
	Av (l)	0.182	0.306	0.073	0.009	4.16	12.91	0.000
Stn2	R (r)	0.793	0.018	0.037	0.009	3.86	11.84	0.396
	R (s)	0.329	0.018	0.021	0.005	3.43	10.19	0.958
	R (l)	1.343	0.102	0.090	0.012	5.96	37.08	0.000
	Ac (r)	3.274	0.038	0.035	0.019	13.58	13.18	0.502
	Ac (s)	0.206	0.020	0.064	0.008	0.00	18.56	0.282
	Ac (l)	0.805	0.061	0.278	0.018	3.10	19.94	0.594
	Av (r)	1.540	0.044	0.047	0.016	13.83	18.48	0.344
	Av (s)	0.209	0.129	0.042	0.005	3.58	7.71	0.212
	Av (l)	0.498	0.329	0.046	0.008	3.82	8.46	0.139
Stn3	R (r)	0.320	0.021	0.170	0.007	1.92	9.95	0.804
	R (s)	0.237	0.053	0.074	0.008	0.14	8.20	0.106
	R (l)	0.493	0.042	0.105	0.007	1.50	9.84	1.109
	Ac (r)	0.077	0.011	0.032	0.004	0.00	9.73	0.271
	Ac (s)	0.136	0.037	0.074	0.005	4.45	14.92	0.311
	Ac (l)	0.428	0.034	0.088	0.010	3.80	15.17	0.122
	Av (r)	1.924	0.047	0.127	0.009	4.43	20.79	1.795
	Av (s)	0.334	0.024	0.073	0.003	2.08	10.14	1.025
	Av (l)	1.041	0.053	0.094	0.007	1.04	12.96	0.891
Stn4	R (r)	1.236	0.027	0.025	0.007	0.04	10.72	0.320
	R (s)	1.389	0.115	0.036	0.010	0.00	7.60	0.033
	R (l)	0.377	0.184	0.017	0.006	0.00	4.88	0.035
	Ac(r)	1.685	0.234	0.114	0.024	7.56	26.26	1.049
	Ac (s)	0.098	0.023	0.022	0.004	0.55	6.28	0.003
	Ac (l)	0.661	0.044	0.071	0.010	9.39	9.49	0.081
	Av (r)	2.984	0.160	0.038	0.010	0.00	8.12	1.410
	Av (s)	1.279	0.077	0.049	0.008	0.53	7.16	0.304
	Av (l)	0.139	0.174	0.042	0.004	1.21	6.97	0.247

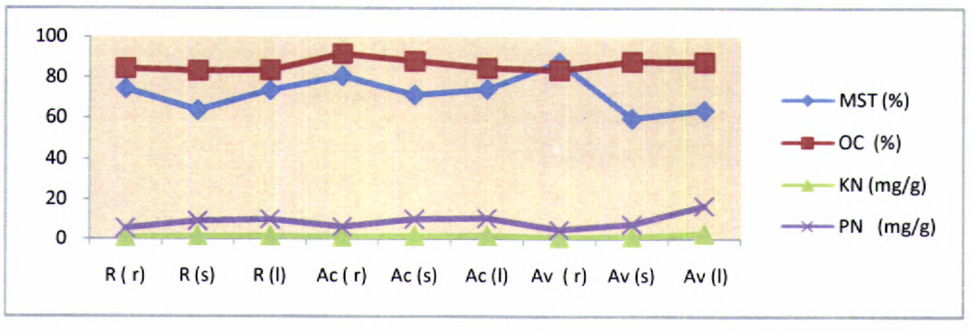
Graphs of plant part data

Premonsoon

Stn 1



Stn 2



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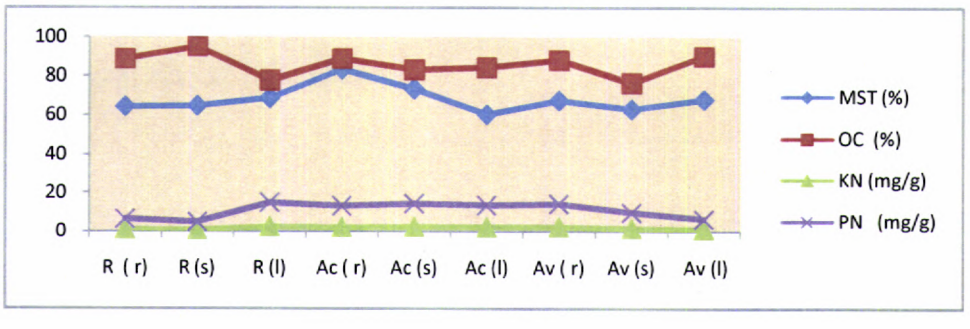

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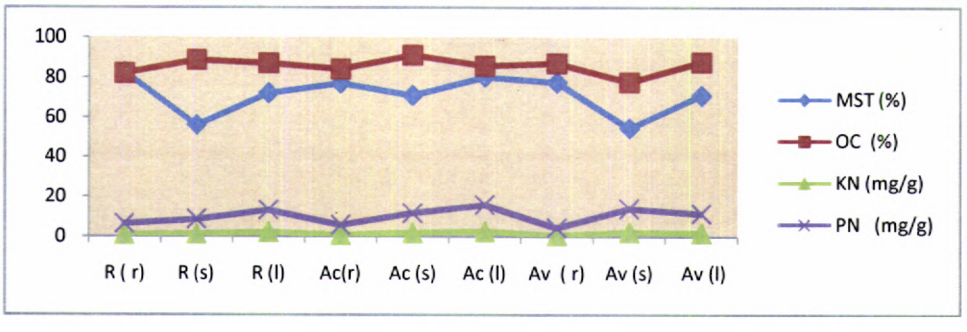
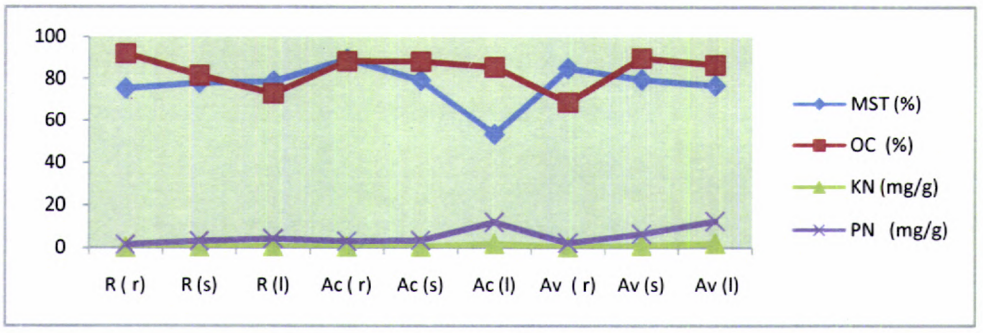


Monsoon

Stn 1



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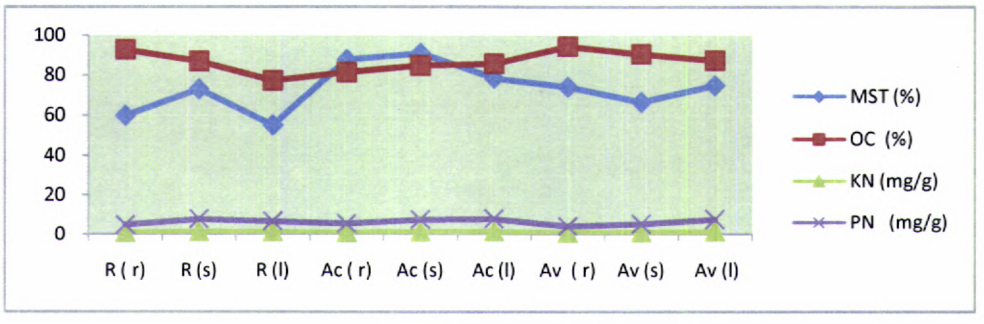

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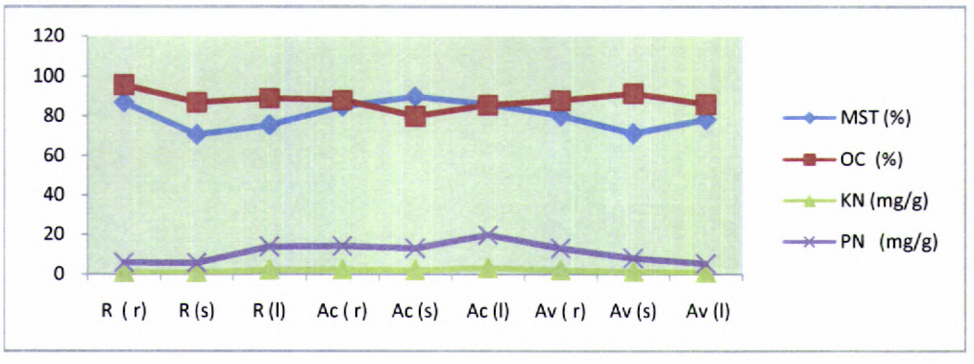

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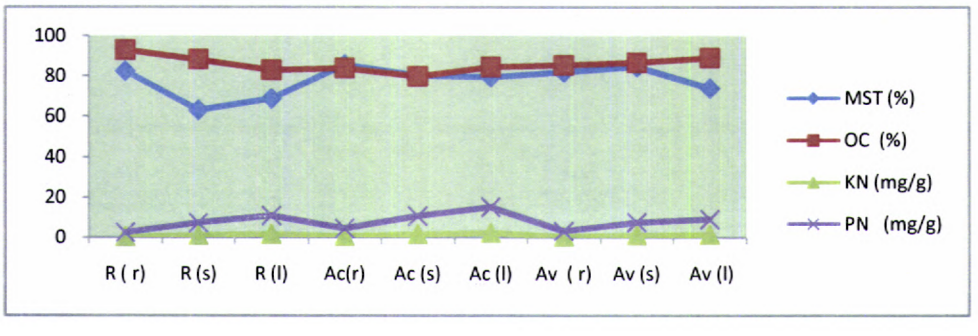
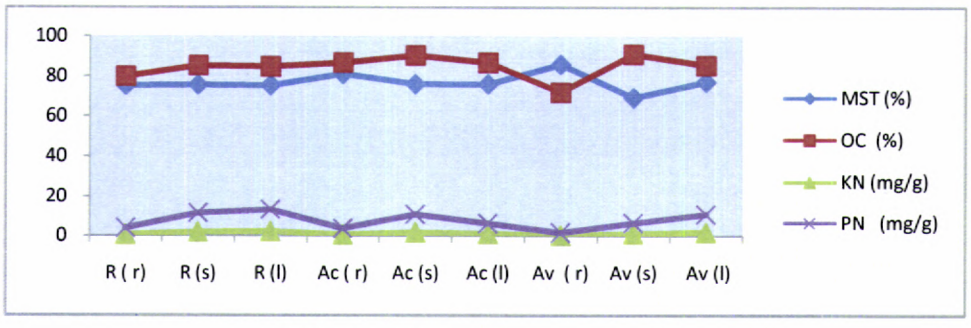


Post Monsoon

Stn 1



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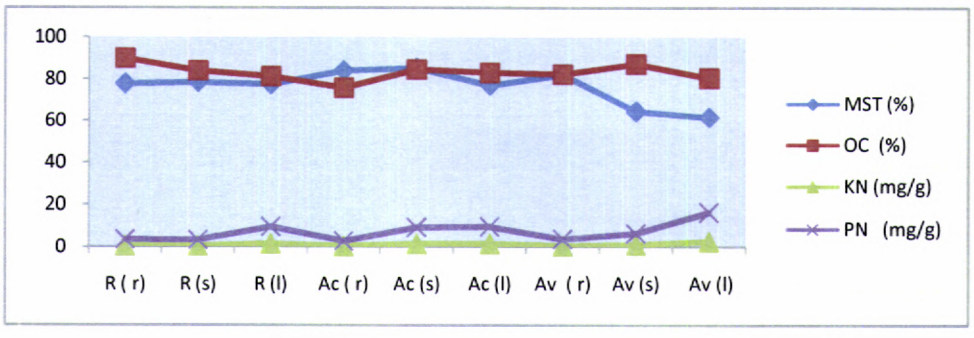

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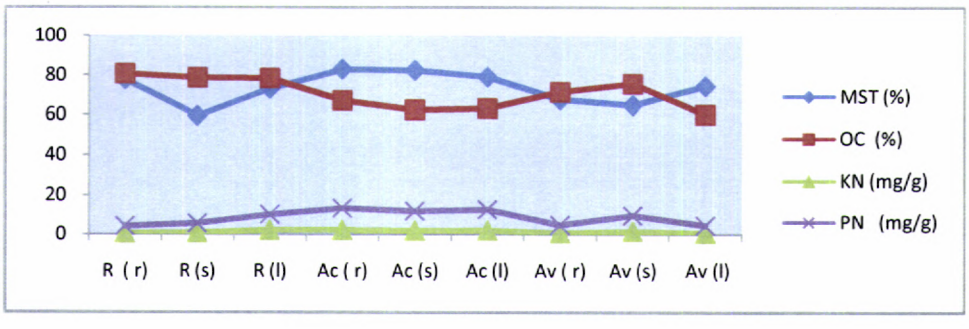

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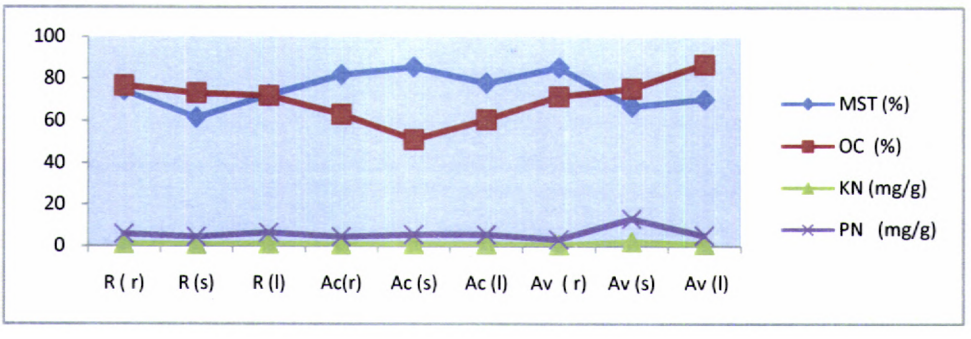
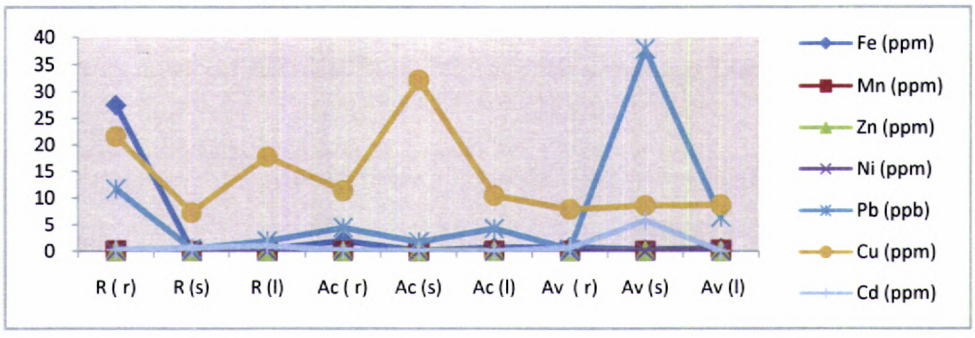


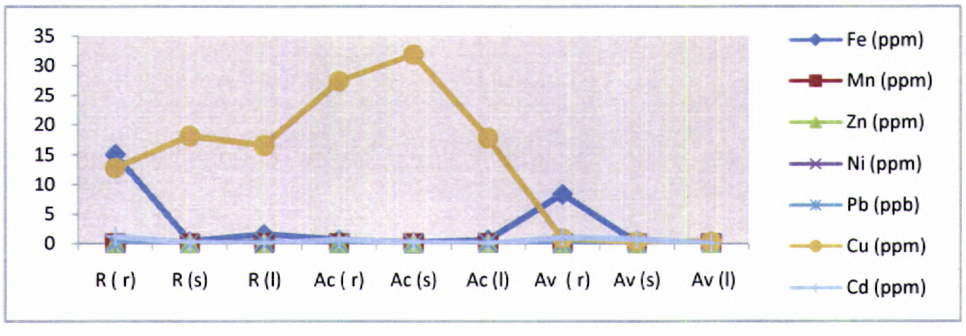
Metals in Plant Parts

Pre Monsoon

Stn 1



Stn2



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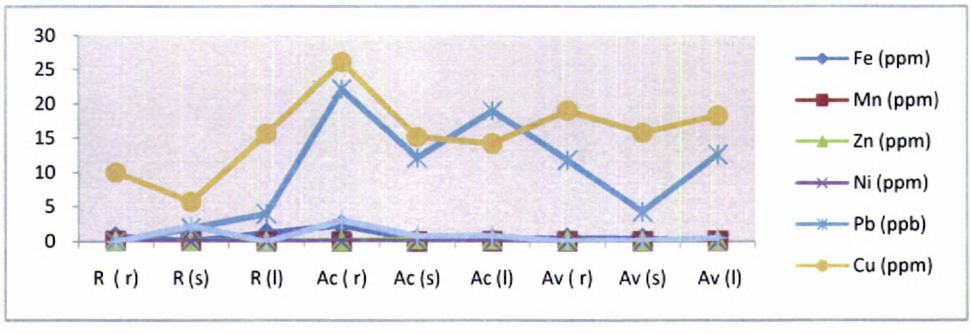

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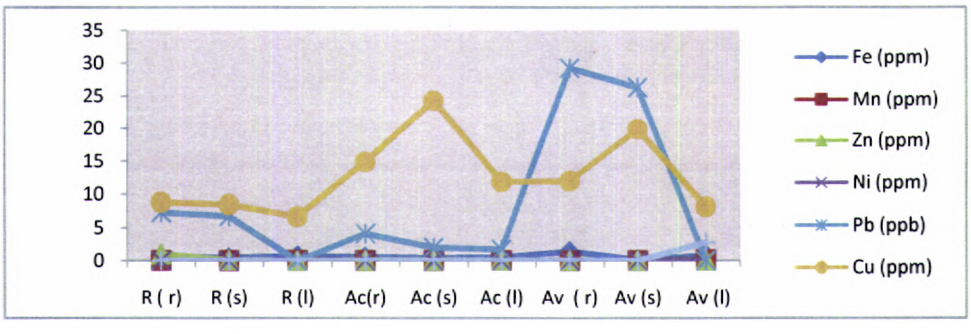
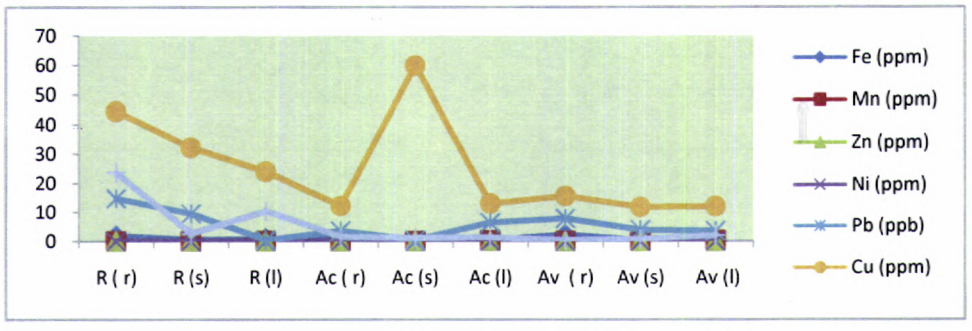
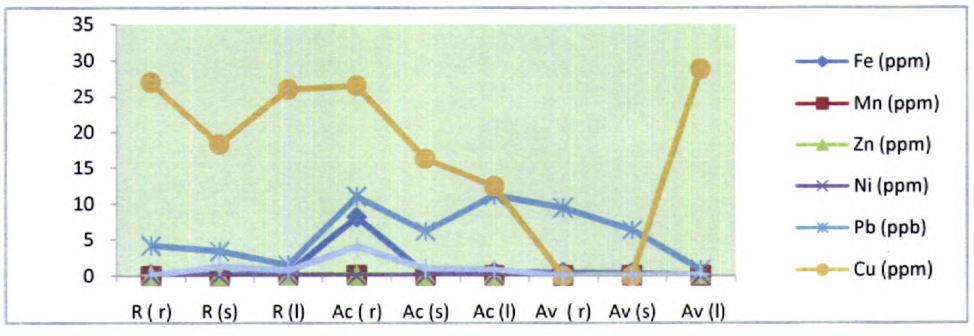


Monsoon

Stn1



Stn2



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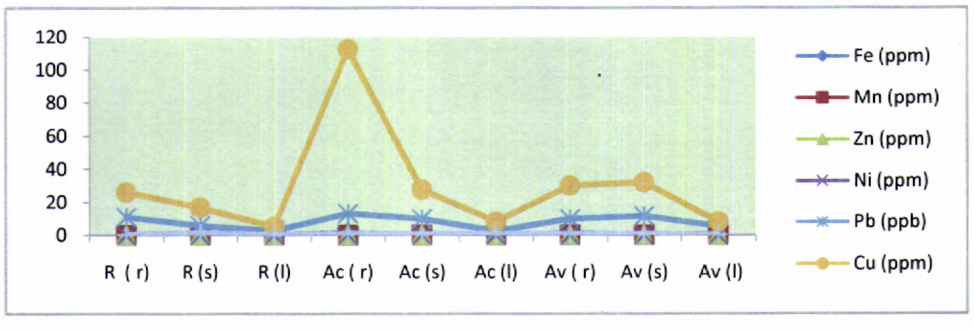

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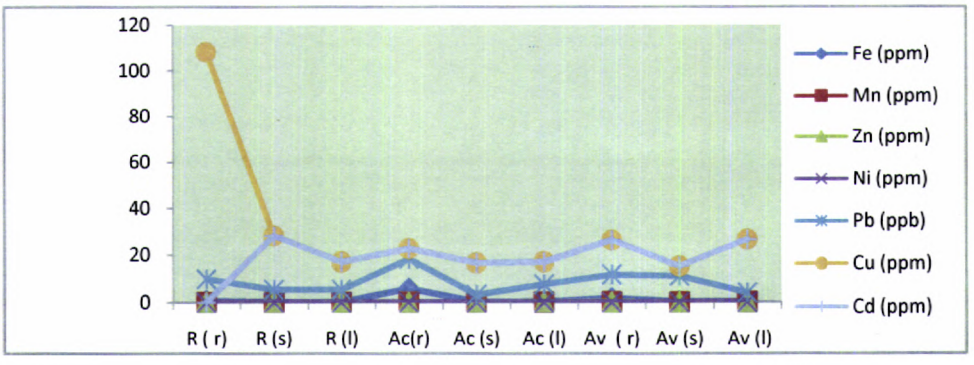
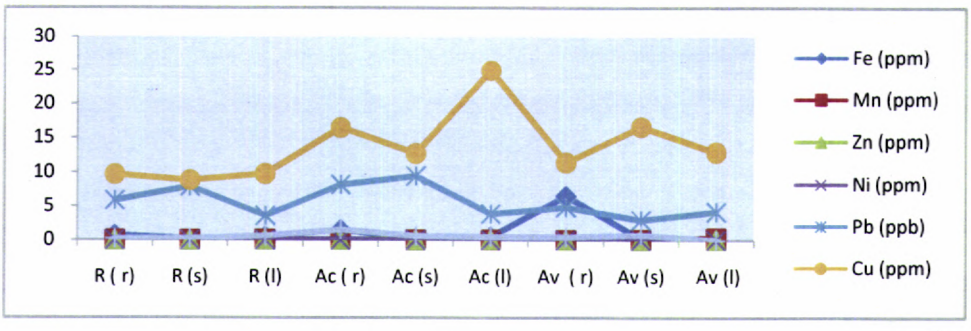
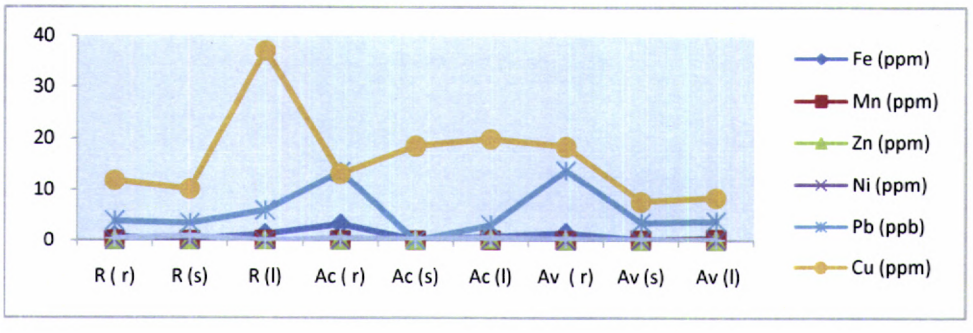


POST MONSOON

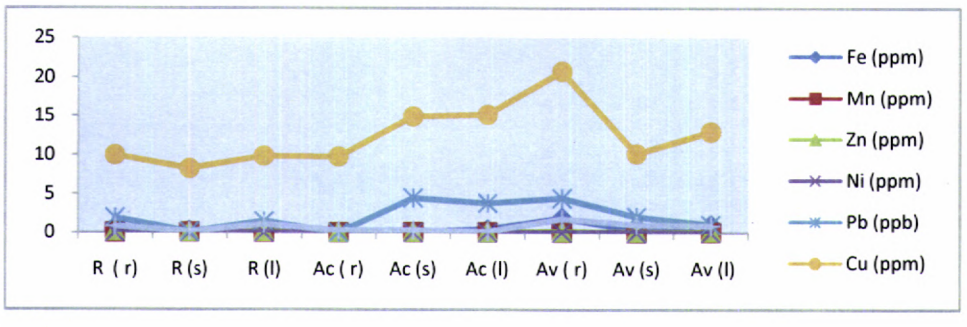
Stn1



Stn2



Stn 3



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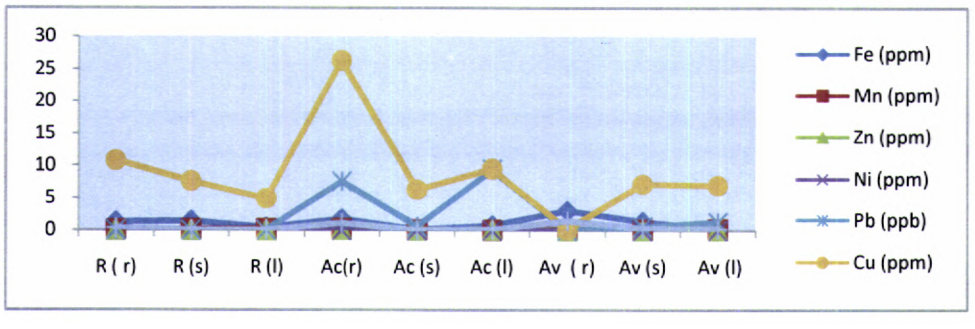
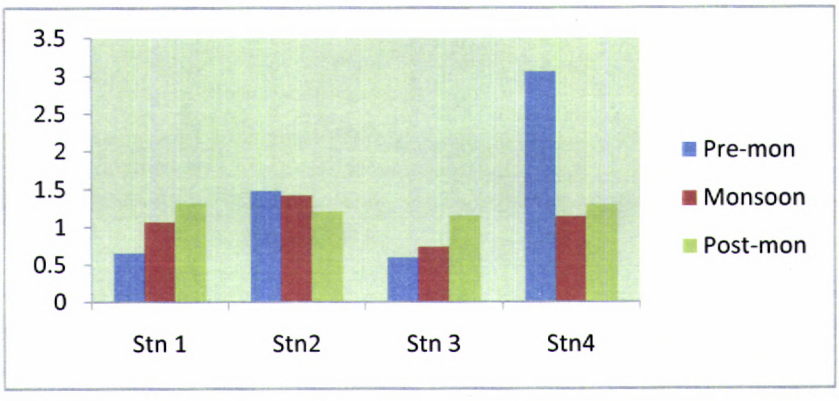


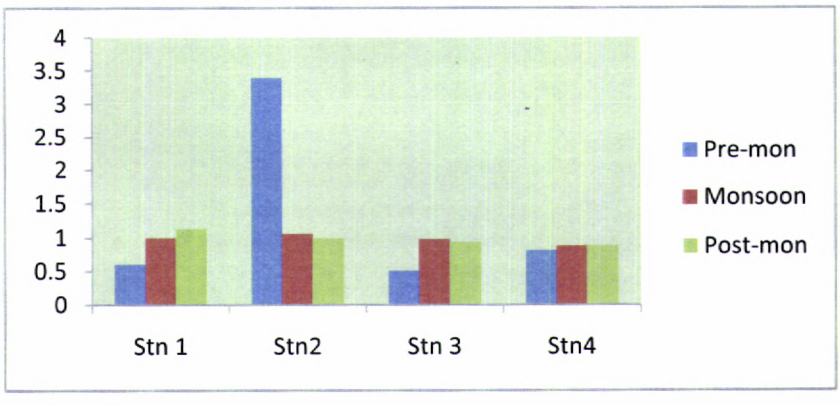
Graphs of leaves alone data

A) Tannin and Lignin

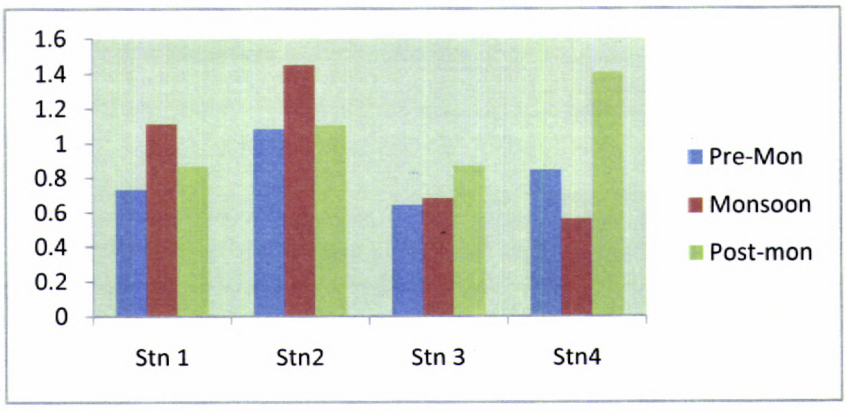
a) R(l)



b)Ac(l)

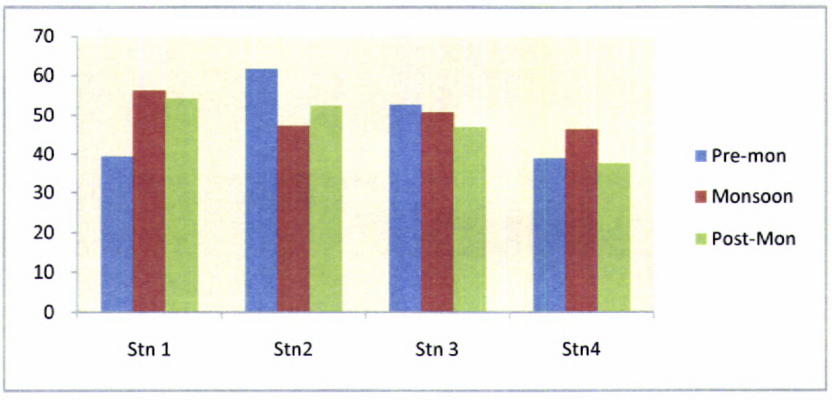


Av(l)

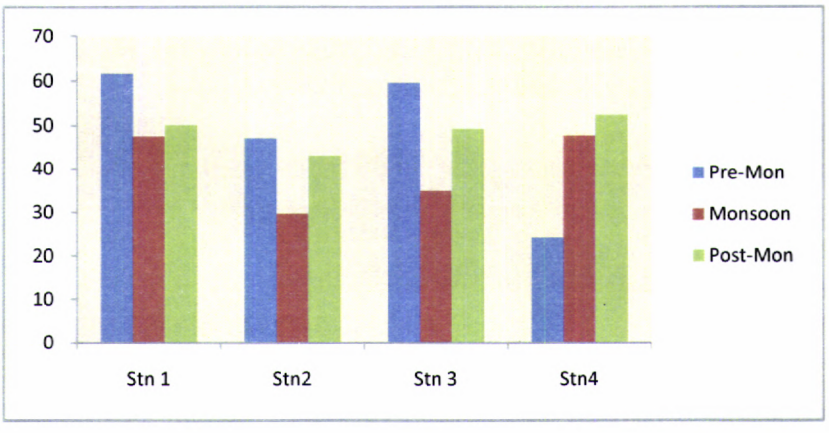


B) Chloride

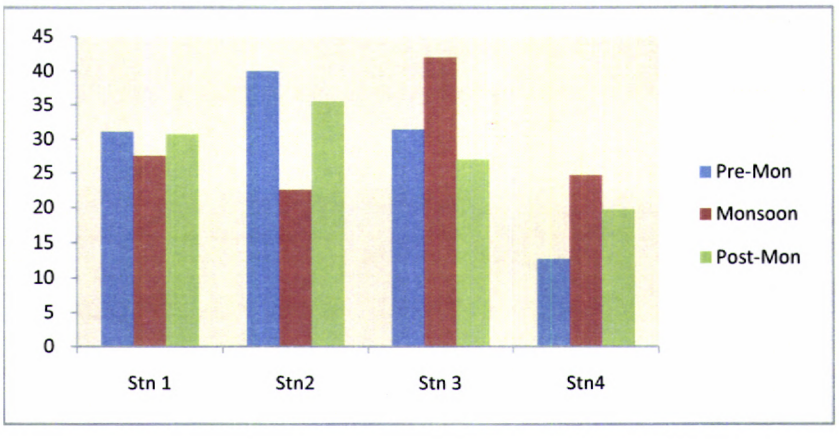
a) R(I)



Ac(I)



Av(I)



Three way Anova

Moisture

Source of Variation	DF	SS	MS	F	P
Season	2	644.067	322.033	5.223	0.008
Station	3	67.934	22.645	0.367	0.777
Plant	2	1033.236	516.618	8.38	<0.001
Season x station	6	360.066	60.011	0.973	0.45
Season x Plant	4	329.202	82.301	1.335	0.265
station x Plant	6	639.75	106.625	1.729	0.126
Season x station x Plant	12	622.081	51.84	0.841	0.609
Residual	72	4438.973	61.652		
Total	107	8135.309	76.031		

Organic carbon

Source of Variation	DF	SS	MS	F	P
Season	2	1907.734	953.867	36.445	<0.001
Station	3	496.776	165.592	6.327	<0.001
Plant	2	160.15	80.075	3.059	0.053
Season x station	6	1253.591	208.932	7.983	<0.001
Season x Plant	4	240.477	60.119	2.297	0.067
station x Plant	6	475.136	79.189	3.026	0.011
Season x station x Plant	12	475.64	39.637	1.514	0.139
Residual	72	1884.452	26.173		
Total	107	6893.956	64.429		

Kjeldhal nitrogen

Source of Variation	DF	SS	MS	F	P
Season	2	3.389	1.695	4.28	0.018
Station	3	3.519	1.173	2.963	0.038
Plant	2	2.395	1.197	3.024	0.055
Season x station	6	2.038	0.34	0.858	0.53
Season x Plant	4	0.608	0.152	0.384	0.819
station x Plant	6	2.967	0.494	1.249	0.292
Season x station x Plant	12	1.918	0.16	0.404	0.958
Residual	72	28.507	0.396		
Total	107	45.342	0.424		

Protein

Source of Variation	DF	SS	MS	F	P
Season	2	139.247	69.624	4.631	0.013
Station	3	125.138	41.713	2.775	0.047
Plant	2	100.406	50.203	3.339	0.041
Season x station	6	83.039	13.84	0.921	0.485
Season x Plant	4	19.8	4.95	0.329	0.857
station x Plant	6	122.601	20.434	1.359	0.243
Season x station x Plant	12	75.94	6.328	0.421	0.95
Residual	72	1082.417	15.034		
Total	107	1748.589	16.342		

Three way Anova of Metals

Fe

Source of Variation	DF	SS	MS	F	P
Season	2	29.516	14.758	1.353	0.265
Station	3	32.134	10.711	0.982	0.406
Plant	2	11.524	5.762	0.528	0.592
Season x station	6	37.234	6.206	0.569	0.754
Season x Plant	4	79.523	19.881	1.823	0.134
station x Plant	6	37.913	6.319	0.579	0.745
Season x station x Plant	12	90.348	7.529	0.69	0.755
Residual	72	785.1	10.904		
Total	107	1103.294	10.311		

Mn

Source of Variation	DF	SS	MS	F	P
Season	2	0.0101	0.00505	1.376	0.259
Station	3	0.0187	0.00625	1.704	0.174
Plant	2	0.0352	0.0176	4.794	0.011
Season x station	6	0.0206	0.00344	0.937	0.474
Season x Plant	4	0.0103	0.00258	0.704	0.591
station x Plant	6	0.00942	0.00157	0.428	0.858
Season x station x Plant	12	0.0274	0.00229	0.624	0.815
Residual	72	0.264	0.00367		
Total	107	0.396	0.0037		

Zn

Source of Variation	DF	SS	MS	F	P
Season	2	0.0365	0.0182	1.797	0.173
Station	3	0.0314	0.0105	1.031	0.384
Plant	2	0.00715	0.00357	0.352	0.704
Season x station	6	0.0757	0.0126	1.243	0.295
Season x Plant	4	0.0311	0.00778	0.767	0.55
station x Plant	6	0.0659	0.011	1.082	0.382
Season x station x Plant	12	0.196	0.0163	1.609	0.108
Residual	72	0.731	0.0102		
Total	107	1.175	0.011		

Ni

Source of Variation	DF	SS	MS	F	P
Season	2	0.00046	0.00023	8.92	<0.001
Station	3	0.00152	0.000506	19.611	<0.001
Plant	2	0.000189	0.0000944	3.659	0.031
Season x station	6	0.000419	0.0000698	2.707	0.02
Season x Plant	4	0.0000301	0.00000751	0.291	0.883
station x Plant	6	0.000313	0.0000522	2.023	0.073
Season x station x Plant	12	0.000264	0.000022	0.854	0.595
Residual	72	0.00186	0.0000258		
Total	107	0.00505	0.0000472		

Pb

Source of Variation	DF	SS	MS	F	P
Season	2	198.717	99.359	3.131	0.05
Station	3	129.339	43.113	1.359	0.262
Plant	2	197.334	98.667	3.11	0.051
Season x station	6	555.17	92.528	2.916	0.013
Season x Plant	4	235.796	58.949	1.858	0.127
station x Plant	6	206.476	34.413	1.085	0.38
Season x station x Plant	12	630.481	52.54	1.656	0.095
Residual	72	2284.487	31.729		
Total	107	4437.8	41.475		

Cu

Source of Variation	DF	SS	MS	F	P
Season	2	3651.725	1825.863	8.179	<0.001
Station	3	157.875	52.625	0.236	0.871
Plant	2	1376.685	688.342	3.083	0.052
Season x station	6	1154.684	192.447	0.862	0.527
Season x Plant	4	727.854	181.964	0.815	0.52
station x Plant	6	1490.266	248.378	1.113	0.364
Season x station x Plant	12	2871.168	239.264	1.072	0.396
Residual	72	16073.358	223.241		
Total	107	27503.615	257.043		

Cd

Source of Variation	DF	SS	MS	F	P
Season	2	784.006	392.003	36.017	<0.001
Station	3	620.609	206.87	19.007	<0.001
Plant	2	4.119	2.059	0.189	0.828
Season x station	6	1366.546	227.758	20.926	<0.001
Season x Plant	4	12.232	3.058	0.281	0.889
station x Plant	6	110.371	18.395	1.69	0.136
Season x station x Plant	12	222.888	18.574	1.707	0.083
Residual	72	783.637	10.884		
Total	107	3904.408	36.49		

Three way Anova of leaves alone

Tannin and lignin of leaves

Source of Variation	DF	SS	MS	F	P
Plant	2	18196.73	9098.364	524.875	<0.001
Season	2	3.676	1.838	0.106	0.9
Station	3	102.894	34.298	1.979	0.171
Residual	12	208.012	17.334		
Total	35	18812.94	537.512		

Chloride of Leaves.

Source of Variation	DF	SS	MS	F	P
Plant	2	2781.553	1390.777	22.705	<0.001
Season	2	28.447	14.223	0.232	0.796
Station	3	649.992	216.664	3.537	0.048
Residual	12	735.055	61.255		
Total	35	5540.475	158.299		

Correlations (Total)												
		MO	OC	KN	PN	Fe	Mn	Zn	NI	Pb	Cu	Cd
MO	Pearson Correlation	1	0.136	-.225(*)	-.225(*)	.196(*)	.198(*)	0.033	0.053	0.003	0.184	0.071
	Sig. (2-tailed)	.	0.161	0.019	0.019	0.042	0.04	0.737	0.586	0.978	0.056	0.468
OC	Pearson Correlation	-0.136	1	0.067	0.072	-0.041	-0.072	-0.033	0.127	0.153	0.185	0.106
	Sig. (2-tailed)	0.161	.	0.491	0.459	0.672	0.459	0.737	0.19	0.115	0.055	0.275
KN	Pearson Correlation	.225(*)	0.067	1	.997(**)	.197(*)	0.097	0.065	0.152	0.038	-0.063	-0.091
	Sig. (2-tailed)	0.019	0.491	.	0	0.041	0.317	0.503	0.115	0.695	0.515	0.351
PN	Pearson Correlation	.225(*)	0.072	.997(**)	1	.197(*)	0.1	0.063	0.149	0.044	-0.06	-0.089
	Sig. (2-tailed)	0.019	0.459	0	.	0.041	0.301	0.516	0.124	0.654	0.537	0.357
Fe	Pearson Correlation	.196(*)	0.041	-.197(*)	-.197(*)	1	0.07	-0.056	0.116	0.092	0.01	0.008
	Sig. (2-tailed)	0.042	0.672	0.041	0.041	.	0.47	0.566	0.232	0.346	0.918	0.938
Mn	Pearson Correlation	.198(*)	0.072	0.097	0.1	0.07	1	-0.025	0	-0.109	-0.11	-0.012
	Sig. (2-tailed)	0.04	0.459	0.317	0.301	0.47	.	0.801	0.998	0.262	0.257	0.898
Zn	Pearson Correlation	0.033	0.033	0.065	0.063	-0.056	-0.025	1	0.005	0.076	-0.005	-0.097
	Sig. (2-tailed)	0.737	0.737	0.503	0.516	0.566	0.801	.	0.956	0.435	0.957	0.319
NI	Pearson Correlation	0.053	0.127	-0.152	-0.149	0.116	0	0.005	1	0.001	0.106	-0.018
	Sig. (2-tailed)	0.586	0.19	0.115	0.124	0.232	0.998	0.956	.	0.992	0.276	0.856
Pb	Pearson Correlation	0.003	0.153	0.038	0.044	0.092	-0.109	0.076	0.001	1	.195(*)	0.186
	Sig. (2-tailed)	0.978	0.115	0.695	0.654	0.346	0.262	0.435	0.992	.	0.043	0.054
Cu	Pearson Correlation	0.184	0.185	-0.063	-0.06	0.01	-0.11	-0.005	0.106	.195(*)	1	0.145
	Sig. (2-tailed)	0.056	0.055	0.515	0.537	0.918	0.257	0.957	0.276	0.043	.	0.134
Cd	Pearson Correlation	0.071	0.106	-0.091	-0.089	0.008	-0.012	-0.097	0.018	0.186	0.145	1
	Sig. (2-tailed)	0.468	0.275	0.351	0.357	0.938	0.898	0.319	0.856	0.054	0.134	.

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

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

Correlations (Premonsoon)

		MO	OC	KN	PN	Fe	Mn	Zn	Nl	Pb	Cu	Cd
MO	Pearson Correlation	1	0.084	-.339(*)	-.339(*)	0.29	-0.142	0.16	0.19	-0.24	0.073	-0.067
	Sig. (2-tailed)	.	0.628	0.043	0.043	0.087	0.407	0.351	0.267	0.159	0.672	0.696
	N	36	36	36	36	36	36	36	36	36	36	36
OC	Pearson Correlation	0.084	1	-0.237	-0.237	-0.11	0.092	-0.23	-0.022	-0.081	-0.004	0.295
	Sig. (2-tailed)	0.628	.	0.163	0.163	0.522	0.594	0.178	0.899	0.64	0.98	0.081
	N	36	36	36	36	36	36	36	36	36	36	36
KN	Pearson Correlation	-.339(*)	-0.237	1	1.000(**)	-0.302	0.013	-0.065	-0.272	0.192	0.13	0.07
	Sig. (2-tailed)	0.043	0.163	.	.	0.074	0.941	0.705	0.108	0.261	0.45	0.685
	N	36	36	36	36	36	36	36	36	36	36	36
PN	Pearson Correlation	-.339(*)	-0.237	1.000(**)	1	-0.302	0.013	-0.065	-0.272	0.192	0.13	0.07
	Sig. (2-tailed)	0.043	0.163	.	.	0.074	0.941	0.705	0.108	0.261	0.45	0.685
	N	36	36	36	36	36	36	36	36	36	36	36
Fe	Pearson Correlation	0.29	-0.11	-0.302	-0.302	1	0.194	-0.097	0.19	0.011	0.066	0.014
	Sig. (2-tailed)	0.087	0.522	0.074	0.074	.	0.258	0.574	0.267	0.951	0.703	0.937
	N	36	36	36	36	36	36	36	36	36	36	36
Mn	Pearson Correlation	-0.142	0.092	0.013	0.013	0.194	1	-0.035	-0.03	-0.067	-0.108	-0.034
	Sig. (2-tailed)	0.407	0.594	0.941	0.941	0.258	.	0.84	0.863	0.696	0.531	0.843
	N	36	36	36	36	36	36	36	36	36	36	36
Zn	Pearson Correlation	0.16	-0.23	-0.065	-0.065	-0.097	-0.035	1	-0.183	0.089	-0.05	-0.112
	Sig. (2-tailed)	0.351	0.178	0.705	0.705	0.574	0.84	.	0.285	0.604	0.77	0.514
	N	36	36	36	36	36	36	36	36	36	36	36
Nl	Pearson Correlation	0.19	-0.022	-0.272	-0.272	0.19	-0.03	-0.183	1	-0.235	0.1	-0.025
	Sig. (2-tailed)	0.267	0.899	0.108	0.108	0.267	0.863	0.285	.	0.168	0.562	0.885
	N	36	36	36	36	36	36	36	36	36	36	36
Pb	Pearson Correlation	-0.24	-0.081	0.192	0.192	0.011	-0.067	0.089	-0.235	1	0.106	.465(**)
	Sig. (2-tailed)	0.159	0.64	0.261	0.261	0.951	0.696	0.604	0.168	.	0.538	0.004
	N	36	36	36	36	36	36	36	36	36	36	36
Cu	Pearson Correlation	0.073	-0.004	0.13	0.13	0.066	-0.108	-0.05	0.1	0.106	1	-0.132
	Sig. (2-tailed)	0.672	0.98	0.45	0.45	0.703	0.531	0.77	0.562	0.538	.	0.441
	N	36	36	36	36	36	36	36	36	36	36	36
Cd	Pearson Correlation	-0.067	0.295	0.07	0.07	0.014	-0.034	-0.112	-0.025	.465(**)	-0.132	1
	Sig. (2-tailed)	0.696	0.081	0.685	0.685	0.937	0.843	0.514	0.885	0.004	0.441	.
	N	36	36	36	36	36	36	36	36	36	36	36

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

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

Correlations (Monsoon)												
		MO	OC	KN	PN	Fe	Mn	Zn	Ni	Pb	Cu	Cd
MO	Pearson Correlation	1	-0.119	0.006	0.006	0.313	-0.259	-0.034	-0.241	0.324	0.156	-0.031
	Sig. (2-tailed)	.	0.491	0.975	0.975	0.063	0.127	0.843	0.157	0.054	0.364	0.856
	N	36	36	36	36	36	36	36	36	36	36	36
OC	Pearson Correlation	-0.119	1	-0.026	-0.026	-0.237	-0.109	0.024	0.051	0.179	0.167	-0.067
	Sig. (2-tailed)	0.491	.	0.882	0.882	0.165	0.525	0.888	0.769	0.296	0.33	0.696
	N	36	36	36	36	36	36	36	36	36	36	36
KN	Pearson Correlation	0.006	-0.026	1	1.000(**)	-0.256	0.155	0.284	-0.101	-0.176	-0.099	-0.075
	Sig. (2-tailed)	0.975	0.882	.	0	0.132	0.368	0.093	0.557	0.306	0.565	0.663
	N	36	36	36	36	36	36	36	36	36	36	36
PN	Pearson Correlation	0.006	-0.026	1.000(**)	1	-0.256	0.155	0.284	-0.101	-0.176	-0.099	-0.075
	Sig. (2-tailed)	0.975	0.882	0	.	0.132	0.368	0.093	0.557	0.306	0.565	0.663
	N	36	36	36	36	36	36	36	36	36	36	36
Fe	Pearson Correlation	0.313	-0.237	-0.256	-0.256	1	0.057	-0.028	-0.049	.501(**)	0.074	0.17
	Sig. (2-tailed)	0.063	0.165	0.132	0.132	.	0.741	0.873	0.776	0.002	0.666	0.322
	N	36	36	36	36	36	36	36	36	36	36	36
Mn	Pearson Correlation	-0.259	-0.109	0.155	0.155	0.057	1	-0.03	-0.054	-0.168	-0.128	0.083
	Sig. (2-tailed)	0.127	0.525	0.368	0.368	0.741	.	0.86	0.753	0.326	0.456	0.629
	N	36	36	36	36	36	36	36	36	36	36	36
Zn	Pearson Correlation	-0.034	0.024	0.284	0.284	-0.028	-0.03	1	.516(**)	0.047	0.095	-0.191
	Sig. (2-tailed)	0.843	0.888	0.093	0.093	0.873	0.86	.	0.001	0.788	0.582	0.264
	N	36	36	36	36	36	36	36	36	36	36	36
Ni	Pearson Correlation	-0.241	0.051	-0.101	-0.101	-0.049	-0.054	.516(**)	1	-0.011	-0.119	-0.252
	Sig. (2-tailed)	0.157	0.769	0.557	0.557	0.776	0.753	0.001	.	0.951	0.491	0.138
	N	36	36	36	36	36	36	36	36	36	36	36
Pb	Pearson Correlation	0.324	0.179	-0.176	-0.176	.501(**)	-0.168	0.047	-0.011	1	0.271	0.243
	Sig. (2-tailed)	0.054	0.296	0.306	0.306	0.002	0.326	0.788	0.951	.	0.109	0.154
	N	36	36	36	36	36	36	36	36	36	36	36
Cu	Pearson Correlation	0.156	0.167	-0.099	-0.099	0.074	-0.128	0.095	-0.119	0.271	1	-0.019
	Sig. (2-tailed)	0.364	0.33	0.565	0.565	0.666	0.456	0.582	0.491	0.109	.	0.911
	N	36	36	36	36	36	36	36	36	36	36	36
Cd	Pearson Correlation	-0.031	-0.067	-0.075	-0.075	0.17	0.083	-0.191	-0.252	0.243	-0.019	1
	Sig. (2-tailed)	0.856	0.696	0.663	0.663	0.322	0.629	0.264	0.138	0.154	0.911	.
	N	36	36	36	36	36	36	36	36	36	36	36

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

Correlations(Postmonsoon)												
		MO	OC	KN	PN	Fe	Mn	Zn	Ni	Pb	Cu	Cd
MO	Pearson Correlation	1	-0.252	-0.215	-0.213	0.326	-0.268	0.016	0.269	0.318	0.208	0.095
	Sig. (2-tailed)	.	0.138	0.208	0.212	0.052	0.114	0.926	0.112	0.059	0.223	0.582
	N	36	36	36	36	36	36	36	36	36	36	36
OC	Pearson Correlation	-0.252	1	0.053	0.051	-0.171	0.041	-0.03	-0.036	0.149	0.123	0.051
	Sig. (2-tailed)	0.138	.	0.76	0.767	0.317	0.811	0.864	0.835	0.387	0.474	0.768
	N	36	36	36	36	36	36	36	36	36	36	36
KN	Pearson Correlation	-0.215	0.053	1	.990(**)	-.466(**)	0.175	0.089	-0.147	-0.173	0.01	-0.257
	Sig. (2-tailed)	0.208	0.76	.	0	0.004	0.309	0.604	0.392	0.312	0.956	0.13
	N	36	36	36	36	36	36	36	36	36	36	36
PN	Pearson Correlation	-0.213	0.051	.990(**)	1	-.470(**)	0.19	0.073	-0.143	-0.162	0.02	-0.297
	Sig. (2-tailed)	0.212	0.767	0	.	0.004	0.267	0.674	0.404	0.346	0.906	0.078
	N	36	36	36	36	36	36	36	36	36	36	36
Fe	Pearson Correlation	0.326	-0.171	-.466(**)	-.470(**)	1	-0.014	-0.012	.369(*)	0.246	0.058	0.258
	Sig. (2-tailed)	0.052	0.317	0.004	0.004	.	0.938	0.943	0.027	0.149	0.738	0.129
	N	36	36	36	36	36	36	36	36	36	36	36
Mn	Pearson Correlation	-0.268	0.041	0.175	0.19	-0.014	1	-0.009	0.216	-0.084	-0.041	-0.138
	Sig. (2-tailed)	0.114	0.811	0.309	0.267	0.938	.	0.96	0.206	0.625	0.81	0.423
	N	36	36	36	36	36	36	36	36	36	36	36
Zn	Pearson Correlation	0.016	-0.03	0.089	0.073	-0.012	-0.009	1	.445(**)	-0.033	.443(**)	0.285
	Sig. (2-tailed)	0.926	0.864	0.604	0.674	0.943	0.96	.	0.007	0.851	0.007	0.092
	N	36	36	36	36	36	36	36	36	36	36	36
Ni	Pearson Correlation	0.269	-0.036	-0.147	-0.143	.369(*)	0.216	.445(**)	1	.470(**)	.509(**)	0.143
	Sig. (2-tailed)	0.112	0.835	0.392	0.404	0.027	0.206	0.007	.	0.004	0.002	0.405
	N	36	36	36	36	36	36	36	36	36	36	36
Pb	Pearson Correlation	0.318	0.149	-0.173	-0.162	0.246	-0.084	-0.033	.470(**)	1	.366(*)	0.056
	Sig. (2-tailed)	0.059	0.387	0.312	0.346	0.149	0.625	0.851	0.004	.	0.028	0.745
	N	36	36	36	36	36	36	36	36	36	36	36
Cu	Pearson Correlation	0.208	0.123	0.01	0.02	0.058	-0.041	.443(**)	.509(**)	.366(*)	1	0.102
	Sig. (2-tailed)	0.223	0.474	0.956	0.906	0.738	0.81	0.007	0.002	0.028	.	0.553
	N	36	36	36	36	36	36	36	36	36	36	36
Cd	Pearson Correlation	0.095	0.051	-0.257	-0.297	0.258	-0.138	0.285	0.143	0.056	0.102	1
	Sig. (2-tailed)	0.582	0.768	0.13	0.078	0.129	0.423	0.092	0.405	0.745	0.553	.
	N	36	36	36	36	36	36	36	36	36	36	36

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

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

Correlations (Station 1)

		MO	OC	KN	PN	Fe	Mn	Zn	Ni	Pb	Cu	Cd
MO	Pearson Correlation	1	-0.28	-.603(**)	-.603(**)	0.177	-0.36	-.402(*)	-0.321	-.414(*)	0.05	-0.055
	Sig. (2-talled)	.	0.157	0.001	0.001	0.378	0.065	0.037	0.103	0.032	0.805	0.785
	N	27	27	27	27	27	27	27	27	27	27	27
OC	Pearson Correlation	-0.28	1	0.359	0.359	-0.128	0.015	0.011	-0.197	0.109	0.094	0.076
	Sig. (2-tailed)	0.157	.	0.066	0.066	0.525	0.94	0.956	0.325	0.587	0.642	0.705
	N	27	27	27	27	27	27	27	27	27	27	27
KN	Pearson Correlation	-.603(**)	0.359	1	1.000(**)	-0.172	.403(*)	0.317	-0.02	0.167	-.404(*)	-0.303
	Sig. (2-tailed)	0.001	0.066	.	.	0.391	0.037	0.108	0.922	0.404	0.037	0.125
	N	27	27	27	27	27	27	27	27	27	27	27
PN	Pearson Correlation	-.603(**)	0.359	1.000(**)	1	-0.172	.403(*)	0.317	-0.02	0.167	-.404(*)	-0.303
	Sig. (2-tailed)	0.001	0.066	.	.	0.391	0.037	0.108	0.922	0.404	0.037	0.125
	N	27	27	27	27	27	27	27	27	27	27	27
Fe	Pearson Correlation	0.177	-0.128	-0.172	-0.172	1	0.127	-0.06	0.113	0.147	0.051	-0.048
	Sig. (2-tailed)	0.378	0.525	0.391	0.391	.	0.529	0.767	0.576	0.465	0.799	0.813
	N	27	27	27	27	27	27	27	27	27	27	27
Mn	Pearson Correlation	-0.36	0.015	.403(*)	.403(*)	0.127	1	.381(*)	0.344	-0.019	-0.229	-0.14
	Sig. (2-tailed)	0.065	0.94	0.037	0.037	0.529	.	0.05	0.079	0.924	0.251	0.487
	N	27	27	27	27	27	27	27	27	27	27	27
Zn	Pearson Correlation	-.402(*)	0.011	0.317	0.317	-0.06	.381(*)	1	.435(*)	-0.129	0.019	-0.236
	Sig. (2-tailed)	0.037	0.956	0.108	0.108	0.767	0.05	.	0.023	0.521	0.926	0.237
	N	27	27	27	27	27	27	27	27	27	27	27
Nl	Pearson Correlation	-0.321	-0.197	-0.02	-0.02	0.113	0.344	.435(*)	1	-0.028	0.192	0.308
	Sig. (2-tailed)	0.103	0.325	0.922	0.922	0.576	0.079	0.023	.	0.89	0.338	0.118
	N	27	27	27	27	27	27	27	27	27	27	27
Pb	Pearson Correlation	-.414(*)	0.109	0.167	0.167	0.147	-0.019	-0.129	-0.028	1	-0.07	0.331
	Sig. (2-tailed)	0.032	0.587	0.404	0.404	0.465	0.924	0.521	0.89	.	0.728	0.092
	N	27	27	27	27	27	27	27	27	27	27	27
Cu	Pearson Correlation	0.05	0.094	-.404(*)	-.404(*)	0.051	-0.229	0.019	0.192	-0.07	1	.445(*)
	Sig. (2-tailed)	0.805	0.642	0.037	0.037	0.799	0.251	0.926	0.338	0.728	.	0.02
	N	27	27	27	27	27	27	27	27	27	27	27
Cd	Pearson Correlation	-0.055	0.076	-0.303	-0.303	-0.048	-0.14	-0.236	0.308	0.331	.445(*)	1
	Sig. (2-tailed)	0.785	0.705	0.125	0.125	0.813	0.487	0.237	0.118	0.092	0.02	.
	N	27	27	27	27	27	27	27	27	27	27	27

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

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

Correlations (Station 2)												
		MO	Oc	KN	PN	Fe	Mn	Zn	Ni	Pb	Cu	Cd
MO	Pearson Correlation	1	-0.16	-0.351	-0.351	0.317	-0.269	0.076	0.223	0.369	0.135	.400(*)
	Sig. (2-tailed)	.	0.426	0.073	0.073	0.107	0.175	0.707	0.264	0.058	0.503	0.039
	N	27	27	27	27	27	27	27	27	27	27	27
OC	Pearson Correlation	-0.16	1	-0.124	-0.124	-0.26	-0.359	0.088	0.305	-0.185	-0.207	-0.251
	Sig. (2-tailed)	0.426	.	0.537	0.537	0.189	0.066	0.664	0.122	0.355	0.3	0.206
	N	27	27	27	27	27	27	27	27	27	27	27
KN	Pearson Correlation	-0.351	-0.124	1	1.000(**)	-0.262	.504(**)	0.092	-0.232	-.427(*)	0.021	-0.273
	Sig. (2-tailed)	0.073	0.537	.	0	0.187	0.007	0.648	0.244	0.026	0.916	0.168
	N	27	27	27	27	27	27	27	27	27	27	27
PN	Pearson Correlation	-0.351	-0.124	1.000(**)	1	-0.262	.504(**)	0.092	-0.232	-.427(*)	0.021	-0.273
	Sig. (2-tailed)	0.073	0.537	0	.	0.187	0.007	0.648	0.244	0.026	0.916	0.168
	N	27	27	27	27	27	27	27	27	27	27	27
Fe	Pearson Correlation	0.317	-0.26	-0.262	-0.262	1	-0.042	-0.114	-0.034	0.016	-0.067	.534(**)
	Sig. (2-tailed)	0.107	0.189	0.187	0.187	.	0.837	0.572	0.865	0.937	0.741	0.004
	N	27	27	27	27	27	27	27	27	27	27	27
Mn	Pearson Correlation	-0.269	-0.359	.504(**)	.504(**)	-0.042	1	-0.002	-0.283	-0.031	0.028	-0.101
	Sig. (2-tailed)	0.175	0.066	0.007	0.007	0.837	.	0.994	0.153	0.88	0.891	0.615
	N	27	27	27	27	27	27	27	27	27	27	27
Zn	Pearson Correlation	0.076	0.088	0.092	0.092	-0.114	-0.002	1	0.296	-0.033	0.139	-0.128
	Sig. (2-tailed)	0.707	0.664	0.648	0.648	0.572	0.994	.	0.134	0.87	0.489	0.524
	N	27	27	27	27	27	27	27	27	27	27	27
Nl	Pearson Correlation	0.223	0.305	-0.232	-0.232	-0.034	-0.283	0.296	1	0.099	-0.07	0.003
	Sig. (2-tailed)	0.264	0.122	0.244	0.244	0.865	0.153	0.134	.	0.624	0.727	0.987
	N	27	27	27	27	27	27	27	27	27	27	27
Pb	Pearson Correlation	0.369	-0.185	-.427(*)	-.427(*)	0.016	-0.031	-0.033	0.099	1	-0.031	0.256
	Sig. (2-tailed)	0.058	0.355	0.026	0.026	0.937	0.88	0.87	0.624	.	0.879	0.197
	N	27	27	27	27	27	27	27	27	27	27	27
Cu	Pearson Correlation	0.135	-0.207	0.021	0.021	-0.067	0.028	0.139	-0.07	-0.031	1	0.126
	Sig. (2-tailed)	0.503	0.3	0.916	0.916	0.741	0.891	0.489	0.727	0.879	.	0.531
	N	27	27	27	27	27	27	27	27	27	27	27
Cd	Pearson Correlation	.400(*)	-0.251	-0.273	-0.273	.534(**)	-0.101	-0.128	0.003	0.256	0.126	1
	Sig. (2-tailed)	0.039	0.206	0.168	0.168	0.004	0.615	0.524	0.987	0.197	0.531	.
	N	27	27	27	27	27	27	27	27	27	27	27
* Correlation is significant at the 0.05 level (2-tailed).												
** Correlation is significant at the 0.01 level (2-tailed).												

Correlations (Station 3)

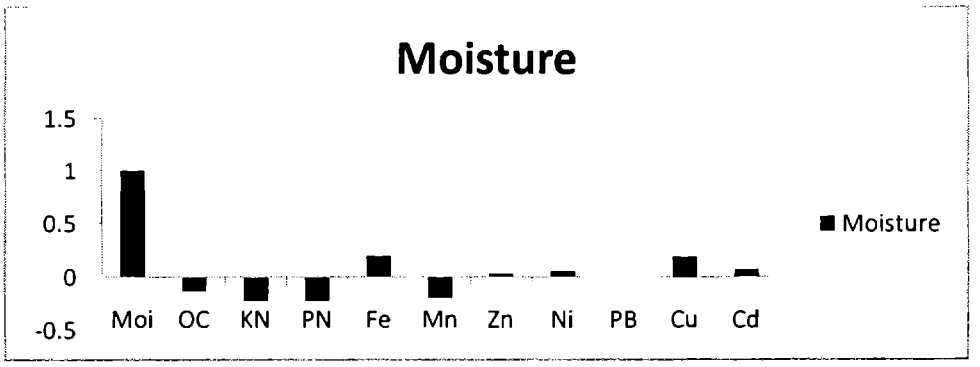
		MO	OC	KN	PN	Fe	Mn	Zn	Ni	Pb	Cu	Cd
MO	Pearson Correlation	1	-0.055	0.35	0.357	0.048	-0.258	-0.177	0.339	0.163	0.342	0.017
	Sig. (2-tailed)	.	0.786	0.073	0.067	0.81	0.194	0.378	0.083	0.418	0.081	0.934
	N	27	27	27	27	27	27	27	27	27	27	27
OC	Pearson Correlation	-0.055	1	-0.041	-0.032	-0.055	0.165	-0.088	0.228	.439(*)	0.199	0.164
	Sig. (2-tailed)	0.786	.	0.838	0.873	0.787	0.411	0.663	0.253	0.022	0.319	0.415
	N	27	27	27	27	27	27	27	27	27	27	27
KN	Pearson Correlation	0.35	-0.041	1	.989(**)	0.048	-0.327	0.169	0.25	0.264	0.18	-0.147
	Sig. (2-tailed)	0.073	0.838	.	0	0.811	0.096	0.401	0.209	0.183	0.369	0.463
	N	27	27	27	27	27	27	27	27	27	27	27
PN	Pearson Correlation	0.357	-0.032	.989(**)	1	0.053	-0.328	0.165	0.259	0.293	0.196	-0.165
	Sig. (2-tailed)	0.067	0.873	0	.	0.794	0.095	0.412	0.191	0.138	0.327	0.41
	N	27	27	27	27	27	27	27	27	27	27	27
Fe	Pearson Correlation	0.048	-0.055	0.048	0.053	1	-0.14	0.031	0.377	0.348	0.332	.499(**)
	Sig. (2-tailed)	0.81	0.787	0.811	0.794	.	0.488	0.878	0.053	0.075	0.091	0.008
	N	27	27	27	27	27	27	27	27	27	27	27
Mn	Pearson Correlation	-0.258	0.165	-0.327	-0.328	-0.14	1	-0.116	-0.256	-0.107	-0.124	-0.191
	Sig. (2-tailed)	0.194	0.411	0.096	0.095	0.488	.	0.565	0.198	0.596	0.537	0.339
	N	27	27	27	27	27	27	27	27	27	27	27
Zn	Pearson Correlation	-0.177	-0.088	0.169	0.165	0.031	-0.116	1	0.183	.412(*)	0.154	0.079
	Sig. (2-tailed)	0.378	0.663	0.401	0.412	0.878	0.565	.	0.361	0.033	0.443	0.694
	N	27	27	27	27	27	27	27	27	27	27	27
Ni	Pearson Correlation	0.339	0.228	0.25	0.259	0.377	-0.256	0.183	1	0.328	.716(**)	0.203
	Sig. (2-tailed)	0.083	0.253	0.209	0.191	0.053	0.198	0.361	.	0.094	0	0.31
	N	27	27	27	27	27	27	27	27	27	27	27
Pb	Pearson Correlation	0.163	.439(*)	0.264	0.293	0.348	-0.107	.412(*)	0.328	1	.438(*)	0.337
	Sig. (2-tailed)	0.418	0.022	0.183	0.138	0.075	0.596	0.033	0.094	.	0.022	0.086
	N	27	27	27	27	27	27	27	27	27	27	27
Cu	Pearson Correlation	0.342	0.199	0.18	0.196	0.332	-0.124	0.154	.716(**)	.438(*)	1	0.054
	Sig. (2-tailed)	0.081	0.319	0.369	0.327	0.091	0.537	0.443	0	0.022	.	0.788
	N	27	27	27	27	27	27	27	27	27	27	27
Cd	Pearson Correlation	0.017	0.164	-0.147	-0.165	.499(**)	-0.191	0.079	0.203	0.337	0.054	1
	Sig. (2-tailed)	0.934	0.415	0.463	0.41	0.008	0.339	0.694	0.31	0.086	0.788	.
	N	27	27	27	27	27	27	27	27	27	27	27

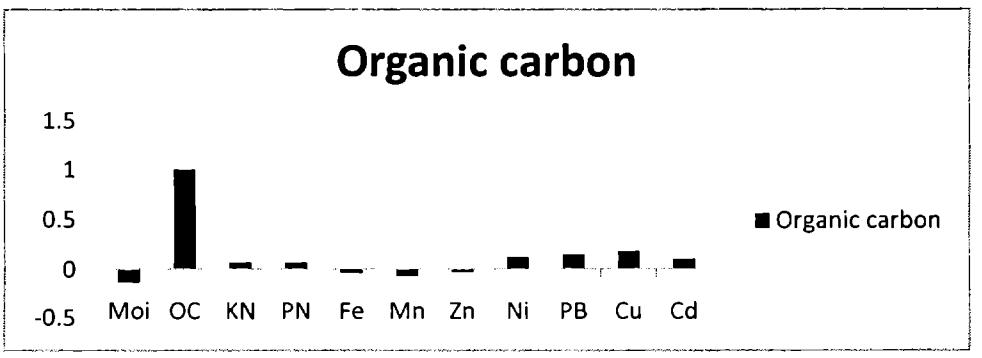
* Correlation is significant at the 0.05 level (2-tailed).

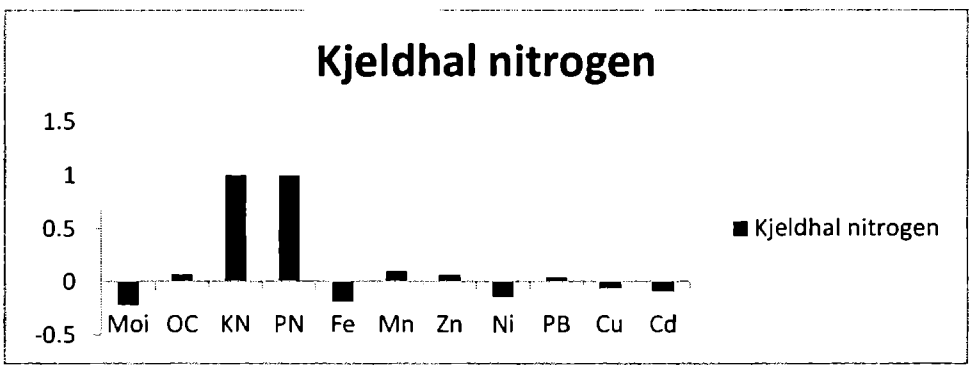
** Correlation is significant at the 0.01 level (2-tailed).

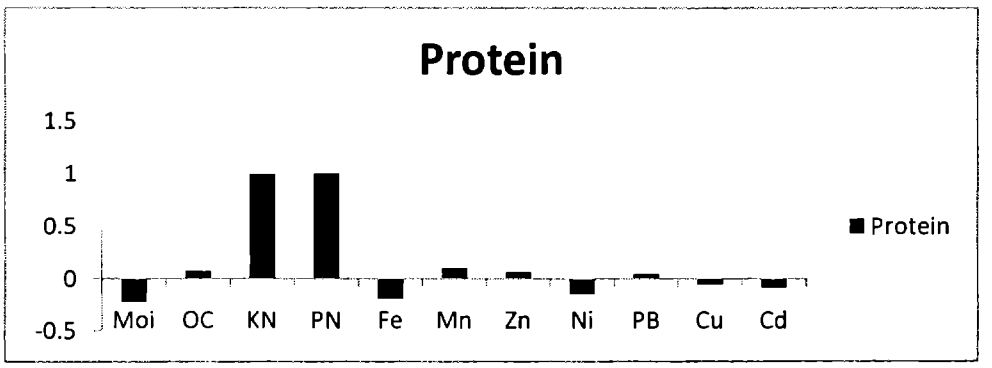
Correlations (Station 4)												
		MO	OC	KN	PN	Fe	Mn	Zn	Nl	Pb	Cu	Cd
OC	Pearson Correlation	1	-0.19	-0.351	-0.351	0.338	0.021	0.183	0.153	0.001	0.163	0.134
	Sig. (2-tailed)	.	0.343	0.072	0.072	0.084	0.916	0.36	0.447	0.995	0.418	0.505
	N	27	27	27	27	27	27	27	27	27	27	27
KN	Pearson Correlation	-0.19	1	0.254	0.254	-0.074	-0.146	0.033	-0.192	0.16	0.346	0.31
	Sig. (2-tailed)	0.343	.	0.201	0.201	0.714	0.467	0.868	0.337	0.426	0.077	0.116
	N	27	27	27	27	27	27	27	27	27	27	27
PN	Pearson Correlation	-0.351	0.254	1	1.000(**)	-.384(*)	-0.206	-0.056	-0.217	-0.119	-0.23	0.028
	Sig. (2-tailed)	0.072	0.201	.	.	0.048	0.302	0.781	0.277	0.556	0.249	0.89
	N	27	27	27	27	27	27	27	27	27	27	27
	Pearson Correlation	-0.351	0.254	1.000(**)	1	-.384(*)	-0.206	-0.056	-0.217	-0.119	-0.23	0.028
	Sig. (2-tailed)	0.072	0.201	.	.	0.048	0.302	0.781	0.277	0.556	0.249	0.89
	N	27	27	27	27	27	27	27	27	27	27	27
Fe	Pearson Correlation	0.338	-0.074	-.384(*)	-.384(*)	1	0.184	-0.057	0.314	0.241	-0.028	0.129
	Sig. (2-tailed)	0.084	0.714	0.048	0.048	.	0.357	0.778	0.11	0.226	0.89	0.522
	N	27	27	27	27	27	27	27	27	27	27	27
Mn	Pearson Correlation	0.021	-0.146	-0.206	-0.206	0.184	1	-0.082	0.324	-0.326	-0.119	-0.13
	Sig. (2-tailed)	0.916	0.467	0.302	0.302	0.357	.	0.685	0.1	0.097	0.554	0.518
	N	27	27	27	27	27	27	27	27	27	27	27
Zn	Pearson Correlation	0.183	0.033	-0.056	-0.056	-0.057	-0.082	1	-0.135	0.031	-0.102	-0.143
	Sig. (2-tailed)	0.36	0.868	0.781	0.781	0.778	0.685	.	0.503	0.878	0.611	0.478
	N	27	27	27	27	27	27	27	27	27	27	27
Ni	Pearson Correlation	0.153	-0.192	-0.217	-0.217	0.314	0.324	-0.135	1	0.283	0.137	0.114
	Sig. (2-tailed)	0.447	0.337	0.277	0.277	0.11	0.1	0.503	.	0.153	0.496	0.572
	N	27	27	27	27	27	27	27	27	27	27	27
Pb	Pearson Correlation	0.001	0.16	-0.119	-0.119	0.241	-0.326	0.031	0.283	1	0.224	0.147
	Sig. (2-tailed)	0.995	0.426	0.556	0.556	0.226	0.097	0.878	0.153	.	0.261	0.465
	N	27	27	27	27	27	27	27	27	27	27	27
Cu	Pearson Correlation	0.163	0.346	-0.23	-0.23	-0.028	-0.119	-0.102	0.137	0.224	1	0.149
	Sig. (2-tailed)	0.418	0.077	0.249	0.249	0.89	0.554	0.611	0.496	0.261	.	0.458
	N	27	27	27	27	27	27	27	27	27	27	27
Cd	Pearson Correlation	0.134	0.31	0.028	0.028	0.129	-0.13	-0.143	0.114	0.147	0.149	1
	Sig. (2-tailed)	0.505	0.116	0.89	0.89	0.522	0.518	0.478	0.572	0.465	0.458	.
	N	27	27	27	27	27	27	27	27	27	27	27
** Correlation is significant at the 0.01 level (2-tailed).												
* Correlation is significant at the 0.05 level (2-tailed).												

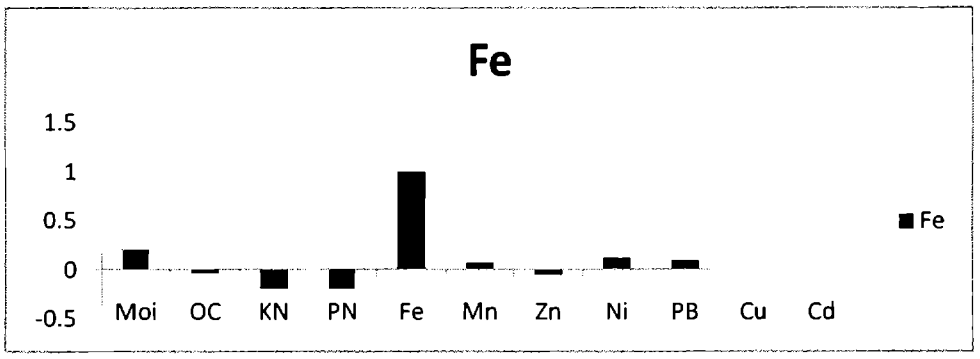
Graphs of Total Correlation - Plant Parts







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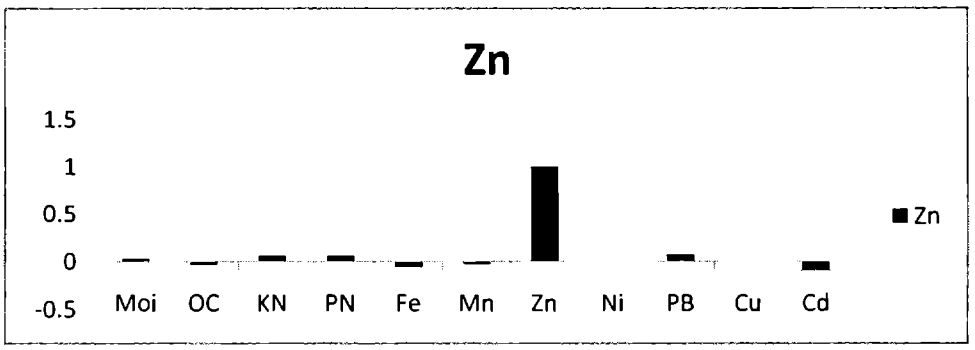
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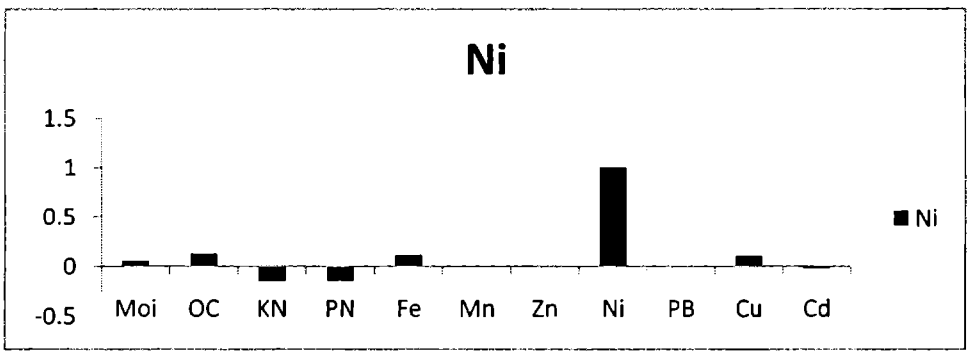
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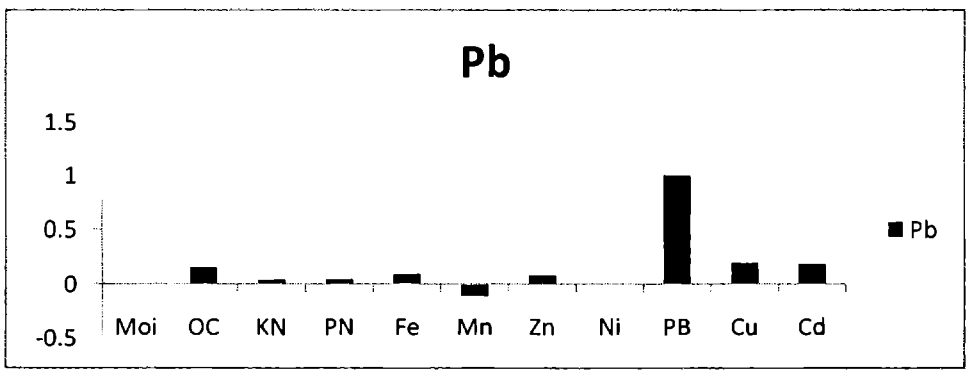
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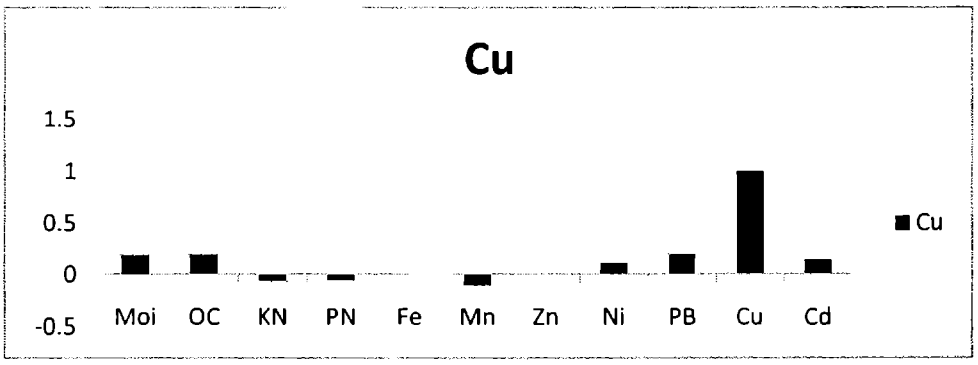
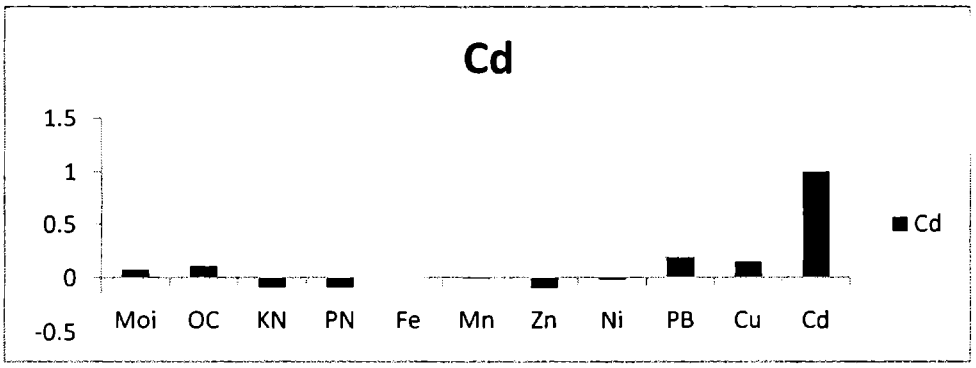
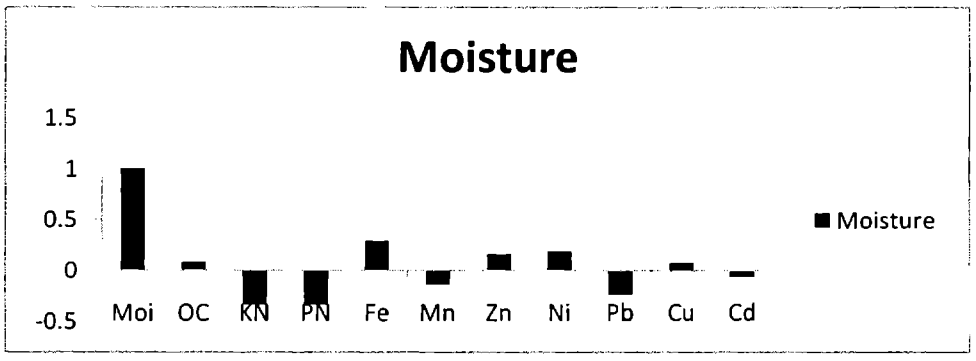
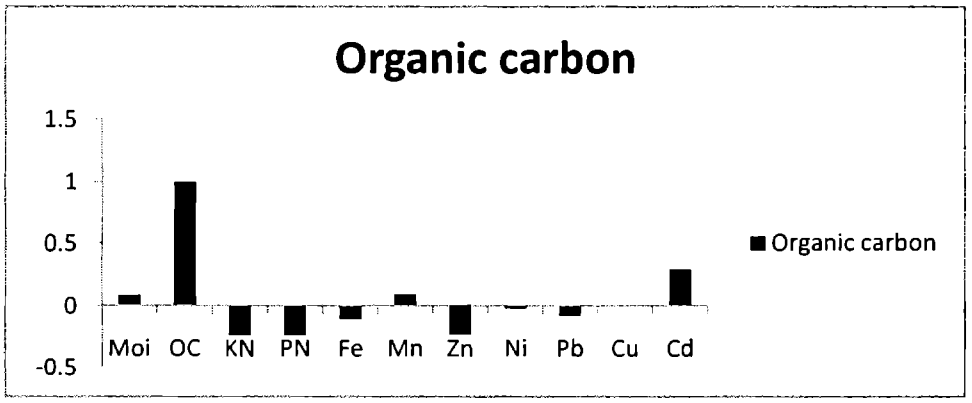


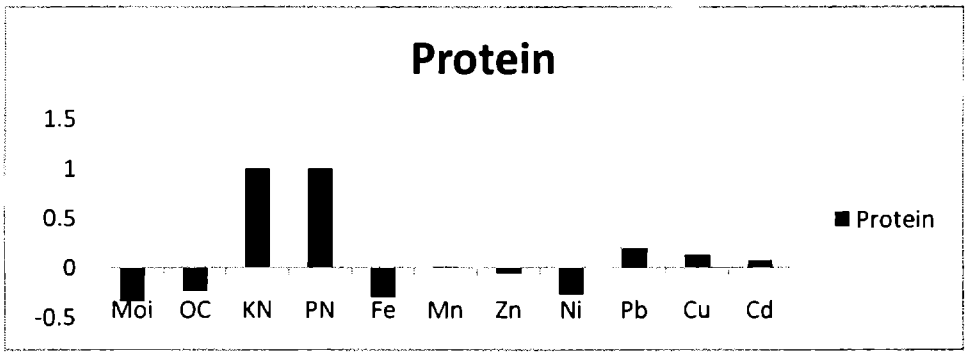


B. Seasonal

Pre Monsoon



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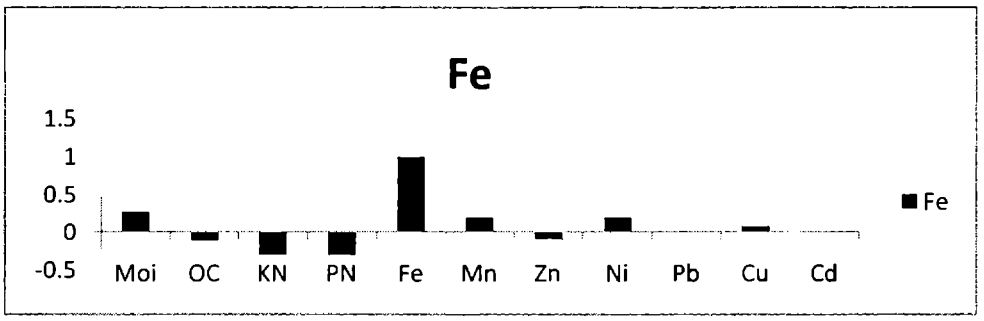
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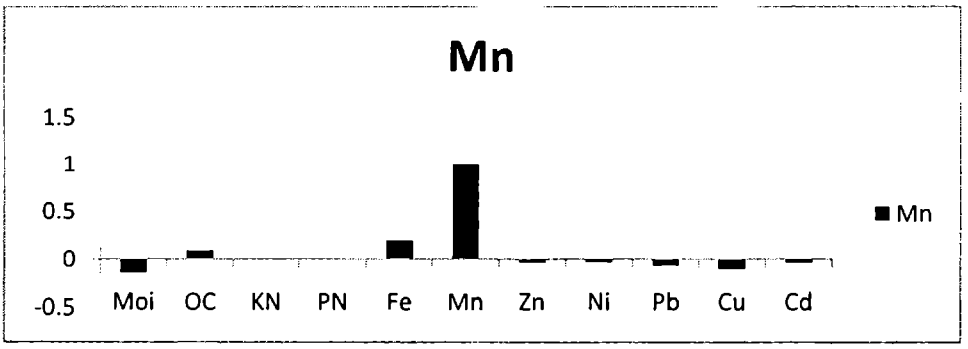
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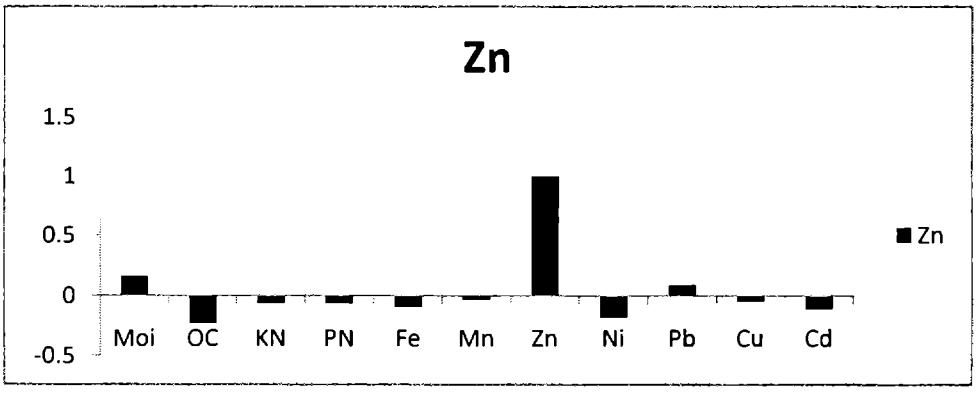
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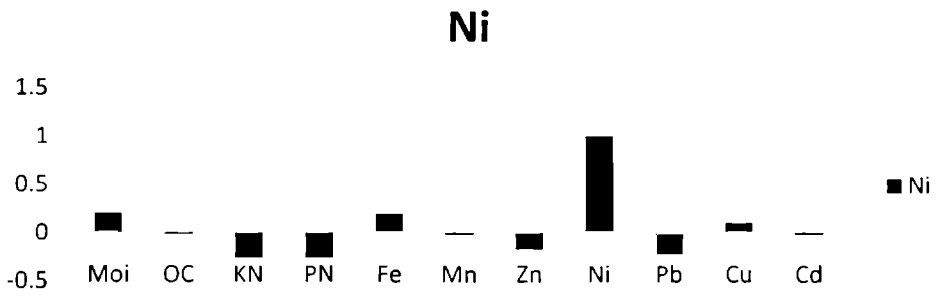
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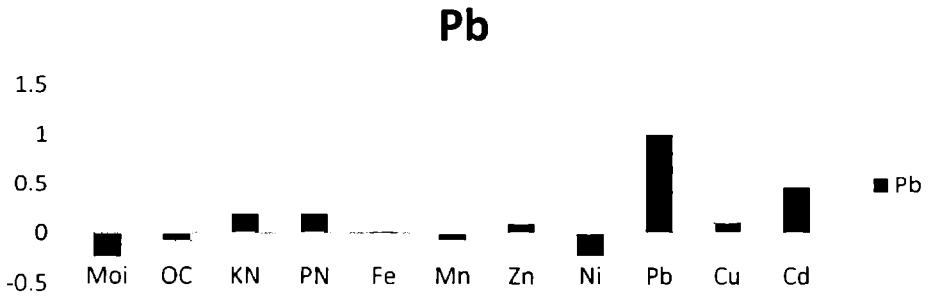
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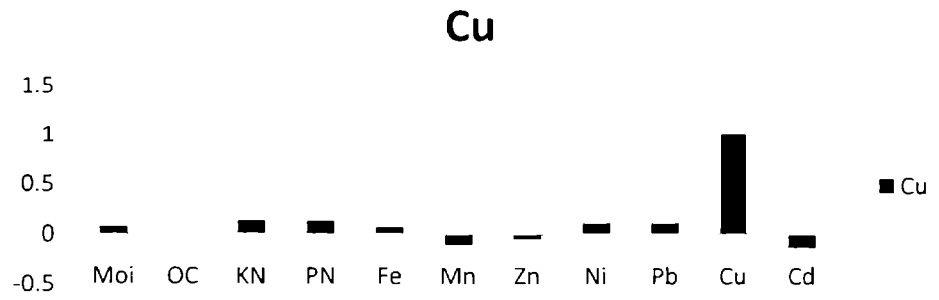
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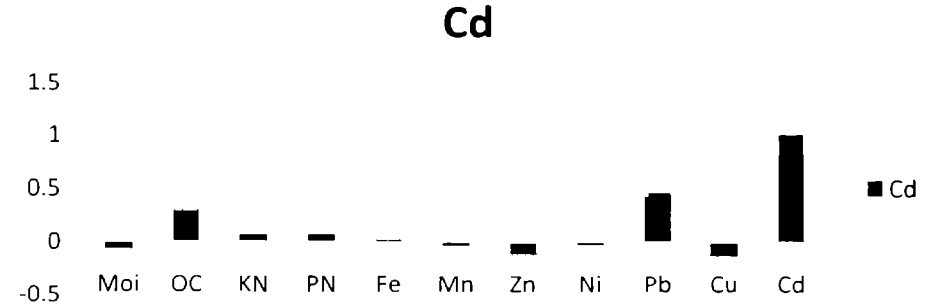
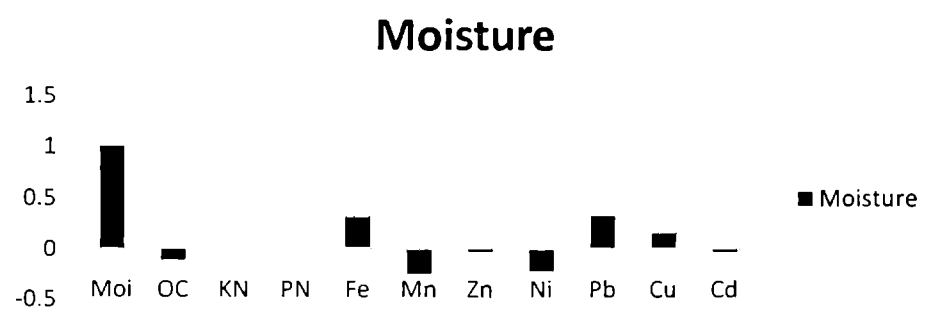
Cu


Cd
1.5
1
0.5
0
-0.5
Moi
OC
KN
PN
Fe
Mn
Zn
Ni
Pb
Cu
Cd
Cd

Monsoon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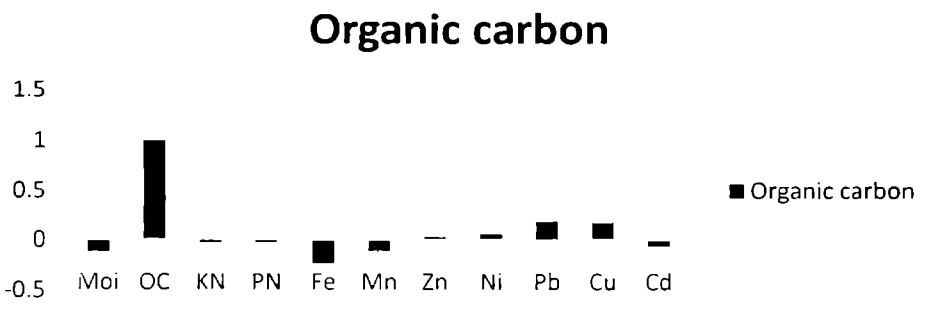
0.5
0
-0.5
Moi OC KN PN Fe Mn Zn Ni Pb Cu Cd
Moisture


Organic carbon
1.5
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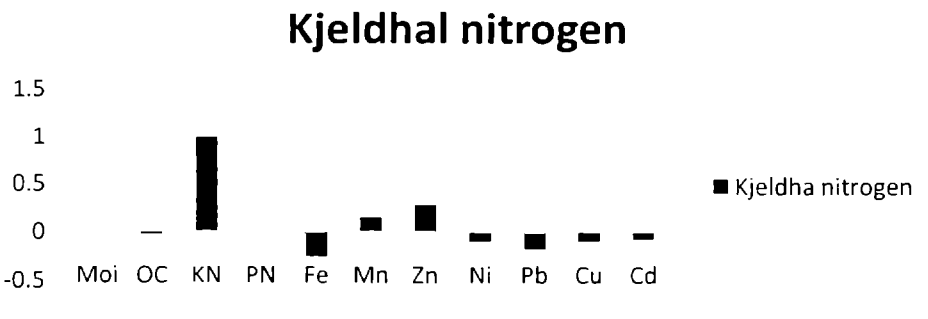
0.5
0
-0.5
Moi OC KN PN Fe Mn Zn Ni Pb Cu Cd
Organic carbon


Kjeldhal nitrogen
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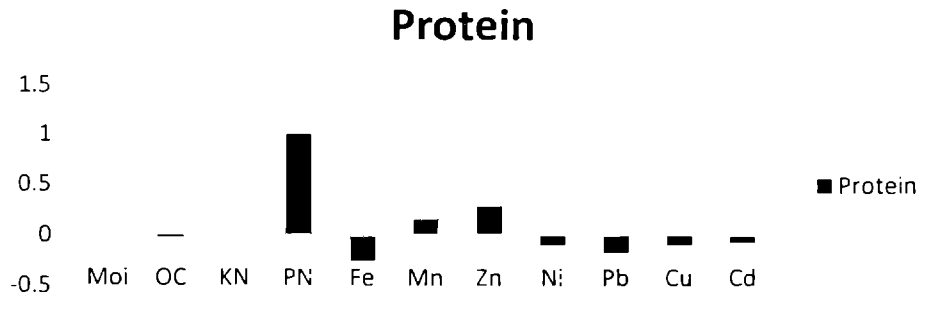
0
-0.5
Moi OC KN PN Fe Mn Zn Ni Pb Cu Cd
Kjeldha nitrogen


Protein
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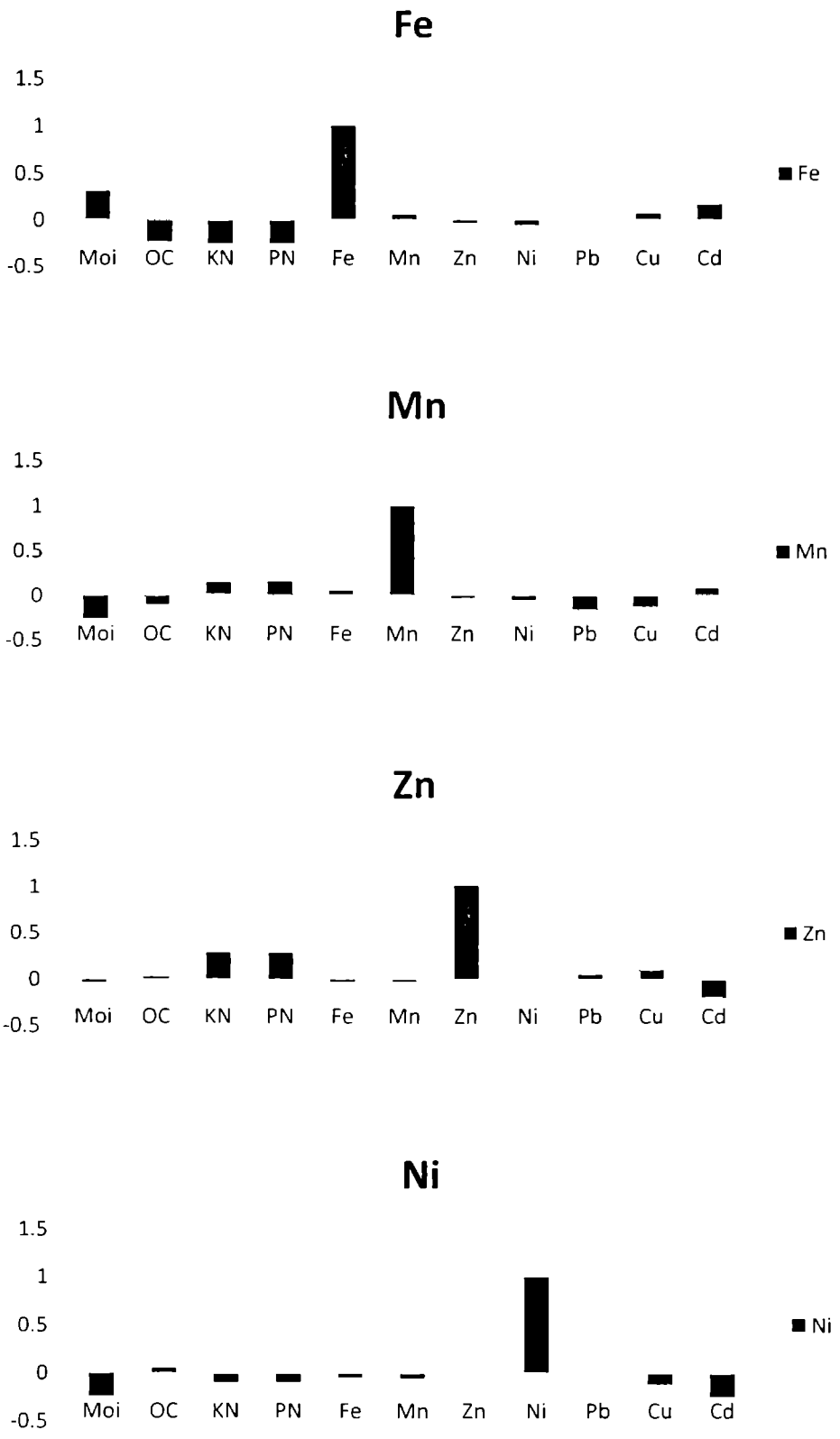
0.5
0
-0.5
Moi OC KN PN Fe Mn Zn Ni Pb Cu Cd
Protein


Fe
1.5
1
0.5
0
-0.5
Moi
OC
KN
PN
Fe
Mn
Zn
Ni
Pb
Cu
Cd
Fe
Mn
1.5
1
0.5
0
-0.5
Moi
OC
KN
PN
Fe
Mn
Zn
Ni
Pb
Cu
Cd
Mn
Zn
1.5
1
0.5
0
-0.5
Moi
OC
KN
PN
Fe
Mn
Zn
Ni
Pb
Cu
Cd
Zn
Ni
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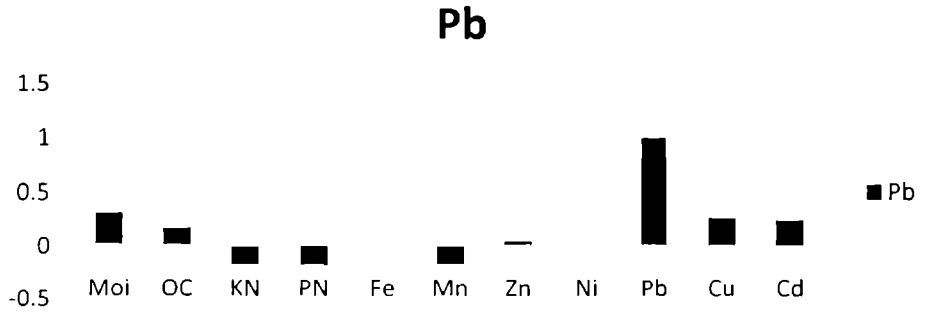
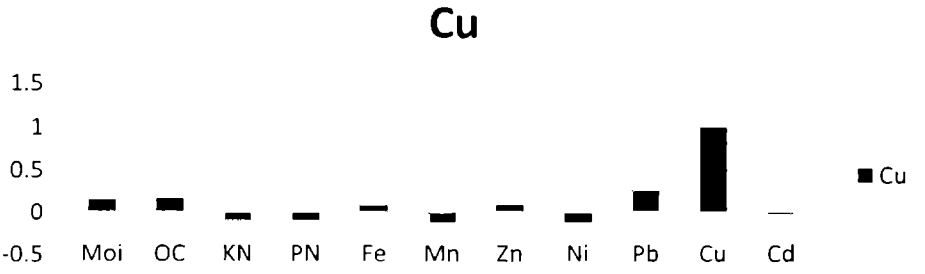
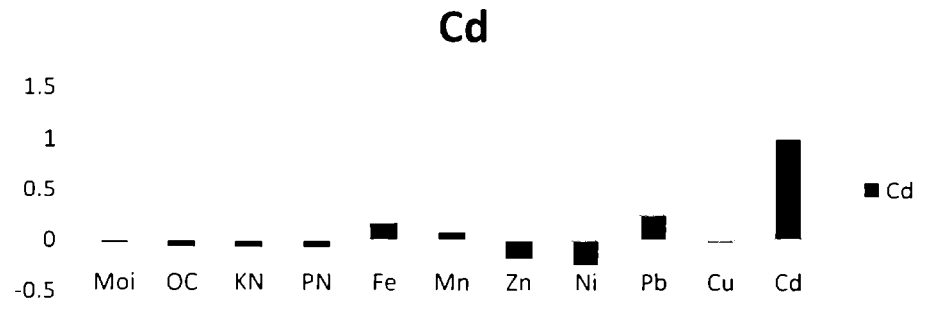
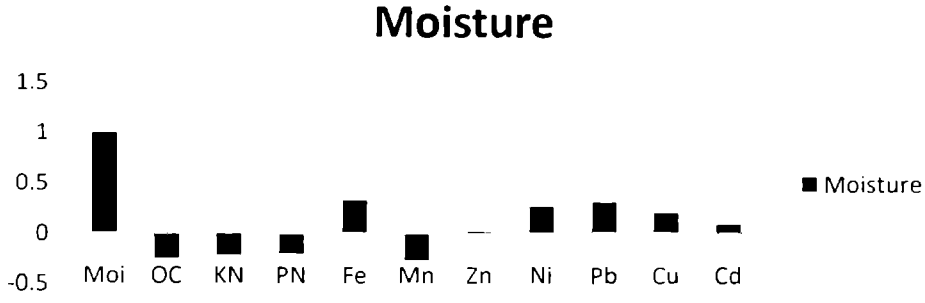
Fe
Mn
Zn
Ni
Pb
Cu
Cd
Ni

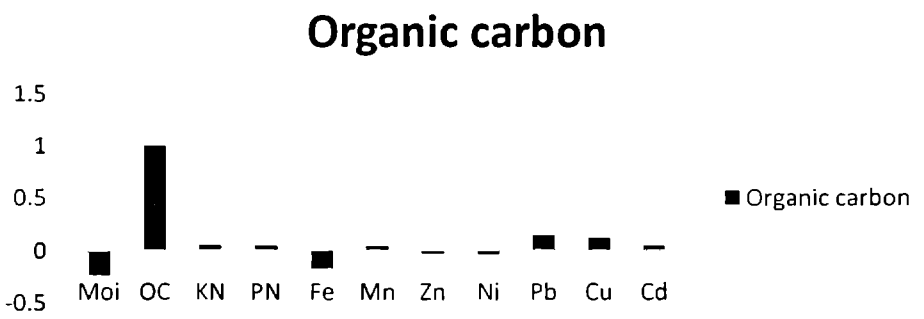






Post Monsoon




Organic carbon
1.5
1
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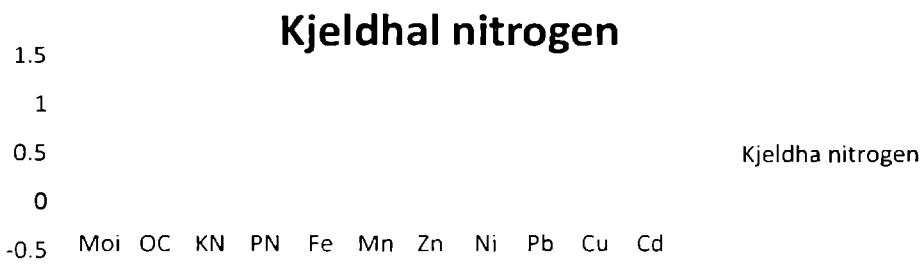
0
-0.5
Moi
OC
KN
PN
Fe
Mn
Zn
Ni
Pb
Cu
Cd
Organic carbon


Kjeldhal nitrogen
1.5
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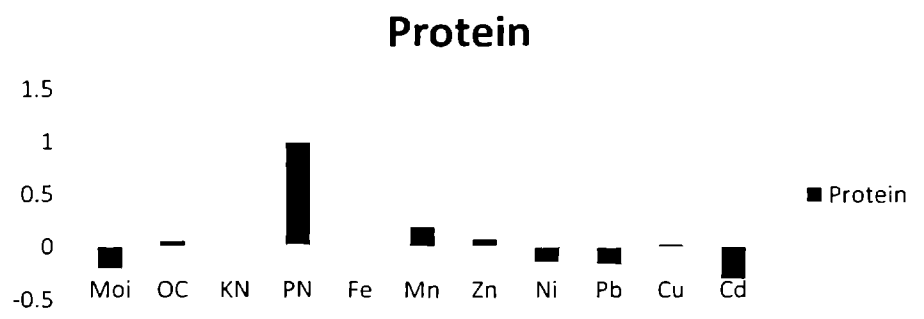
-0.5
Moi
OC
KN
PN
Fe
Mn
Zn
Ni
Pb
Cu
Cd
Kjeldha nitrogen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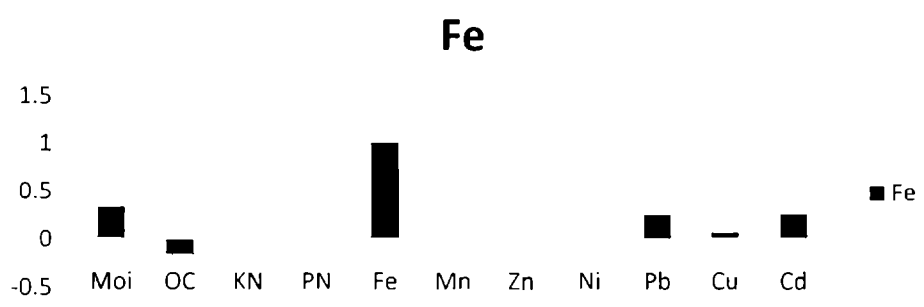
Moi
OC
KN
PN
Fe
Mn
Zn
Ni
Pb
Cu
Cd
Protein


Fe
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0
-0.5
Moi
OC
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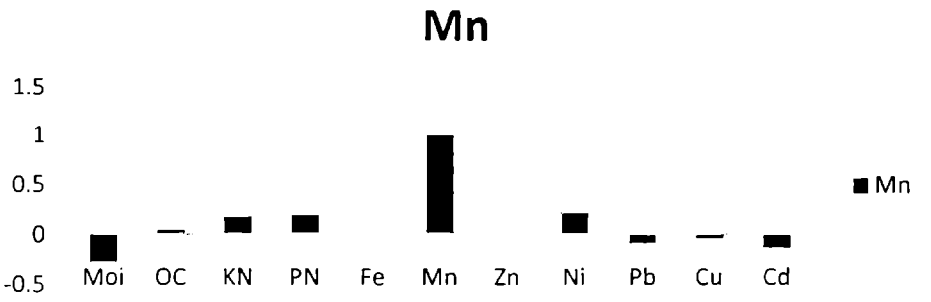
PN
Fe
Mn
Zn
Ni
Pb
Cu
Cd
Fe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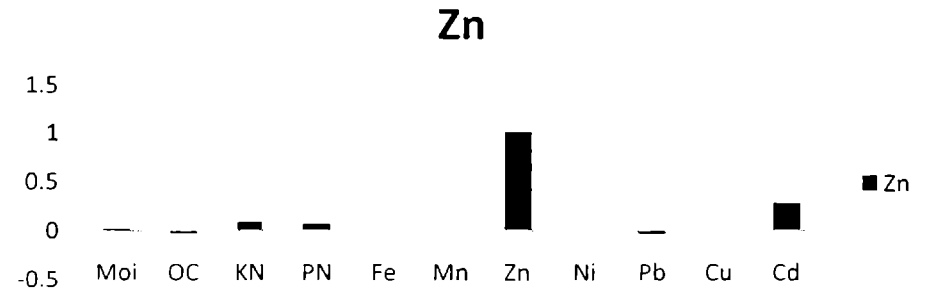
-0.5
Moi
OC
KN
PN
Fe
Mn
Zn
Ni
Pb
Cu
Cd
Mn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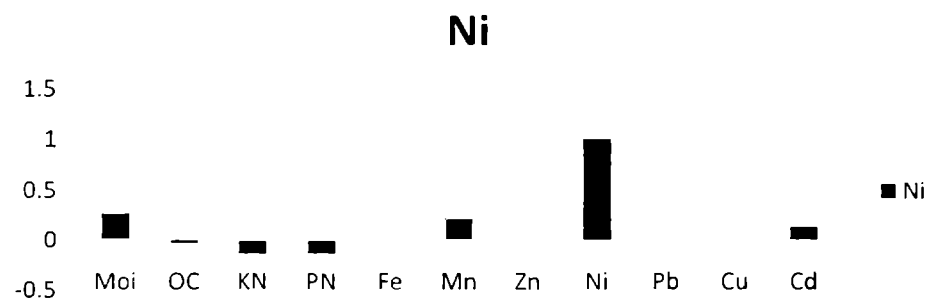
OC
KN
PN
Fe
Mn
Zn
Ni
Pb
Cu
Cd
Zn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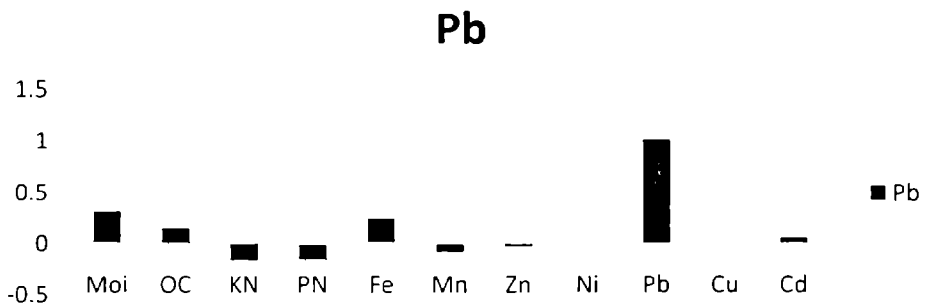
Moi
OC
KN
PN
Fe
Mn
Zn
Ni
Pb
Cu
Cd
Ni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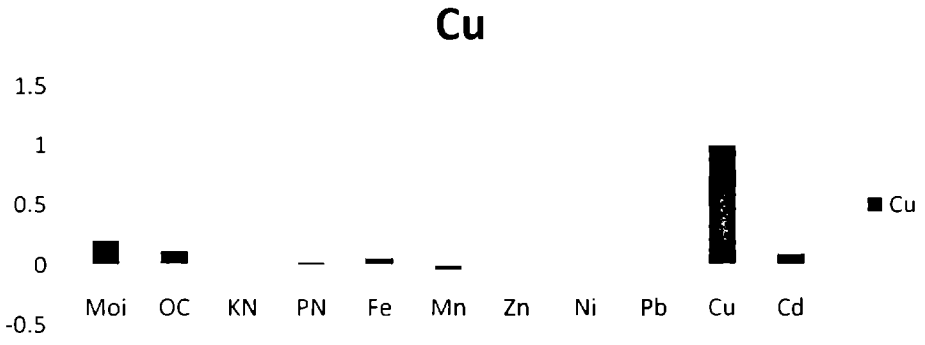
OC
KN
PN
Fe
Mn
Zn
Ni
Pb
Cu
Cd
Pb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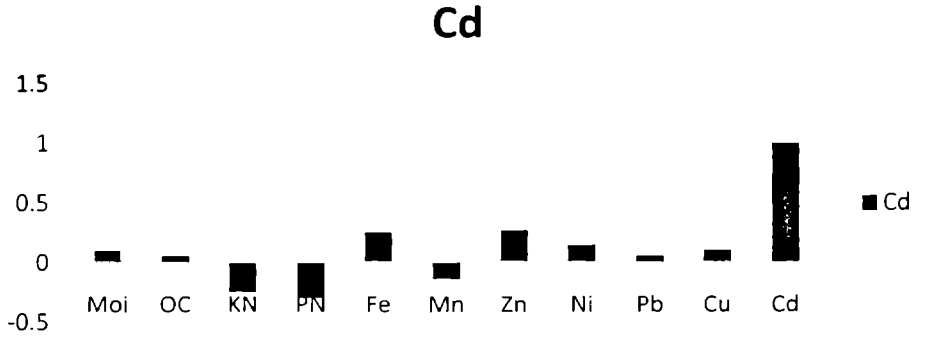
OC
KN
PN
Fe
Mn
Zn
Ni
Pb
Cu
Cd
Cu


Cd
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0.5
0
-0.5
Moi
OC
KN
PN
Fe
Mn
Zn
Ni
Pb
Cu
Cd
Cd