Biomarker Geochemistry of Core Sediments in the Mangrove Ecosystems along Northern Kerala Coast

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Certificate

*This is to certify that the thesis entitled "**Biomarker Geochemistry of Core Sediments in the Mangrove Ecosystems along Northern Kerala Coast**" is an authentic record of the research work carried out by Ms. Manju M.N, under my supervision and guidance at the Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, Kochi-682016, in partial fulfilment of the requirements for Ph.D degree of Cochin University of Science and Technology and no part of this has been presented before for any degree in any University. I further certify that all the relevant corrections and modifications suggested by the audience during the Pre-synopsis Seminar and recommended by the Doctoral Committee of Ms. Manju M. N has been incorporated in the thesis.*

Dr. N. Chandramohanakumar
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Declaration

I hereby declare that the thesis entitled "**Biomarker Geochemistry of Core Sediments in the Mangrove Ecosystems along Northern Kerala Coast"** is an authentic record of the research work carried out by me under the guidance and supervision of Dr. N. Chandramohanakumar, Professor, Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, and no part of this has previously formed the basis of the award of any degree, diploma, associateship, fellowship or any other similar title or recognition from any University/Institution.

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Preface

Mangroves are diverse group of trees, palms, shrubs, and ferns that share a common ability to live in waterlogged saline soils exposed to regular flooding, and are highly specialised plants which have developed unusual adaptations to the unique environmental conditions. They are sites of accumulation and preservation of both allochthonous and autochthonous organic matter owing to their strategic loction at the interface between land and sea and prevailing reducing environment. They are among the most productive ecosystems and are efficient carbon sinks with most of the carbon stored in sediments.Mangrove ecosystems play a significant role in global carbon cycle and hence the knowledge on the processes controlling the delivery of organic matter to coastal sediments, and how these signatures are preserved in the sediment is a prerequisite for the understanding of biogeochemical cycles.

The evaluation of nature and sources of organic matter can be accomplished by the determination of biochemical constituents like carbohydrates, proteins and lipids. When characterised at molecular level, lipids provide valuable information about the sources of organic matter, even though they account only small fraction of organic matter. They are useful for the paleo-environmental reconstruction because of their low reactivity, high preservation potential and high source specificity relative to other organic class of compounds. The application of recent analytical techniques has produced a wealth of useful information but has also indicated the gaps in our knowledge on cycling of organic matter in the coastal ecosystems. The quantity and quality of organic matter preserved in sediments vary depending up on the nature of material delivered to the sediment and on the depositional environment. The input from both autochthonous and allochthonous sources sharpens the complexity of biogeochemistry of mangrove ecosystem and hence bulk sedimentary parameters are not

completely successful in evaluating the sources of organic matter in mangrove sediments. An effective tool for the source characterisation of organic matter in coastal ecosystems is biomarker approach. Biomarkers are chemical "signatures" present in environmental samples whose structural information can be linked to its biological precursor. The usefulness of molecular biomarkers depends on high taxonomic specificity, potential for preservation, recalcitrant against geochemical changes, easily analysable in environmental samples and should have a limited number of well-defined sources.

The thesis entitled "Biomarker Geochemistry of Core Sediments in the Mangrove ecosystems along Northern Kerala Coast" is an attempt to characterise the sources of organic matter in the core sediments of mangrove forests providing special emphasis on lipid biomarkers such as n-alkanes and fatty acids. Core sediment samples were collected from five mangrove ecosystems along Northern Kerala coast, Southwest India. In this study, a combination of bulk geochemical parameters and different groups of molecular biomarkers has been used to define organic matter sources and thereby identifying various biogeochemical processes acting in the study region. Core sediments were used in this study because they can provide long term and continuous past historical records and act as a useful tool for the effective reconstruction of past environmental conditions.

The thesis is divided into six chapters. Chapter 1 is ***Introduction*** *and it contains general aspects of mangrove ecosystems, the aim and scope of the study. Chapter 2 is* ***Materials and methods****. This chapter deals with the nature and general geographical features of the study area. It also contains the details of the sampling and analytical methodology. Chapter 3 is* ***Geochemistry of heavy metals****, which includes the down core variations of the general sedimentary parameters,*

heavy metal distribution and contamination status. Chapter 4, ***Biogeoorganics****, covers the biochemical composition of organic matter in the core sediments to examine the quality and quantity of organic matter. Bulk sedimentary parameters such as elemental ratios and stable carbon isotope ratio are also employed for the source characterisation of organic matter. Chapter 5,* ***n-Alkanes and hopanes as biomarkers in core sediments*** *characterize the organic matter in the sediments of the mangrove ecosystems under study, to assess the possible sources in core sediments with the help of n-alkanes as biomarkers. The n- alkanes ranging from* C_{11} *to* C_{33} *were detected in the sediment samples. The hopanes were also detected in the core sediment samples. Chapter 6,* ***Fatty acids as biomarkers in core sediments*** *employs fatty acids as biomarkers to distinguish the source of organic matter in core sediments from study area. The short chain saturated fatty acids, monounsaturated fatty acids, polyunsaturated fatty acids and bacterial fatty acids were detected in the core sediment samples.* ***Summary*** *provides the conclusions in brief, the achievements and indication of the scope for future work. References are provided at the end of each chapter.*

Contents

List of Abbreviations

ACL	Average Chain Length
ANOVA	Analysis of Variance
APHA	American Public Health Association
BAFAs	Bacterial Fatty Acids
BHPs	Bacterio Hopane Polyols
BHT	Bacterio Hopane Tetrol
BPC	Bio Polymeric Carbon
BSA	Bovine Serum Albumin
CAM	Crassulacean Acid Metabolism
Chl-a	Chlorophyll a
Chl-b	Chlorophyll b
Chl-c	Chlorophyll c
CHO	Carbohydrates
CMFRI	Central Marine Fisheries Research Institute
CPI	Carbon Preference Index
DGS	Dissolved Gas Super saturation
DO	Dissolved Oxygen
EF	Enrichment Factor
ERL	Effects Range Low
ERM	Effects Range Median
FAME	Fatty Acid Methyl Ester
GC-MS	Gas Chromatography-Mass Spectrometer
HBI	Highly Branched Isoprenoid
Igeo	Geoaccumulation Index
LOM	Labile Organic Matter

LPD	Lipids
MUFAs	MonoUnsaturated Fatty Acids
PCA	Principal Component Analysis
PDB	Pee Dee Belemnite
PEL	Probable Effect Level
Phaeo	Phaeophytin
Ph	Phytane
Pr	Pristane
PRT	Proteins
PUFAs	PolyUnsaturated Fatty Acids
SCSFAs	Short Chain Saturated Fatty Acids
SLR	Short to Long chain n-alkane Ratio
SPSS	Statistical Package for Social Sciences
SQG	Sediment Quality Guidelines
TAR	Terrigenous to Aquatic Ratio
TEL	Threshold Effect Level
TN	Total Nitrogen
TOC	Total Organic Carbon
TOM	Total Organic Matter
TP	Total Phosphorous
TS	Total Sulphur

Chapter 1

INTRODUCTION

1.1 Mangrove ecosystems

Mangrove ecosystems are unique collections of plants, animals and microorganisms adapted in a fluctuating environment of tropical intertidal zone (Samanta et al., 2014). Mangrove forests have been regarded as highly productive ecosystem along most tropical coastlines. The special physiological adaptations favor them to thrive in the deoxygenated soils, variable flooding and salinity stress conditions prevailing in the coastal zone. They flourish mostly in an environment with a humidity range of 60-90% and an annual rainfall varying between 1000 and 3000mm. The richest mangrove forest ecosystems occur in tropical and sub-tropical areas (30°N and 30°S latitudes). The tidal inundation, water and soil salinity, pH, redox status, availability of anions and cations, hydrodynamics and stresses are the most important factors which control the distribution of species.

1.2 Important ecological functions of mangrove forests

Mangroves are endowed with a number of physico-chemical characteristics capable of altering the species composition and trophic structure of benthic communities (Levin et al., 2006; Alongi, 2009). Many organisms live in the mangrove forests. An interdependent relationship is established between the many kinds of living things inside mangrove forests. Plants in mangrove forest provide organic crumbs for crabs, fishes and shellfishes, and they provide food for raptors of different sizes. These ecosystems also act as sanctuaries for a variety of birds. The extensive root systems trap and stabilize huge quantities of sediments, thereby reducing siltation of waterways and estuaries and protect reefs from upstream sediment loads. These tidal forest ecosystems can limit coastal erosion and protect the coast from tropical storms and tsunamis. Mangrove ecosystems play an important role in nutrient cycling (Lacerda et al., 1993; Silva and Mozeto, 1997; Bouillon et al., 2008) and the nutrients required to maintain the high productivity of these ecosystems are met by inputs from rivers, tides and benthic activities (Jennerjahn and Ittekot, 2002). They reduce water flow and trap sediments, which can lead to enhanced densities of deposit feeding fauna (Demopoulos, 2004; Demopoulos and Smith, 2010), limit coastal erosion, and provide a buffer to tropical storms and tsunamis. They also effectively sequester nutrients (Middelburg et al., 1996; Bouillon et al., 2008), and may enhance water quality in surrounding habitats by reducing eutrophication and turbidity (Valiela and Cole, 2002; Victor et al., 2004).

Mangroves are complex ecosystems which play an imperative role in ecological balance of the nature through food chain relationship and an energy transfer processes. They supply nutrients and oxygen to animals and plants in the ecosystem with the help of photosynthesis. As mangrove forests link up

the ecosystems of the land and sea, their importance in stabilising and reserving the peripheral ecosystems is unquestionable.

1.3 Mangrove biogeochemistry

Mangrove forests serve as interface for the carbon cycle in tropical coastal environments and exert profound influence on the carbon balance of tropical coastal ecosystems (Jennerjahn and Ittekkot, 2002; Feller et al., 2003). These wetland ecosystems have been recognised as potential sources of organic matter to nearby estuarine and coastal region (Jennerjahn and Ittekkot, 2002; Wardle et al., 2004; Dittmar et al., 2006). Sedimentary organic matter constitutes a major reservoir of organic carbon in the global carbon cycle. The litter fall is the most important source of organic carbon to mangrove ecosystems (Wafar et al., 1997; Clough et al., 2000). Leaf litter from trees and subsurface root growth provide significant inputs of organic carbon to mangrove sediments (Alongi et al., 2005). Other important sources of organic carbon inputs to mangrove ecosystems consist of allochthonous riverine or marine material and autochthonous production by benthic or epiphytic algae and phytoplankton (Bouillon et al., 2004). The primary food source for aquatic organisms in the mangrove dominated estuaries occurs in the form of particulate organic matter derived chiefly from the litter fall. The decomposition of mangrove debris occurs primarily through microbial action and the leaching of water soluble compounds. It is through the decomposition process that nutrients and organic compounds such as lipids are released to adjacent estuarine waters and sediments via tidal transport. Mangrove ecosystems play a prominent role as sources of organic matter which may be transported to adjacent coastal ecosystems through the export of detritus (Robertson and Duke, 1990). These tidal forests contribute 11% of the total input of terrestrial carbon into the ocean and 15% of the total carbon

accumulating in modern marine sediments (Jennerjahn and Ittekkot, 2002). In spite of the comparatively lower area relative to other ecosystems, mangroves contribute approximately 10% of the terrestrially derived dissolved organic carbon to the global carbon budget in the ocean (Dittmar et al., 2006).

Mangrove detritus is a source of nutrients for many organisms living in the mangrove ecosystem. Litter handling by the fauna not only affects microbial carbon transformations, but also the amount of organic carbon available for export. Irrespective of the pathways of organic matter consumption and food web structure, all the organic matter that is not exported by tidal action enters the sediment where it is consumed, degraded and chemically modified. The preservation of organic matter appears to be favored by the development of anoxia which in turn aided by high accumulation rate rather than degradation by detrivores and decomposers (Killops and Killops, 2005). Organic matter preserved in sediment act as a direct indicator of environmental conditions at the time of deposition and thus is important in paleoenvironmental studies (Castañeda and Schouten, 2011).

In organic geochemistry, the key challenge is to trace the source of organic matter in a complex marine environment like mangroves (Hernes and Benner, 2003). The unravelling of long and continuous past historical records and the reconstruction of past environmental conditions can be achieved through the study of marine core sediments. These reconstructions are based on the measurement of physical or chemical properties of the sediments, which varies with the changes in environmental conditions. Labile compounds are less likely to be preserved for a long period than a refractory one's since these undergo several hundred years of oxygen exposure and hence allochthonous component of such labile compound would be smaller than a more refractory compound at a given site, assuming uniform initial production

of both compounds take place over an area of interest. Preferential in situ degradation of labile compound can take place, which result in a strong down core decrease in abundance of compounds. These variations can be considered as an artificially rapid down core "aging" of the compound (Mollenhauer and Eglinton, 2007). Core sediments are very important as it provide useful information on the changes in the quality of the study area from a past period.

1.4 Source assessment of organic matter- Bulk parameter approach

The information on processes controlling the delivery of organic matter to sedimentary environments and the reflection of these inputs in newly deposited sediments is important to our understanding of global biogeochemical cycles. The mineralisation process occurring in the sedimentary environments is closely linked with organic matter and hence the characterisation of organic matter is an essential requirement for biogeochemical studies. Several methodological approaches have been employed for the determination of the origin of organic matter and the processes occurring in the transformation of organic materials in sediments. The approach of determination of biochemical components of sediments (i.e., carbohydrates, lipids and proteins) not only can be used to determine the origin of particles and the factors controlling their diagenesis (Colombo et al., 1996a); but also can be useful to properly value the quality of organic materials available for benthic consumers (Fabiano and Danovaro 1994; Gremare et al., 1997; Cividanes et al., 2002). In addition, the biochemical composition of sediments is proposed for assessing the tropic status of coastal marine systems (Dell'Anno et al., 2002; Pusceddu et al., 2003).

Among the various methods employed to characterise sources of organic matter in aquatic environments, the application of stable carbon isotope ratio and elemental composition is a common trend (Dittmar et al., 2001; Bouillon et al., 2003). A number of important bulk sediment parameters are available for the evaluation of organic matter sources and its fate within marine sediments including C/N ratios (Yamamuro, 2000; Perdue and Koprivnjak, 2007) and $\delta^{13}C$ signatures (Goñi et al., 2003; Alt-Epping et al., 2007). The use of these bulk parameters as source indicators is reliant on the fact that there exist markedly different signatures between the different organic matter sources. The C/N ratios have been widely used to distinguish the origin of organic matter based on the generalisation that algal organic matter has atomic C/N ratios between 4 and 10, whereas organic matter from terrestrial vascular plants has C/N ratios of 20 and greater (Ishiwatari and Uzaki,1987; Lehmann et al., 2002). This marked variation arises from the absence of cellulose in algae and its greater content in vascular plants. Microbial immobilisation of nitrogenous material accompanied by the remineralization of carbon might also result in the lowering of C/N ratios (Sollins et al., 1984). Selective degradation of organic matter components during early diagenesis also results in the modification of C/N ratios (Meyers, 1997).

The basic principle behind the application of stable isotopes in natural ecosystems is based on the variations in relative abundance of lighter isotopes from chemical rather than nuclear processes (Hoefs, 1980). Due to the faster reaction kinetics of the lighter isotope of an element, reaction products in nature are enriched with lighter isotopes. These fractionation processes have proven to be useful in determining source of organic matter in biogeochemical studies. Stable carbon isotopic ratios are particularly useful to distinguish

between marine and continental plant sources of sedimentary organic matter and to identify organic matter from different types of land plants.

1.5 Biomarker concept

Variations in productivity, as well as fluctuations in delivery, make it difficult to resolve processes contributing to the storage of organic matter in coastal environments. Moreover, natural organic matter originates from a diverse sources, i.e., from marine organisms as well as from higher plants (Keil et al., 1994; Hedges and Keil, 1995). The biochemical composition of organic matter sources varies and the differences in source signatures are not always unique enough to identify components in complex environment such as mangrove sediments. The C/N ratio is known to be seriously affected by the preferential remineralisation of nitrogen in marine sediments or nitrogen sorption onto clay minerals (Schubert and Calvert, 2001) and $\delta^{13}C$ of total organic carbon values of a mixture of C3 and C4 plants could mimic marine algae (Goñi et al., 1998). Furthermore, both indices cannot provide detailed information about specific organic matter sources. Due to the aforementioned limitations, a detailed study of lipid biomarkers (biomarker approach) enables the recognition of the major sources contributing to the sedimentary organic matter. The incorporation of biomarkers and carbon isotope geochemistry are widely used to infer the depositional environment conditions and source input of organic matter preserved in the sediments (Peters and Moldowan, 1993; Peters et al., 2005a, b; Hakimi and Abdullah, 2014).

Biomarkers are organic molecules, which are derived from formally living organisms through biological processes and show marked resistance to chemical changes. Minimal alteration of the original biological chemistry during burial and maturation would take place thereby keeping the fundamental carbon skeleton

intact. The term biomarker has been pointed by Meyers (2003) as organic compounds that possess the capability to characterise certain biotic sources and retain the source information after burial in sediments. Simply it can be defined as organic compounds found in sediments which have properties that can be directly linked to a known biological precursor. These are organic compounds derived from formerly living organisms and are ubiquitous in sedimentary organic matter. This molecular level information provided by biomarkers has been found to be more specific and sensitive compared to bulk elemental and isotopic techniques in source characterisation of organic matter, and further allows for identification of multiple sources (Meyers, 2003). Moreover, the high degree of structural complexity of these organic molecules is particularly informative and thus suitable for studying geochemical reactions because they provide the possibility of relating a certain product to a specific precursor. The stable carbon skeletons of such compounds are enriched with restore data on the habitat, nature and fate of the ancestral flora and fauna which can facilitate the paleo-environmental reconstruction of sedimentary environments (Brocks and Summons, 2003). In spite of the various biogeochemical reactions in the sediments, these compounds retain their basic skeletal structures and can be used as characteristic molecular markers (Peters et al., 2005a, b). The functional groups may be lost but the biological origins can be still recognised (Briggs, 2007; Affouri et al., 2013). As a result, these biomarkers can be employed as molecular fossils to trace changes in flora, fauna and microbes, and to form linkages with ecological, environmental and climatic evolution (Zhang et al., 2009). Lipid biomarkers are particularly useful tracers because they can reveal valuable information on organic matter sources at the molecular level. Furthermore they exhibit strong carbon-number predominance inherited from biosynthesis. The distribution of their homolog can reflect origin (marine versus terrestrial vegetation). Of the available biomarkers,

lipids provide better source characterisation than other biochemical classes due to a number of unique biosynthetic pathways which organisms use to produce these compounds as well as their relatively high geochemical stability. Earlier studies in coastal areas, estuaries, rivers and lakes have successfully used this approach to assess sedimentary organic matter sources (Jaffé et al., 2001; Bianchi et al., 2002; Mead et al., 2005). Sedimentary lipids have been successfully used to infer environmental changes that have impacted their sources (Zimmerman and Canuel, 2000).

1.6 Major classes of lipid biomarkers

1.6.1 Hydrocarbons

Among the lipid biomarkers, n-alkanes with odd chain such as n-C_{15}, n-C_{17} and n-C_{19} are indicative of algal and cyanobacterial inputs (Harji et al., 2008). Long chain (n-C_{20} to n-C_{35+}) alkanes that display strong predominance of odd chain lengths indicates a contribution from terrestrial plants (Volkman et al., 1997). Presence of hopanes in the sediments of Santos Bay and Estuary pointed towards the petrogenic origin of hydrocarbon (Medeiros and Bícego, 2004). Hydrocarbons from eroded sediments often display sterane and hopane distribution (Rowland and Maxwell, 1984) The C_{19} isoprenoid alkane, pristane, is common in marine samples, reflecting its abundance in some zooplankton species (Blumer et al., 1963; Zaghden et al., 2007; Ratheesh Kumar, 2012). The presence of phytane, a C_{20} isoprenoid in marine sediments, can be synthesised by the methanogenic and photosynthetic bacteria (Steinhauer and Boehm, 1992; Sakata et al., 1997). Simple branched alkenes such as 7- and 8- methyl heptadecene are found in many species of cyanobacteria (Han et al., 1968), and in algal mats and lagoonal sediments. Unusual classes of highly branched isoprenoid (HBI) alkanes are highly

specific biomarkers for diatoms (Castañeda and Schouten, 2011). The appearance of unsaturated C_{25} HBI alkanes along with increased concentrations of other algal biomarkers was recorded at Lake Koucha, eastern Tibetan Plateau (Aichner et al., 2010).

1.6.2 Long chain ketones

Very long straight chain (C_{35} to C_{40}) unsaturated methyl and ethyl ketones with trans double bonds are termed alkenones (Volkman et al., 1995). Long-chain unsaturated alkenones and alkyl alkenoates have been investigated as biomarkers of marine source material (Westerhausen et al., 1993), as thermometers (Chapman et al., 1996; Doose et al., 1997; Ikehara et al., 1997; Madureira et al., 1997) and as reconstruction proxies of environments such as variations of monsoon influence in the Arabian Sea (Rostek et al., 1993), the past surface current system in the equatorial Atlantic (Schneider et al., 1995), and El Niño events (McCaffrey et al., 1990; Kennedy and Brassell, 1992).

1.6.3 Terpenoids

The terpenoids are valuable markers for the determination of the biological source of organic material in geological samples (Simoneit, 1986, 1998, 1999). The diterpenoids originate mainly from conifers while the triterpenoids are derived mainly from angiosperms (Simoneit, 1977, 1986; Sukh Dev, 1989; Pisani et al., 2013). Sterols (tetracyclic triterpenoids) and compounds derived from them by diagenetic reactions are ubiquitous in sediments. A number of studies have shown that phytosterols could be used as tracers of various inputs and transformation processes to environments due to their structural diversity, biosynthesis and stability (Mudge and Norris, 1997; Ranjan et al., 2015). Numerous researchers have utilized pentacyclic terpenoids as biomarkers for the source determination of organic matter from mangrove ecosystems on account of

the peculiar stability during sedimentation and diagenesis (Killops and Frewin, 1994; Versteegh et al., 2004; Koch et al., 2005). Usually pentacyclic triterpenoids are mostly synthesised by higher plants and consist of a highly diverse group of molecules (Mahato and Sen, 1997; Kristensen et al., 2008).

1.6.4 Fatty acids

Fatty acids are essential components of every living cell and have been used as sediment biomarkers by many researchers (Harvey, 1994; Colombo et al., 1996b; Laureillard et al., 1997). They have great structural diversity coupled with high biological specificity (Parkes, 1987; Hu et al., 2006) and have therefore been used as taxonomic indicators (Minnekin and Goodfellow, 1980; Meziane et al., 2007). Fatty acid biomarkers are usually used to identify sources and fate of organic matter in marine environments (Harvey, 1994; Laureillard et al., 1997; Budge and Parrish, 1998; Carrie et al., 1998; Mudge et al., 1998; Fahl and Stein, 1999).

1.6.4.1 Saturated fatty acids

Fatty acids are simple in structure and can be subdivided into well-defined families. Among straight-chain fatty acids, the simplest are referred to as saturated fatty acids (SFAs). They possess the general formula: $CH_3 (CH_2)_n COOH$ (Table 1.1). Fatty acids have predominantly even numbers of carbon atoms because of their formation from acetyl (C_2) units, which are derived from glucose in the presence of various enzymes, coenzymes and carrier proteins. These are typically of C_{12} to C_{36} chain length. Saturated fatty acids (called alkanoic acids) are predominant in animals. They have no unsaturated linkages and cannot be altered by hydrogenation or halogenation. Saturated fatty acids are commonly straight chains with even carbon number. C_{14} to C_{18} fatty acids are ubiquitous and present

in many sources of organic matter, including vascular plants, algae, and bacteria (Goñi and Hedges, 1995; Zegouagh et al., 1996).

1.6.4.2 Unsaturated fatty acids

Fatty acids are said to be unsaturated when double bonds are present. When one double bond is present, the fatty acids are considered as mono unsaturated (alkenoic acids) and if the fatty acids contain more than one double bond, then they are termed as polyunsaturated. Polyunsaturated fatty acids are more common in algae than in higher plants. Unsaturated fatty acids are generally associated with algae (Colombo et al., 1996b; Meziane and Tsuchiya, 2000).

The important attributes of fatty acids are its carbon chain length, the number of double bonds present and the positions of double bond, which can be represented by a simple notation scheme (Table 1.2). For example, oleic acid can be represented by *cis*-$C_{18:1n9}$, where *cis* refers to the stereochemistry about the C=C bond. 18 is the number of carbon atoms, the number of double bonds (1) is given after the colon, and the number following 'n' is the position of the double bond from the opposite end to the acid group. As double bonds in polyunsaturated acids are usually conjugated, it is only necessary to give the position of the first double bond because all others follow on alternate carbon atoms. Hence eicosapentanoic acid is $C_{20:5n3}$ in which the first C=C bond occurs between C_3 and C_4, numbering from the opposite end of acid group and other four C= bonds are between C_6 and C_7, C_9 and C_{10}, C_{12} and C_{13}, and C_{15} and C_{16} (Killops and Killops, 2005). The number of double bonds and their geometric configuration are important factors in the function of these compounds.

Table 1.1 Common saturated fatty acids in nature

Trivial Name	Notation	Structure
Butyric acid	$C_{4:0}$	$CH_3(CH_2)_2COOH$
Valeric acid	$C_{5:0}$	$CH_3(CH_2)_3COOH$
Caproic acid	$C_{6:0}$	$CH_3(CH_2)_4COOH$
Caprylic acid	$C_{8:0}$	$CH_3(CH_2)_6COOH$
Pelargonic acid	$C_{9:0}$	$CH_3(CH_2)_7COOH$
Capric acid	$C_{10:0}$	$CH_3(CH_2)_8COOH$
Lauric acid	$C_{12:0}$	$CH_3(CH_2)_{10}COOH$
Myristic acid	$C_{14:0}$	$CH_3(CH_2)_{12}COOH$
Palmitic acid	$C_{16:0}$	$CH_3(CH_2)_{14}COOH$
Margaric acid	$C_{17:0}$	$CH_3(CH_2)_{15}COOH$
Stearic acid	$C_{18:0}$	$CH_3(CH_2)_{16}COOH$
Arachidic acid	$C_{20:0}$	$CH_3(CH_2)_{18}COOH$
Behenic acid	$C_{22:0}$	$CH_3(CH_2)_{20}COOH$
Lignoceric acid	$C_{24:0}$	$CH_3(CH_2)_{22}COOH$
Cerotic acid	$C_{26:0}$	$CH_3(CH_2)_{24}COOH$
Carboceric acid	$C_{27:0}$	$CH_3(CH_2)_{25}COOH$
Montanic acid	$C_{28:0}$	$CH_3(CH_2)_{26}COOH$
Melissic acid	$C_{30:0}$	$CH_3(CH_2)_{28}COOH$
Lacceroic acid	$C_{32:0}$	$CH_3(CH_2)_{30}COOH$
Ceromelissic acid	$C_{33:0}$	$CH_3(CH_2)_{31}COOH$
Geddic acid	$C_{34:0}$	$CH_3(CH_2)_{32}COOH$
Ceroplastic acid	$C_{35:0}$	$CH_3(CH_2)_{33}COOH$

Table 1.2 Most common unsaturated fatty acids

Trivial name	Notation	Structural Formula
Myristoleic acid	$C_{14:1n5}$	$CH_3(CH_2)_3\mathbf{CH=CH}(CH_2)_7COOH$
Palmitoleic acid	$C_{16:1n7}$	$CH_3(CH_2)_5\mathbf{CH=CH}(CH_2)_7COOH$
Oleic acid	$C_{18:1n9}$	$CH_3(CH_2)_7\mathbf{CH=CH}(CH_2)_7COOH$
Linoleic acid	$C_{18:2n6}$	$CH_3(CH_2)_4\mathbf{CH=CH}CH_2\mathbf{CH=CH}(CH_2)_7COOH$
α-Linolenic acid	$C_{18:3n3}$	$CH_3CH_2\mathbf{CH=CH}CH_2\mathbf{CH=CH}CH_2\mathbf{CH=CH}(CH_2)_7COOH$
Arachidonic acid	$C_{20:4n6}$	$CH_3(CH_2)_4\mathbf{CH=CH}CH_2\mathbf{CH=CH}CH_2\mathbf{CH=CH}CH_2$ $\mathbf{CH=CH}(CH_2)_3COOH$
Eicosapentaenoic acid	$C_{20:5n3}$	$CH_3CH_2\mathbf{CH=CH}CH_2\mathbf{CH=CH}CH_2\mathbf{CH=CH}CH_2\mathbf{CH=CH}CH_2$ $\mathbf{CH=CH}(CH_2)_3COOH$
Erucic acid	$C_{22:1n9}$	$CH_3(CH_2)_7\mathbf{CH=CH}(CH_2)_{11}COOH$
Docosahexaenoic acid	$C_{22:6n3}$	$CH_3CH_2\mathbf{CH=CH}CH_2\mathbf{CH=CH}CH_2\mathbf{CH=CH}CH_2\mathbf{CH=CH}CH_2$ $\mathbf{CH=CH}CH_2\mathbf{CH=CH}(CH_2)_2COOH$

1.6.4.3 Branched chain fatty acids

These are common constituents of the lipids of bacteria and animals, although they are rarely found in the integral lipids of higher plants. Normally, the fatty acyl chain is saturated and the branch is a methyl-group. Branched chain fatty acids (mono- branched) may have also a methoxy or a hydroxy substitution. However, unsaturated branched-chain fatty acids are found in marine animals, and branches other than methyl may be present in microbial lipids. The most common branched chain fatty acids are mono-methyl-branched, but di- and poly-methyl-branched fatty acids are also known. Branched fatty acids have usually either an iso-structure (methyl group at the penultimate carbon atom) or an anteiso-structure (methyl group on the third carbon from the end). The odd carbon numbered and branched chain (iso- and anteiso-) fatty acids are generally considered to be synthesised by bacterial communities (Volkmann et al., 1980), and are therefore used as biomarkers of bacteria (Parkes,1987).

1.7 Aim and scope of the study

Mangrove forests are among the most threatened habitats in the world. Growing human populations are increasingly converting, polluting, or otherwise disturbing mangrove ecosystems, often with greater or long term impacts than natural disturbances. Mangrove deforestation contributes to fisheries decline, erosion and land subsidence, as well as lead to the release of carbon dioxide into the atmosphere. The biodiversity and the nursery character shown by them authenticate the evaluation of the biogeochemistry of these ecosystems. Since mangroves are considered to be a major supporter of the coastal aquatic life, the present study has a special significance in predicting

the management requirements of this coastal ecosystem. These unique ecosystems need immediate protection and conservation.

The biogeochemistry of mangroves is the least understood one because of their sediment complexity due to the tidal influx of allochthonous organic matter and also due to the input of local vegetation. In order to understand the relative importance of biogeochemical processes, it is not only necessary to characterise and quantify the organic matter but also to identify its sources. Mangrove environments are sites of intense carbon processing (Borges et al., 2003; Dittmar et al., 2006; Alongi, 2007). The synthesis, degradation, and storage of terrestrial organic matter form an important component of the global carbon cycle (Feng et al., 2013). Common chemical parameters are insufficient to describe the biogeochemical character of this fragile ecosystem effectively. Even though bulk geochemical parameters such as elemental and isotopic compositions of sedimentary organic matter have commonly been used to distinguish organic matter from autochthonus versus allochthonous sources, they do not explain the chemical nature of the organic matter deposited. The biochemical composition of organic matter sources varies widely and the differences in source indications are not always unique enough to distinguish the constituents in complex mixtures like sediments. Therefore biomarker approach has been employed as one of the most suitable tool for the source characterisation of organic matter in coastal ecosystems. The n-alkanes and fatty acid biomarkers were selected as the reliable proxy for monitoring the preservation and degradation of organic matter in the core sediments.

The mangrove coverage in Kerala coast has diminished from 70,000 hectares to less than 4200 hectares (Mohanan, 1997). Even though preliminary assessment of sources organic matter in the surficial sediments of mangrove

sediments of Cochin has been carried out employing biochemical composition and fatty acid biomarkers (Joseph et al., 2008; Joseph et al., 2012), biogeochemical evaluation of mangroves in North of Cochin still remain un-attempted. Source characterisation of organic matter is an essential criterion for the better understanding of the ecological functioning as well as biogeochemical processes which can aid to formulate a better sustainable management strategy for the conservation of these vulnerable ecosystems. Core sediment samples are employed in the present study since they can provide useful information on the changes in the quality of the study area from past period. They are useful in paleoenvironmental reconstruction, paleoclimatic and paleolimnological studies. The objectives of the present investigation was to derive information on the sources of organic matter in the sedimentary organic matter using lipid biomarkers along with bulk elemental parameters like biochemical composition, elemental ratios and stable carbon isotope signature and to study historical records imprinted in the core sediments.

The objectives the investigation were to:

1. Assess the principal sources of organic matter in the study region.
2. Estimate the distributional character of lipid biomarkers in the ecosystem.
3. To determine the application of lipids as biomarkers thereby evaluating the major biogeochemical processes.
4. To study the historical records of distribution of lipid biomarkers using core sediments.

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Chapter 2
MATERIALS AND METHODS

2.1 Description of the Study Area

Once Kerala had a mangrove vegetation cover of about 70,000 hectare (Mohanan, 2004). According to Radhakrishnan et al., 2006, the mangrove vegetation in four Northern districts of Kerala (Kasargod, Kannur, Kozhikode and Malappuram) represents about 83% of mangrove forest covers in the state. Most of the research works on various aspects of mangrove ecosystems are confined to central part of Kerala and studies in Northern Kerala coast has not been reported so far. A reconnaissance survey was conducted to find out the true mangrove ecosystems in Northern Kerala coast and five sampling sites were identified and the selected stations were: Kunjimangalam (S1), Pazhayangadi (S2), Pappinissery (S3), Thalassery (S4) and Kadalundi (S5). The focus of the present study is restricted to mangroves occurring in the two Northern districts of Kerala; Kannur and Kozhikode. The choice of the districts was based on the fact that a significant portion of mangroves in Kerala is currently restricted to these two districts and the major share of these

wetland ecosystems are distributed in Kannur District. The geographical location of the study area is given in figure 2.1.

Kunjimangalam (S1)

The station is situated in an estuarine environment formed by Pullamcode puzha and Kunjimangalam River which is located at 2 km away from coastline with an area of around 18 hectares. The major species occurred in this region include: *Avicennia sp.*, *Acanthus ilicifolius*, *Rhizophora sp., Kandelia candel, Clerodendron inerme, Aegiceras corniculatium* and *Excoecaria sp*., *Lumnitzera racemosa*. In Kunjimangalam, there exist vast extents of mangroves, which remain untouched.

Pazhayangadi (S2)

The site is situated at a distance about 3-4 km from coastline and was found to be almost free from anthropogenic activities. Major species found at this station include: *Avicennia marina, Avicennia officinalis, Aegiceras corniculatium and Rhizophora mucronata*.

Pappinissery (S3)

It is formed on the banks of Valapattanam estuary (area of about 20 hectare), covering a distance of 4-5 km from the coastline. Valapattanam River is connected to the Lakshadweep Sea through a tidal inlet at Azheekal, about 6.5km downstream. It is found to exhibit rich mangrove species diversity (Khaleel, 2005). Major mangrove species found at this site includes: *Avicennia, Rhizophora, Kandelia and Acanthus* with isolated growths of *Aegiceras corniculatum* and creeper *Derris trifoliata*.

Thalassery (S4)

The mangrove vegetation cover in Thalassery spans over an area of 0.313 km^2 and falls within 50 meters of the shoreline (i.e., in the vicinity of Arabian Sea). Mangrove forests of Thalassery are characterised by the presence of *Avicennia-Sonneratia-Rhizophora* combination. The dense growth of *Rhizophora* species, *Avicennia officinalis*, *Acanthus ilicifolius*, *Excoecaria agallocha*, *Aegiceras corniculatum* and *Thespesia populnea* with isolated column of old trees of *Sonneratia* species and *Kandelia candel* were found.

Kadalundi (S5)

The Kadalundi mangrove system is situated on the banks of Kadalundi River which joins the Arabian Sea through a permanent bar mouth. Mangroves cover an area of 10 hectare which includes: *Rhizophora mucronata, Excoecaria agallocha, Aegiceras corniculatum*, and *Acanthus ilicifolius Avicennia officinalis* etc. (CMFRI, 2002; Manju et al., 2012). Mangrove cover in Kadalundi is a notable destination for migratory birds in Kerala. The mangrove forest cover is estimated to contain ten mangrove species. The stations S4 and S5 are situated along the close proximity to Arabian Sea and experiences semi-diurnal tidal action in the range between 0.09 to 1.84m.

Table 2.1 Location of the sampling sites

Stations	Code	Latitude	Longitude	Distance from the Coast
Kunjimangalam	S1	12° 03' 43" N	75° 14' 44" E	2 Km
Pazhayangadi	S2	12° 01' 45" N	75° 16' 28" E	3.5 Km
Pappinissery	S3	11° 56' 53" N	75° 21' 55" E	4.5 Km
Thalassery	S4	11° 45' 57" N	75° 28' 53" E	0.05 Km
Kadalundi	S5	11° 07' 49" N	75° 49' 47" E	1 Km

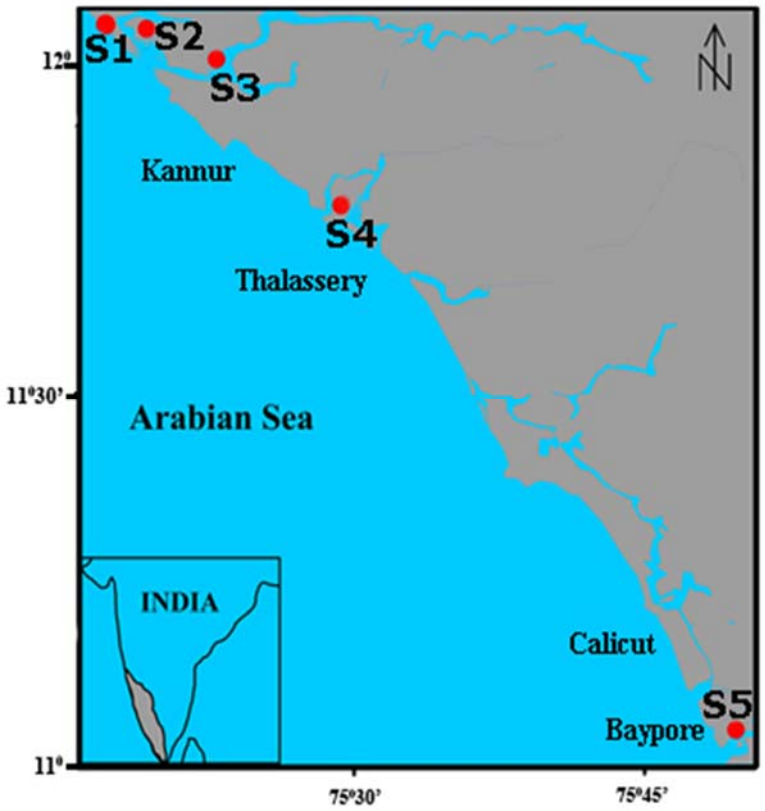


Figure 2.1 Geographical location map of the sampling stations

2.2 Sampling and Analytical Methodology

Samples of water and core sediments were taken from the five mangrove locations during October 2009, May 2010 and August 2010. Surface water samples were collected during high tide using a clean plastic bucket. The water samples were stored in previously washed plastic bottles, which were rinsed with the sample at the collection site. Core sediment samples from each station were collected manually using PVC tubes with 75mm diameter and 70 cm length. Core sediment samples collected during October 2009 was employed for the analysis. The core samples were sliced into segments as: 0-5cm (surface) and the rest at 10 cm intervals. The pH and Eh of the samples was measured in situ using portable pH meter (Eutech, pH

Tester 10) and Eh meter (Eutech, ORP Tester 10) respectively without delay. The samples were carried to laboratory in ice box and kept in deep freezer at -20^{0}C until analysis. All the analyses were carried out in triplicates and the average values were reported.

2.2.1 General Hydrography

Analysis of general hydrographical parameters and nutrients of the water samples were carried out employing standard methods. Values of pH in the water column were measured in situ using portable pH meter and temperature was recorded using a sensitive thermometer. Salinity of the water samples were estimated by Mohr- Knudsen method (Muller, 1999). Modified Winkler method was used for the estimation of dissolved oxygen (Hansen, 1999). Alkalinity of the water samples was estimated by the method of Koroleff (Anderson et al., 1999). Nutrients (nitrite, nitrate phosphate and silicate) were estimated using a spectophotometer (Genesys 10UV Thermospectronic). Nitrite was converted to an azo dye with sulphanilamide and N- (1-naphthyl) ethylene diamine dihydrochloride (Grasshoff et al., 1999). Nitrate was reduced to nitrite using a glass column containing copper-coated cadmium granules and estimated as nitrite (Grasshoff et al., 1999). Formation of phospho- molybdate complex employing ascorbic acid as reducing agent was used for phosphate determination (Grasshoff et al., 1999). Silicate was converted into silicomolybdate complex, which was reduced by ascorbic acid, to produce a blue solution and estimated spectrophotometrically (Grasshoff et al., 1999). The total nitrogen and total phosphorous content were measured after alkaline persulphate oxidation (Hansen and Koroleff, 1999). Chlorophyll pigments and pheophytin in water samples were filtered through 0.45µm GF/F paper, extracted using 90% acetone and measured spectrophotometrically (APHA, 1995).

2.2.2 Methods for Determination of Geochemical Parameters

Redox potential of the fresh wet sediment was measured using Eh meter (Eutech, ORP Tester 10) and Zobell's solution was used for the calibration of the electrodes (Brassard, 1997). The grain size characteristics of the sediments (sand, silt, and clay) were determined by pipette analysis (Folk, 1974), after removing the inorganic carbonates using 10% HCl and organic matter using H_2O_2. Sediment was then wet sieved through a 63µm sieve to collect the sand fraction. The mud fraction was divided into silt (63- 4 µm) and clay (<4 µm) fractions by timed gravimetric extraction of the dispersed sediments. Sediment samples were freeze-dried (Beetta Freeze drier, Chennai, India) and finely powdered using agate mortar for further analyses. Total carbon, nitrogen and sulphur were determined using Vario EL III CHNS Analyser. Total organic carbon (TOC) was estimated by TOC analyser (VARIO TOC SELECT- Elementar), calibrated using standard sediment supplied by VARIO TOC SELECT-Elementar, after decarbonation with 2N HCl (Chairi et al., 2010). The detection limit for TOC was 0.06%. Heavy metals in the sediment were estimated using Flame Atomic Absorption Spectrometry (Perkin Elmer-3110) after digestion using 1:5 $HClO_4$:HNO_3 (Loring and Rantala, 1992; Machado et al., 2002). Accuracy of the analytical procedure was checked using standard reference material BCSS-1 (standard reference material for marine and estuarine sediments). Triplicate analysis of BCSS-1 showed a good accuracy and the recovery rate ranged between 82.7 % for Mn and 103.9 % for Zn (Table 2.2).

Table 2.2 Analysis of standard reference material for heavy metals (BCSS-1)

Metal	Certified Value	Obtained Concentration (n=3)
Co (µg/g)	11.4 ± 2.1	10.67 ± 2.68
Cr (µg/g)	123 ± 1.4	112 ± 0.65
Cu (µg/g)	18.5 ± 2.7	18.2 ± 0.25
Fe (%)	4.7± 0.14	4.64± 0.41
Mg (%)	2.44 ± 0.23	2.32 ± 0.36
Mn (µg/g)	229 ± 15	189.47 ± 10.75
Ni (µg/g)	55.3 ± 3.6	49.16 ± 2.01
Pb (µg/g)	22.7 ± 3.4	24.9 ± 0.08
Zn (µg/g)	119 ± 12	123.64 ± 2.51

2.2.3 Estimation of Biochemical Constituents

Spectrophotometric methods were employed for the determination of biochemical components in sediments. Analysis of total proteins (PRT) were carried out following the procedure of Lowry et al., (1951), as modified by Rice, (1982) with Bovine Serum Albumin as the calibration standard. Total carbohydrates (CHO) were analysed according to Dubois et al., (1956), using glucose as the standard. Total lipids (LPD) were extracted according to Bligh and Dyer, (1959), and estimated according to Barnes and Blackstock, (1973) using cholesterol as the standard. All the analyses were carried out on triplicates and the average concentration is reported. The sum of all proteins (PRT), carbohydrates (CHO) and lipids (LPD) was defined as the labile or easily assimilable organic matter (Danovaro et al., 1993; Cividanes et al., 2002). PRT, CHO and LPD concentrations were converted to carbon equivalents by using the conversion factors: 0.49 to estimate protein equivalence of carbon, 0.40 to evaluate carbohydrate equivalents of carbon and 0.75 to determine lipid equivalence of carbon (g of C/g), respectively (Fabiano and Danovaro, 1994). The sum of PRT, CHO and LPD carbon is

referred to as biopolymeric carbon (BPC) (Fichez, 1991; Fabiano et al., 1995). Tannin and lignin in sediments were extracted using 0.05M NaOH at 60^{o}C for 90 minutes and estimated spectrophotometrically by the sodium tungstate-phosphomolybdic acid method (Nair et al., 1989; APHA, 1995), using tannic acid as the standard. The principle involved is the development of a blue colour on reduction of Folin phenol reagent by the aromatic hydroxyl groups present in tannins and lignins. The effects of Mg and Ca hydroxides and/or bicarbonates present in the seawater were suppressed by the addition of trisodium citrate solution (Nair et al., 1989).

Stable carbon isotope analysis of Total Organic Matter ($\delta^{13}C_{TOM}$) was carried out using Delta Plus XP Continuous flow Mass Spectrometer, after the removal of inorganic carbon using 2M HCl. Stable carbon isotope abundances were reported as $\delta^{13}C$ (‰) values and are expressed relative to the PDB (Pee Dee Belemnite) standard:

$$\delta^{13}C = \{\frac{\left(^{13}C/^{12}C\right)_{Sample}}{\left(^{13}C/^{12}C\right)_{PDB\ Standard}} - 1\}\ X\ 100$$

2.2.4 Lipid Biomarkers in sediments

Finely milled freeze-dried sediment samples (collected during post monsoon) were extracted in an automatic Solvent extractor (SOCS PLUS, SCS08R from PELICAN EQUIPMENTS, India) with a mixture of dichloromethane methanol (2:1, v/v) (Yi Duan and Lanhua Ma, 2001). The solvent extract was filtered and concentrated using a rotary evaporator (Heidolph, Germany) and then dried under high purity nitrogen. The extracted material was saponified overnight with 6% KOH-methanol at room temperature. Both neutral and fatty acid fractions were successively recovered with HPLC-grade n-hexane and dichloromethane respectively, the latter after

acidification with concentrated HCl to pH 1. The neutral lipid fraction was partitioned from the alkaline solution using n-hexane and then fractionated into individual class of compounds by column chromatography on silica gel (activated for 24 hours at 160^0C), n-hexane was used to isolate aliphatic hydrocarbon fraction (Otto and Simoneit, 2001, Wu et al., 2001). Excess solvent was removed by vacuum rotary evaporation and fractions were transferred to vials by dissolving in HPLC grade n- hexane, dried under high purity nitrogen gas, and stored at 4°C until analysis. The remaining aqueous layer containing the fatty acid salts was acidified to pH 1. Fatty acids in this polar-lipid fraction were recovered separately into dichloromethane.

The hydrocarbon fraction eluted with n-hexane using silica gel column was evaporated to 1 ml under high purity nitrogen and determined by gas chromatography-mass spectrometry (GC-MS) using a Perkin Elmer Clarus GC 620, with MS detector equipped with a non-polar HP ultra-double-fused silica capillary column (30 m, 0.32 mm internal diameter, 0.25 mm film thickness). Oven temperature was held at 60^0C for 2 minutes and then increased to 180^0C at 8^0C per minute and held for 2 minutes and then increased to 280^0C at 3^0C per minute and held for 7 minutes. The injector temperature was kept at 260^0C and the detector temperature was maintained at 300^0C. N_2 was used as carrier gas with flow rate of 2 ml per minute. Identification of individual compounds was achieved by comparison of GC retention times with those of standard compounds. Quantification was based on the calibration with authentic standards (C_7 -C_{40}, Sigma Aldrich, USA).

The polar lipid fraction containing the fatty acids was evaporated to dryness using rotary evaporation. It is then converted to fatty acid methyl esters (FAMEs) by treating with 10 ml of 10% BF_3-Methanol (Sigma Aldrich, USA) (70^oC for 30 minutes). The FAMEs were subsequently partitioned from

the reaction solution into dichloromethane. The dichloromethane layer was evaporated to dryness, and the extract was then re-dissolved into HPLC grade dichloromethane for gas -chromatographic analysis. Analysis of FAME was carried out by gas chromatography-mass spectrometry (GC-MS) using a Perkin Elmer Clarus GC 620, with MS detector equipped with a non-polar HP ultra-double-fused silica capillary column (30 m, 0.32 mm internal diameter, 0.25 mm film thickness). Operating conditions were as follows: ion source of 200°C and electron voltage 70 eV. Spectra were scanned from 50 to 600 m/z with a scan time of 1.50 seconds. A two-step temperature program was used: from 50°C to 200°C at 2°C per minute- then held for 5minutes. Then temperature again increased from 200°C to 280°C at 10°C per minute (held for 10minutes). The detector was operated at 290°C and helium was used as carrier gas. Full data acquisition was obtained with the use of MS (turbo mass version 5.3.2). Quantification was achieved by calibration of FAMEs standards supplied by Sigma Aldrich (Supelco, 37 Component FAME Mix, 18919-1AMP). Sample FAMEs were also injected in the above mentioned condition and their concentrations were determined from the calibration plot.

Data were acquired and processed with the MS Turbomass version 5.4.2. Individual compounds were identified by comparison of mass spectra with literature and library data, comparison with authentic standards and interpretation of mass spectrometric fragmentation patterns. Structural assignments were based on comparison of the gas chromatographic retention times with those of authentic standards and by interpretation of mass spectra or comparison with published mass spectral data. The compounds were identified by their GC retention times and published mass spectra (Philip, 1985). Mass spectral identification was confirmed by comparing the obtained mass spectra with those of authentic standards or mass spectra stored in the

NIST MS Library (version: NIST MS Search 2.0) and then comparing mass fragmentation pattern with available literature. The hopanes, eluted along with hydrocarbon fraction, were identified by scanning the mass spectra at m/z 191 and compared with mass fragmentation pattern of hopanes in NIST MS library (version: NIST MS Search 2.0) and that of published mass spectral data.

All the glasswares were cleansed by washing with tap water, chromic acid and distilled water. After this, it was rinsed with methanol and dichloromethane. All solvents and silica gel (230-400 mesh) were purchased from Merck (India/Germany). The materials used for the experiments (silica gel, glass and cotton wool, anhydrous sodium sulphate, etc.) were soxhlet extracted with methanol: acetone (50:50) overnight and twice with methylene chloride for 24 hrs, and kept dry (in desiccator) until use.

2.2.5 Statistical Analysis

Statistical analysis was performed using Statistical Program for Social Sciences (SPSS version 13.0). Two-way analysis of variance (ANOVA) without replication was carried out to find out the spatial and seasonal variations of water quality parameters in the study area and it was also employed to find out spatial and depth wise variation in sediment parameters. Pearson correlation analysis was performed to identify inter-elemental relationship with sediment properties. Prior to further statistical analysis, the data were normalised to create uniformity in the units of variables (Shaw, 2003). Principal component analysis (PCA) was employed to explore the origin and geochemical factors influencing the distribution of various parameters in sediments (Loska and Wiechula, 2003). The principal components (PCs), derived through Varimax rotation, and the number of significant factors within the data were established by considering only those with an Eigen value >1.0.

2.3 Results of the General Hydrography

Range of analysed parameters in three seasons is furnished in table 2.3. The seasonal and spatial variation is depicted in figure 2.2. pH varied from 7.1 to 8.05 and comparatively lower values were detected during post monsoon and minimum was recorded at S3. Salinity exhibited profound seasonal variation ($P<0.01$) recording minimum value during monsoon season (0.24), which might be due to fresh water runoff. The maximum was reported from S1 (35.97), on account of the land locked nature of the sampling site. Compared to other stations, S4 and S5 are situated in the close proximity of Arabian Sea and therefore prominent tidal activity can alter salinity of these systems. Dissolved Oxygen (DO) showed variation in concentration from 2.86 to 9.34 mg/L. In aquatic systems, oxygenation is the result of an imbalance between the process of photosynthesis, degradation of organic matter, re-aeration (Granier et al., 2000), and physicochemical properties of water (Aston, 1980).The organic pollution by domestic sewage at S3 resulted in the depletion of dissolved oxygen. The dissolved oxygen supersaturation (132 %) was observed at S1 (pre monsoon), which may be resulted from higher photosynthetic rate by phytoplankton, and was confirmed by higher chlorophyll content (Manju et al., 2012). Limited tidal rhythm and flushing also might have contributed to the dissolved oxygen super saturation. Dissolved gas super saturation can be produced in rivers and lakes which have high densities of plankton, aquatic plants, and algae (White et al., 1991). Alkalinity also displayed significant seasonal variation ($P<0.01$), exhibiting higher values during pre monsoon and lower values during monsoon. It varied from 44.55 to 167.33 mg $CaCO_3$/L.

Table 2. 3 Range of temporal variation of general hydrographic parameters, nutrients and pigments in water column

Parameters	Post monsoon	Pre monsoon	Monsoon	ANOVA- P value	
				Spatial	Seasonal
pH	7.1 to 7.4	7.2 to 8.00	7.81 to 8.05	0.51	0.003
Salinity	4.26 to 9.25	29.31 to 35.97	0.24 to 26.94	0.43	0.0004
Dissolved oxygen, mg/L	2.86 to 6.41	0.51 to 9.34	3.76 to 7.35	0.43	0.62
Alkalinity, mg $CaCO_3$/L	44.55 to 79.2	121.25 to 167.33	22.31 to 83.42	0.87	0.0003
Nitrite, µmol/L	0.15 to 0.55	0.29 to 0.99	0.31 to 0.99	0.35	0.10
Nitrate, µmol/L	1.37 to 8.43	0.29 to 4.33	3.14 to 20.79	0.09	0.001
Ammonia, µmol/L	4.73 to 27.95	ND to 98.09	5.52 to 80.36	0.10	0.33
Total nitrogen, µmol/L	34.55 to 63.9	32.74 to 102.78	124.78 to 188.38	0.67	0.001
Phosphate, µmol/L	0.59 to 1.37	1.32 to 6.56	9.98 to 15.07	0.47	0.0001
Total Phosphorous, µmol/L	2.96 to 8.61	1.53 to 6.65	10.04 to 21.96	0.39	0.0002
Chlorophyll a, µg/L	0.77 to 17.29	2.18 to 40.86	ND to 3.09	0.07	0.04
Chlorophyll b, µg/L	ND to 1.61	1.12 to 6.00	ND to 1.71	0.38	0.02
Chlorophyll c, µg/L	ND to 4.34	1.7 to 13.8	ND to 2.44	0.18	0.01
Phaeophytin, µg/L	4.01 to 31.01	1.01 to 22.27	ND to 23.2	0.05	0.08

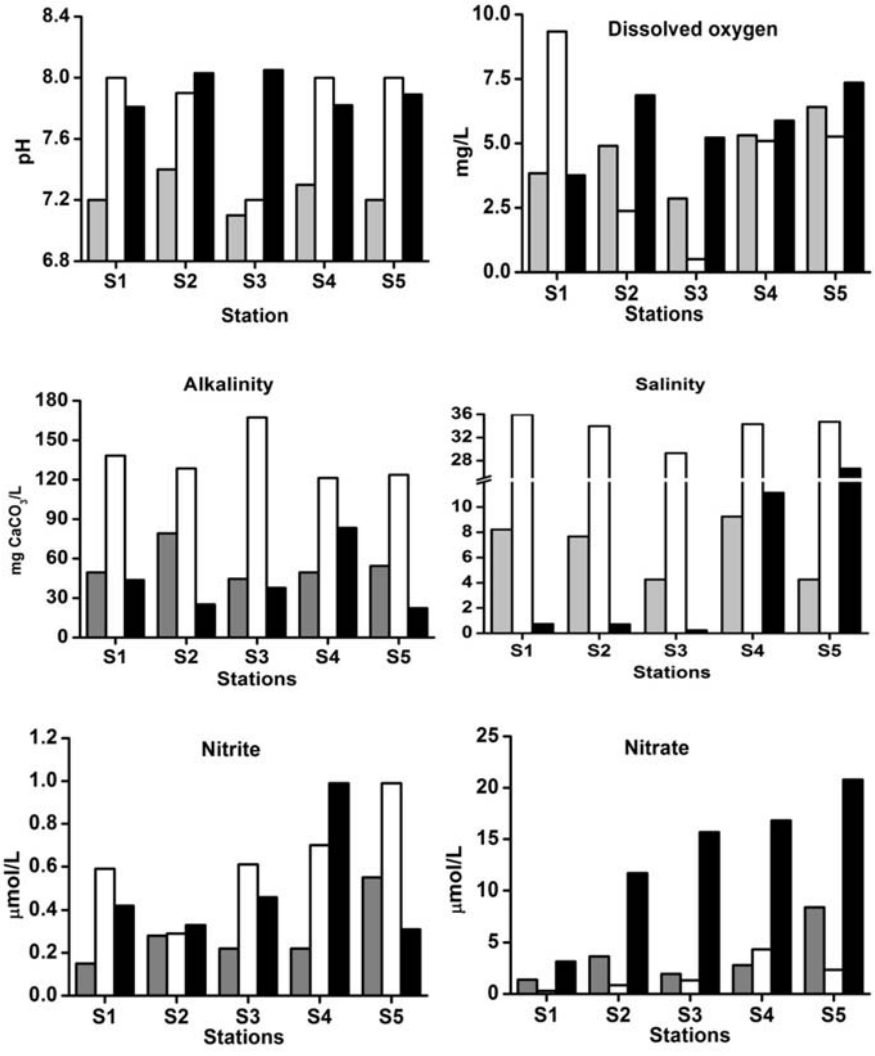
ND - not detected

Concentration of nitrite ranged from 0.15 to 0.99 µmol/L and minimum was observed at S1 during post monsoon. Nitrate displayed a significant seasonal variation ($P<0.01$) and it recorded variation in concentration from 0.29 to 20.79 µmol/L. It exhibited higher concentration during monsoon (at S5) and lower content during pre monsoon (at S1). Ammonia content varied from 4.73 to 98.09 µmol/L recording minimum values during post monsoon and maximum during monsoon season. A significant seasonal variation was observed for TN ($P<0.01$), with its minimum content reported during pre monsoon (32.74 µmol/L) and maximum during monsoon (188.38 µmol/L). According to Solanki et al., 2010, the proportion of different forms of nitrogen in any water body is determined by the balance between assimilation, mineralisation, nitrification, denitrification and nitrogen fixation. Pappinissery (S3) received large quantity of domestic garbage and poultry waste resulting into the reducing environment and

recorded elevated concentration of nutrients (especially NH_4^+) and low DO. The occurrence of burrowing crabs at S2 and S3, produce sediment micro-pores, which are reducing in nature, result in the build-up of ammonium by the process of anaerobic ammonification (Smith et al., 1991). Inorganic phosphate showed significant seasonal variations and its concentration varied from 0.59 to 15.07 µmol/L recording minimum value during post monsoon and maximum during monsoon season. Total phosphorous (TP) displayed highly significant seasonal variation ($P<0.01$) with its maximum concentration recorded during monsoon and the minimum during pre monsoon (1.53 to 21.96 µmol/L).

Significant seasonal variation for chlorophyll pigments was indicated by ANOVA ($P<0.05$). Chlorophyll a (Chl-a) recorded variation in concentration from ND to 40.86 µg/L. The samples collected during pre monsoon (at S1) recorded comparatively higher Chl-a content; whereas comparatively lower concentration was reported during monsoon. Concentration of chlorophyll b (Chl-b) varied from ND to 6 µg/L recording maximum value during pre monsoon. Comparatively higher Chl-b content was recorded at S5 (pre monsoon). Chlorophyll c (Chl- c) ranged from ND to 13.80 µg/L. All stations recorded higher phaeophytin (phaeo) content post monsoon season with a maximum at S1 (31.01 µg/L). Chlorophyll pigments are considered as the most reliable index of phytoplankton biomass. Also, Chl-a to phaeophytin ratio provides the first hand information on the physiological status of phytoplankton, which ranged from 0.15 to 2.14. Higher concentration of phaeophytin compared to Chl-a during post monsoon and monsoon seasons indicated the presence of more detrital matter in these environments, which could be attributed to decomposition of organic matter from the sediment and community structure, harbouring in the surrounding water (Tripathy et al., 2005). In pre monsoon season, the reverse trend was observed due to the growth of phytoplankton in the high light intensity and

low turbulent waters of mangrove ecosystems. The presence Chl-b revealed the contribution of green algae to the productivity of mangrove ecosystems. Chl- b to Chl- a and Chl- c to Chl-a ratios were <1 suggesting the possibility of healthy phytoplankton populations in region with lower light intensity and lower turbulence (Takahashi and Nakamoti, 1972).



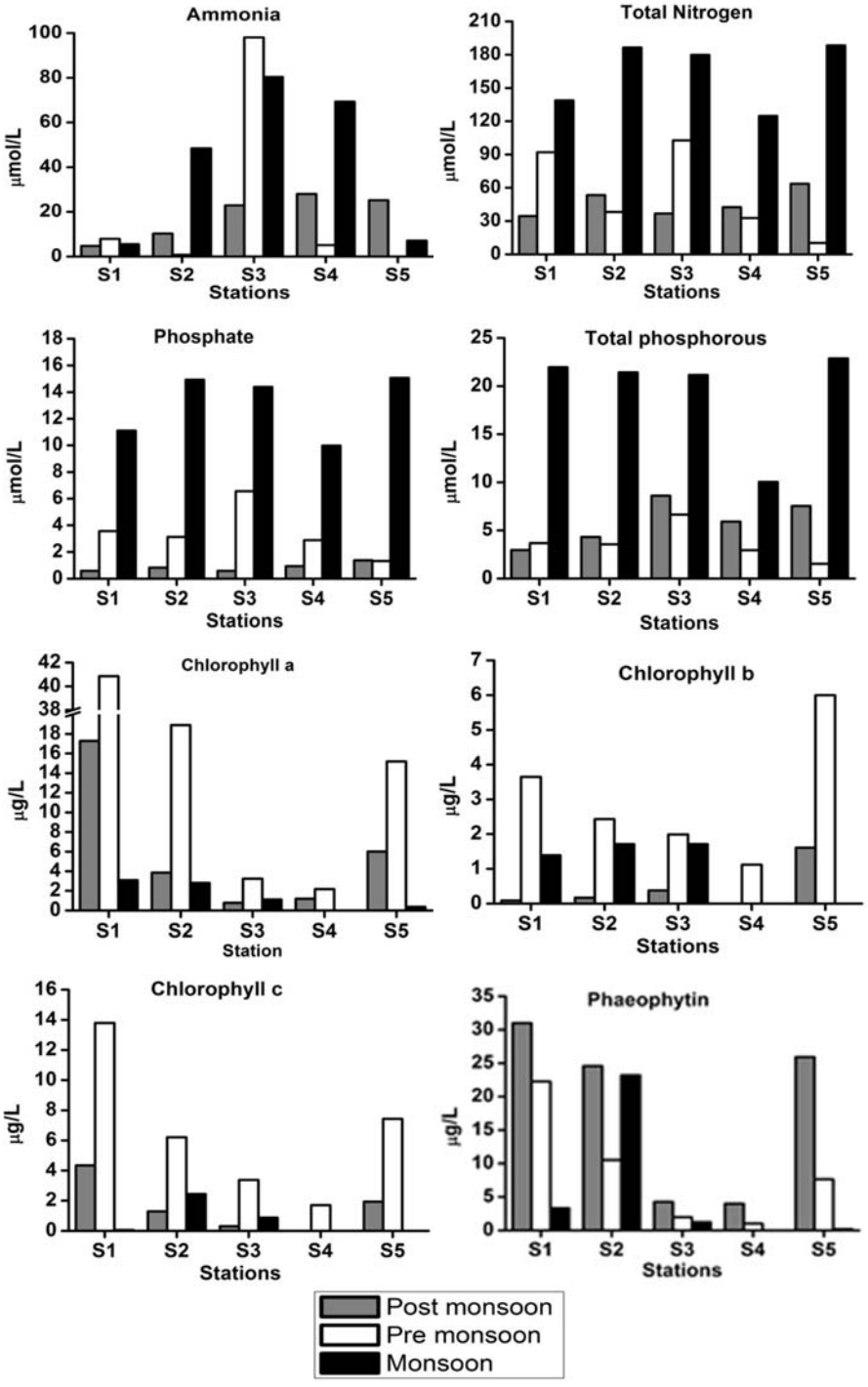


Figure 2.2 Spatial and seasonal variation of various hydrographic parameters

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Chapter 3

GEOCHEMISTRY OF HEAVY METALS

3.1 Introduction

The geochemical variables such as pH, Eh, grain size and organic carbon content play significant role in the spatial distribution of heavy metals (Marchand et al., 2011). Iron and sulphur cycling triggered by redox condition and quality and quantity of organic matter also have major influence on variation in heavy metal content. The redox potential of the sediment can affect trapping of metal directly through a change in the oxidation state of the metal itself, or indirectly through a change in the oxidation state of ions that can form complexes with the metal. The chemical forms of metals in aquatic sediments are usually governed by transformations during early diagenesis and changing redox conditions. Thus the accumulation of heavy metals in sediments is intimately linked with the general geochemical variables and hence the study on its distribution can provide useful implications on the redox status, pH and diagenetic processes involving organic matter and sulphur. The process of cycling of organic matter by means of litter production, degradation

and tidal export ultimately transfer a portion of the accumulated heavy metals to the detritus food chain (Silva et al., 2006).

Inland and coastal wetlands along Kerala Coast have been lost over years due to reclamation, conversion for industrial purposes, dumping of solid waste, discharge of untreated sewage and municipal waste, effluents from industries and human encroachment for construction. Even though trace metal accumulation in mangrove sediments from central part of Kerala Coast have been seriously investigated, studies pertaining to the trace metal accumulation on Northern Kerala Coast has not been reported so far. In the present investigation, an attempt is made to assess the general environmental conditions and health of the mangrove ecosystems by analysing the spatial and down core variations of heavy metals in the sediments. Core sediments are important for tracing past historical records in the sediments. The extent of accumulation and contamination status of the metals due to anthropogenic influence was evaluated employing enrichment factor and geoaccumulation index.

3.2 Results

The spatial and vertical distributions of different geochemical parameters in the core sediments of the study region viz., grain size, total organic carbon, total nitrogen, total sulphur content and concentrations of heavy metals are presented in this chapter. The range of the estimated parameters is furnished in table 3.1 and spatial as well as vertical distributions of various parameters estimated are depicted in figure 3.1. The ternary diagram for grain size data is shown in figure 3.2.

3.2.1 General sedimentary parameters

pH of the sediments varied from 5.7 to 7.12 and a gradual decrease was observed down the core. The maximum negative value for Eh was

recorded at S3 (5-15cm) and the minimum at S1 (45-55cm). The vertical profile of grain size showed no peculiar trend. Sand content recorded the minimum at S2 (0-5cm; 1.22%) while maximum was at S1 (5-15cm; 89.72%). Clay content ranged between 9.2 (S1; 5-15cm) to 71.36 % (S2; 0-5cm) in the study region. Silt was the lowest fraction, with minimum content of 1.08% at S1 (5-15cm) and highest content of 41.69% at S3 (5-15cm). The ternary diagram displayed that at S1, the sediment samples remained sandy down the core from 0-5 to15-25cm and the sample from depth range 25-35cm exhibited a silty sand nature and thereafter the sediment samples became mixed type (sand+silt+clay). The sediment samples from S2 showed a silty clay nature at 0-5cm and 5-15cm and then turned to mixed type of nature down the core to 45-55cm. At S3, the surface sample (0-5cm) and the segment sample 15-25cm displayed mixed type of nature while all the other segments lay on the border of silty clay and clayey silt. At S4, the surface sample (0-5cm) and the sample at 5-15cm displayed a mixed type of nature while all the other segment samples displayed a clayey sand nature. At S5, the samples from 0-5cm, 15-25cm and 35-45cm remained as mixed type of nature while the sample from 5-15cm showed a silty sand nature and the other samples (25-35cm and 45-55cm) displayed clayey sand nature. Total organic carbon (TOC) and total nitrogen (TN) contents showed almost similar vertical trend for the samples from S1 and S2, which revealed that both the contents decreased downwards from 0-5 to 5-15cm and then remained more or less constant value down the core. The content of TN at S3 decreased from 0-5 to 15-25cm and then remained almost invariant down the core. The variation in concentration of TOC was from 0.4% (S1; 25-35cm) to 6.88% (S3; 0-5cm) and the concentration of TN varied from 0.02% (S1; 25-35cm) to 0.31% (S3; 0-5cm).

The total sulphur ranged from 0.01 to 2.73% and exhibited the minimum at S1 and maximum at S3.

3.2.2 Distribution of heavy metals

Concentrations of copper (Cu), cadmium (Cd), cobalt (Co), lead (Pb), nickel (Ni), iron (Fe), manganese (Mn) and zinc (Zn) were determined.

Copper: Concentration of Cu in core S1 decreased downwards from 0-5 to 5-15cm and even though it increased at 15-25cm, the Cu content was found to decrease down the core from 15-25 to 45-55cm. However at S2, a down ward decrease in content from 0-5 to 25-35cm was noticed and it increased at 35-45cm and then remained more or less uniform. At S3, the concentration increased from 0-5 to 5-15cm and then decreased at 15-25cm. Even though it increased slightly down the core from 15-25 to 35-45cm, a slight decrease in copper content at 45-55cm was noticed. A decline in Cu levels down the core, from 0-5 to 15-25cm was observed at S4, and then the content increased down wards from 15-25 to 35-45cm followed by a decrease in concentration further down the core. A downward decrease in content from 0-5 to 15-25cm was recorded at S5, and then a zig-zag pattern of distribution was exhibited by sample segment from 15-25 to 45-55cm. Cu content displayed marked variation in the study area ranging from 8.55 (S1; 45-55cm) to 38.17 mg/kg (S5; 0-5cm).

Cadmium: Vertical profile of Cd at S1, recorded a content of 0.19 mg/kg at surface sediment (0-5cm) and then remained not detectable level downwards to a depth range of 15-25cm, and then its content increased downwards at 35-45cm and then a decrease in concentration was observed at 45-55cm. It was found that, at S2, Cd exhibited values only at 0-5cm and 15-25cm. Decrease in concentration downwards from 0-5 to15-25cm followed by zig-zag type of variation was

noticed at S3. In the present investigation, a decrease in Cd content down the core from 0-5 to 15-25cm was observed at S4, and then it remained more or less uniform down the core from 25-35 to 45-55cm. Prominent down ward decrease in concentration from 0-5 to 5-15cm was observed at S5, and the concentration of Cd increased reaching at the depth of 15-25cm, even though a decrease in Cd content was recorded down the core from 15-25 to 25-35cm, the Cd content increased from 25-35cm to 45-55cm. Cadmium recorded values between not detectable level and 1.84 mg/kg (S2;0-5cm)

Cobalt: Co content increased downwards from 0-5cm to 25-35cm and thereafter it decreased downwards at S1. It was observed that, at S2, an increase in Co levels from 0-5cm to 5-15cm was noticed and then it decreased vertically downwards to 35-45cm followed by a sharp increase at 45-55cm. Meanwhile, S3 recorded a hike down the core from 0-5 to 5-15cm followed by decrease at 15-25cm and thereafter an increase in concentration to a depth of 35-45cm was noticed which again decreased at 45-55cm. A zig-zag pattern of down-core variation was recorded at S4. However in the case of S5, decrease in content down the core to a depth of 15-25cm was observed and then exhibited a zig-zag pattern of distribution down the core. The concentration of Co displayed variation ranging from 10.70 (S1) to 36.94 mg/kg (S3).

Lead: Concentration of Pb decreased to a depth range of 5-15cm, there after the content increased downwards to 25-35cm and then decreased down the core in the case of samples from S1. An increase in concentration of Pb was noticed from 0-5cm to 5-15cm (sub-surface peak was observed), and decrease in content down the core to 25- 35cm was observed and after that depth its concentration increased downwards at S2. In the case of samples from S3, an increase from 0-5 to 5-15cm (subsurface peak) followed by decrease at 15-25cm was noted, there after it increased and remained almost constant to a depth of 35-45cm and

then decreased at 45-55cm. A zig-zag manner of distribution was observed at S4 for lead. Concentration of Pb decreased down the core from 0-5 to 25-35cm was noticed down the core at S5 and thereafter a prominent increase in concentration was observed. Lowest concentration for Pb was found at S1 (5-15cm; 6.09 mg/kg) and the highest at S5 (0-5cm; 29.93 mg/kg).

Nickel: Slight decrease in concentration of Ni from 0-5cm to 5-15cm was recorded and then the Ni content increased down the core in the case of samples from S1. A sharp decrease downwards to 25-35cm followed by increase in content to the depth of 45-55cm was noticed at S2. Ni exhibited a zig-zag pattern of distribution at S3 and S4. Ni content was found to decrease down the core from 0-5 to 5-15cm followed by an increase in concentration up to 25-35cm and though a slight decrease in concentration was observed at 35-45cm, again an increase in concentration was recorded at 45-55cm for S5. It was observed that the estimated Ni content ranged between 26.65 and 78.02 mg/kg in the study region.

Iron: Estimated Fe content at S1 recorded a more or less constant value at 0-5cm and 5-15cm and then the Fe content increased downwards to 25-35cm. However the concentration decreased at 35-45cm, thereafter Fe content increased downwards to 45-55cm. A zig-zag type of vertical distribution pattern was recorded at S2. The downward profile of Fe at S3 revealed a decrease in distribution from 0-5 to 15-25cm and then an increase in content was noticed from 15-25 to 35-45cm which again decreased on reaching 45-55cm. Decrease in concentration was observed at S4 from surface (0-5cm) to the depth of 15-25cm and thereafter a zig-zag type of distribution was noticed. Fe content decreased down the core from 0-5cm to 15-25cm and then it increased at 25-35cm followed by a decrease in content at 35-45cm and an increase in content was found at 45-55cm at S5. Concentration of Fe was

found to fluctuate between 1.25 and 5.53% at S1 (0-5cm) and S5 (0-5cm) respectively.

Manganese: The content of Mn displayed an increasing trend down the core from 0-5 to 45-55cm at S1. In the case of samples from S2, Mn content exhibited a zig-zag pattern of distribution down the core. At S3, a decrease in concentration from 0-5 to 15-25cm was noticed and then the concentration increased from 15-25 to 35-45cm, which again decreased at 45-55cm. The Mn content at S4 decreased from 0-5 to 5-15cm and then increased from 5-15 to 25-35cm. Even though, a decrease in content was observed down the core from 25-35 to 35-45cm, the Mn concentration increased reaching at 45-55cm. At S5, the Mn content decreased downwards from 0-5 to 5-15cm and then increased at 15-25cm and again decreased down the core from 15-25 to 35-45cm which further increased at 45-55cm. The concentration of Mn was found to vary between 71.45 (S3; 15-25cm) and 341.55 mg/kg (S5; 0-5cm).

Zinc: Concentration increased from 0-5cm down to 25-35cm and then decreased downwards at S1 but reverse was true for the samples from S2. A zig-zag distribution was noticed for Zn from 0-5 to 25-35cm and then decreased down wards for the sediment samples from S3. At S4 and S5, Zn content decreased down wards from 0-5 to 15-25cm and then showed a zig-zag distribution down to 45-55cm. The concentration of Zn displayed values ranging between 23.01 (S1; 0-5cm) and 82.21mg/kg (S3; 25-35cm).

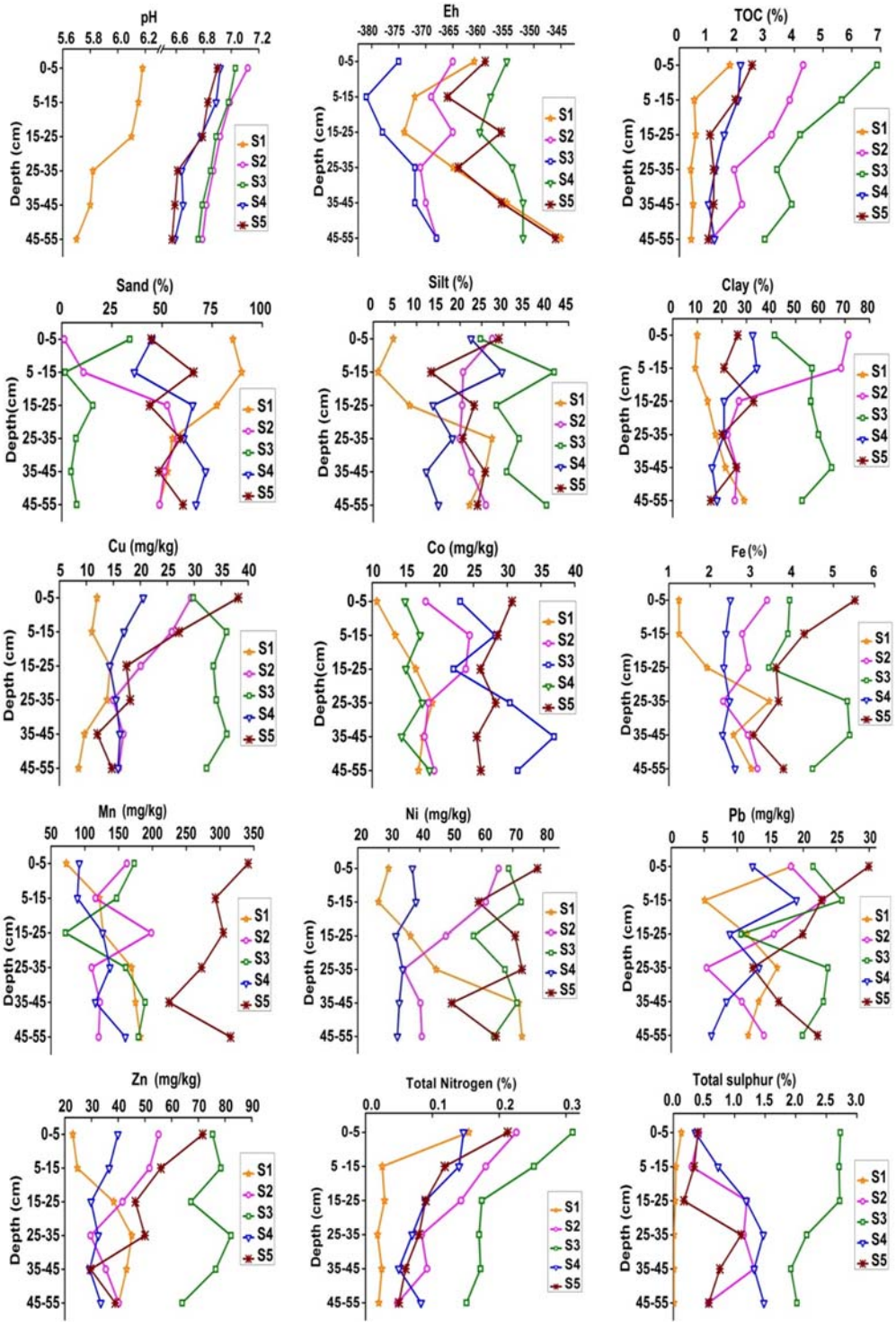
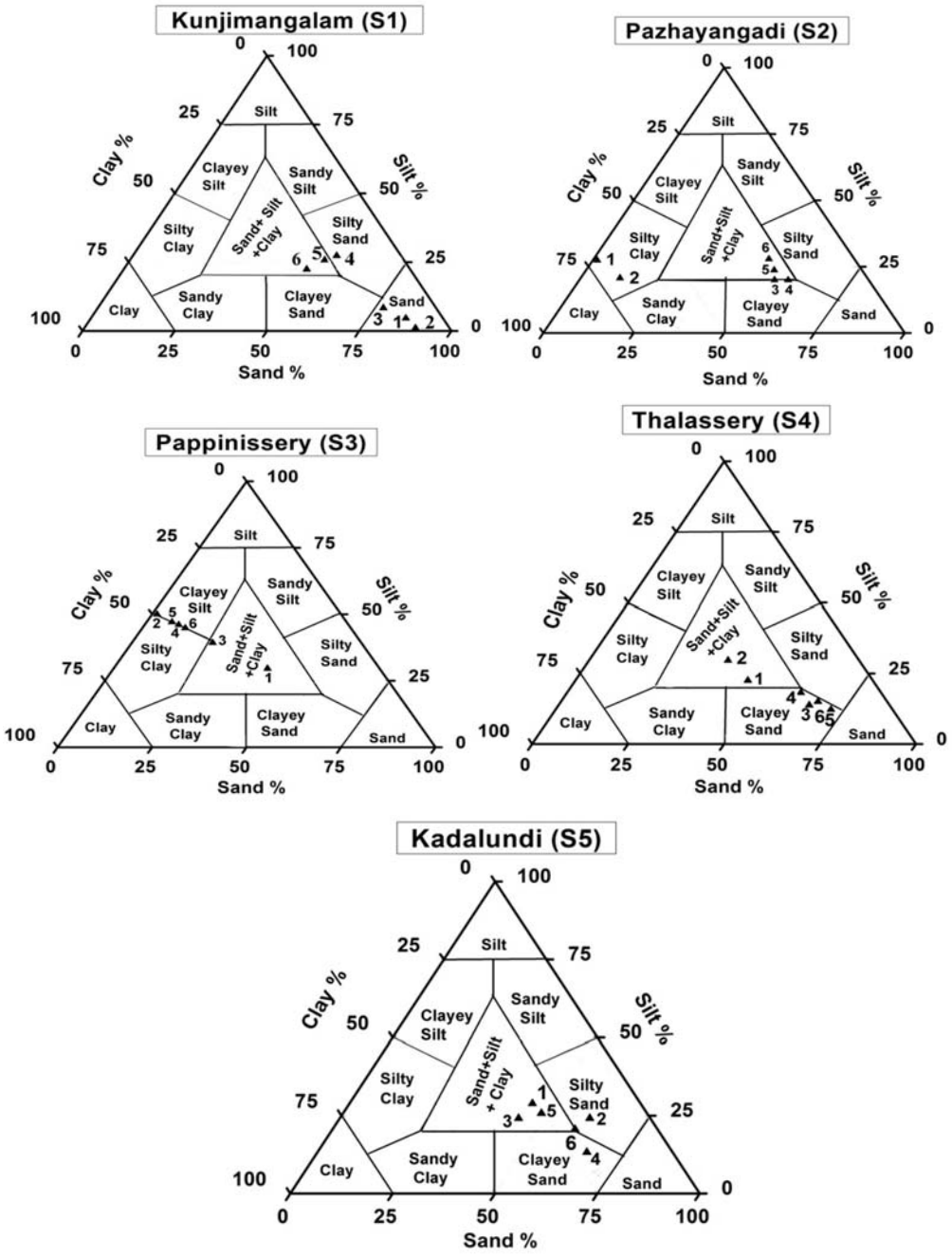


Figure 3.1 Vertical profiles of estimated parameters



1= 0-5cm, 2= 5-15cm, 3= 15-25cm, 4=25-35cm, 5= 35-45cm, 6= 45-55cm

Figure 3.2 Ternary diagram for the sediment samples

Table 3.1 Range of concentration of estimated parameters in the study area (Average ±Standard deviation).

Parameters	Stations				
	S1	S2	S3	S4	S5
pH	5.7 to 6.18 (5.96±0.21)	6.79 to 7.12 (6.92±0.12)	6.76 to 7.03 (6.88±0.11)	6.59 to 6.92 (6.75±0.14)	6.57 to 6.9 (6.72±0.14)
Eh (mv)	-374 to -345 (-355±3)	-371 to -365 (-374±5)	-381 to -368 (-368±3)	-360 to -352 (-362±11)	-366 to -346 (-358±7)
Sand (%)	48.76 to 89.72 (68.21±18.04)	1.22 to 57.78 (37.07±24.40)	1.66 to 33.92 (11.70±11.82)	36.2 to 71.73 (57.67±13.97)	43.87 to 65.78 (53.73±9.26)
Silt (%)	1.08 to 27.34 (14.90 ± 11.54)	19.94 to 27.42 (22.86 ± 3.14)	41.69 to 24.7 (33.18 ± 6.62)	12.24 to 29.65 (18.58 ± 6.54)	13.32 to 28.94 (22.67 ± 5.34)
Clay (%)	9.2 to 29.06 (16.90 ± 7.52)	22.28 to 71.36 (40.07 ± 23.18)	41.39 to 64.63 (55.12± 7.82)	16.04 to 34.15 (23.75 ± 7.66)	15.5 to 32.86 (23.60 ± 6.06)
TOC (%)	0.4 to 1.76 (0.69±0.53)	1.12 to 4.31 (2.76±1.23)	2.97 to 6.88 (4.50 ±1.48)	1.02 to 2.13 (1.54±0.46)	1.01 to 2.53 (1.49±0.61)
TN (%)	0.02 to 0.15 (0.05±0.02)	0.05 to 0.23 (0.13±0.07)	0.15 to 0.31 (0.20±0.06)	0.05 to 0.15 (0.10±0.04)	0.05 to 0.21 (0.10± 0.06)
TS (%)	0.10 to 0.13 (0.04 ± 0.05)	0.3 to 1.32 (0.83 ± 0.45	1.92 to 2.73 (2.38 ± 0.38)	0.36 to 1.48 (1.09 ± 0.45)	0.17 to 1.11 (0.56 ± 0.34)
Cd (mg/kg)	ND to 0.56 (0.25 ±0.24)	ND to 1.84 (0.34 ± 0.74)	ND to 1.30 (0.52 ±0.53)	0.05 to 0.77 (0.42±0.35)	0.12 to 1.78 (0.79±0.71)
Co (mg/kg)	10.7 to 18.92 (15.66±2.76)	17.75 to 24.43 (20.25±2.80)	22.04 to 36.94 (28.70±5.09)	14.37 to 18.52 (16.22±1.54)	25.49 to 30.72 (27.54 ±1.84)
Cu (mg/kg)	8.55 to 14.39 (11.57±2.30)	14.96 to 29.42 (20.52±5.87)	29.81 to 36.05 (33.63 ± 2.37)	14.33 to 20.55 (16.57±2.13)	12.03 to 38.17 (21.27±9.73)
Fe (%)	1.25 to 3.44 (2.24±0.92)	2.32 to 3.39 (2.92±0.36)	3.43 to 5.40 (4.41±0.81)	2.31 to 2.61 (2.43±0.11)	3.06 to 5.53 (3.99±0.85)
Mn (mg/kg)	72.58 to 182.05 (141.28±42.16)	110.09 to 198.27 (138.26±34.75)	71.45 to 189.12 (153.47±42.76)	89.15 to 159.96 (120.07±27.19)	224.47 to 341.55 (292.05±40.27)
Ni(mg/kg)	26.65 to 72.99 (47.30±20.52)	34.77 to 65.43 (48.48±12.41)	57.33 to 72.71 (66.92±5.62)	32.28 to 38.78 (34.90±2.69)	50.26 to 78.02 (65.95±10.16)
Pb (mg/kg)	5.06 to18.24 (12.61±4.54)	5.35 to 23.02 (14.46±6.09)	10.57 to 25.83 (20.76±5.39)	6.09 to 18.95 (11.32±4.59)	12.36 to 29.93 (20.57±6.02)
Zn (mg/kg)	23.01 to 45.11 (36.25±9.85)	29.66 to 55.1 (42.28±9.64)	63.94 to 82.21 (73.93±6.96)	29.34 to 39.88 (33.62±4.05)	29.69 to 71.66 (48.79±14.45)

3.3 Discussion

3.3.1 General sedimentary parameters

Analysis of the general sedimentary parameters showed highly negative values for redox potential which pointed towards the existence of anoxic (highly reducing) condition in the study region. ANOVA revealed significant vertical variation for sand, silt and clay ($P<0.01$), however the spatial variation was found to be insignificant. Highly significant spatial as well as depth wise variation was noticed for TOC and TN ($P<<0.01$). Surface samples (0-5cm) recorded higher TOC and TN contents at all stations. The maximum TOC and TN contents were recorded at S3 and the minimum at S1. It has already been established that mangrove environments act as reservoir of organic carbon (Matsui, 1998; Fujimoto et al., 1999) and in some mangroves; organic rich sediment extended to several meters of depth had already been established (Twilley et al., 1992; Lallier-Vergès et al., 1998). In the present study, the total organic carbon ranging from 0.4 to 6.88 % was recorded. However, a down core decrease in TOC was noticed in the present investigation. According to John, 2003, macrobenthic activities in sediment may lead to the variation of total organic carbon among the top 3cm of the sediment (mangrove macrobenthos are those species that live in mangrove muds or depend on mangroves for all or part of their life-cycle). The observed down core decrease in TOC might be attributed to bacterial mineralisation. Mangrove organic-rich sediments are subjected to various diagenetic processes. Sulphate reduction is thought to be the dominant process, but aerobic respiration as well as Fe and Mn respiration also may have important role in organic matter decomposition pathways in mangrove sediments (Alongi et al., 1998; 2000; Kristensen, 2000). According to Kristensen, 1997, the most significant primary source of detritus in mangrove environment is the litter fall. Higher concentrations of

TOC at S2 and S3 might be due to the greater availability of litter at these stations compared to the other stations. Present investigation deduced the fact that the grain size has effectively played a significant role in the retention of organic matter in the sediments of the study area. The fine grained sediment at S2 and S3, facilitated trapping of particles enriched with organic matter entering the mangrove ecosystem, resulting in higher TOC at these stations, whereas the inability of sandy sediment to trap fine particles resulted in lower TOC content at S1. Elevated levels of TOC may be attributed to decomposition of dead organisms and mangrove detritus, domestic sewage and anthropogenic inputs. The restricted tidal activity and thick population of mangroves enhanced the retention of organic carbon at S2 and S3. High tidal flushing at S4 and S5 which are located near the Sea front exhibited low organic carbon content since it could have removed as readily as it was formed. Concentration of total nitrogen in sediments can be used as a suitable indicator to assess the contribution from aquatic flora to marine sediments (González- Vila et al., 2003). The observed high levels of TN at the surface might be due to the direct input of nitrate compounds from external sources; mainly from the agricultural runoff and domestic sewage (Purvaja and Ramesh, 2000; Subramanian, 2004). Lesser nitrification rate and degradation of organic nitrogen compounds into inorganic form might have resulted in the lower levels of nitrogen with depth (Krishna Prasad and Ramanathan, 2008).

3.3.2 Distribution of metals in core sediments

The study of sediment cores has been considered as an excellent tool for establishing the effects of anthropogenic and natural processes on depositional environments (Vinodhini and Narayanan, 2008; Nadia, 2009; Seshan et al., 2010). Most of the contaminants leave their finger prints in sediments. The only condition is the stability within sedimentary column, i.e., no or insignificant

post-depositional mobility is allowed (Tam and Wong, 2000). The geochemical mobility of heavy metals in sediments depends on the nature of sediment phase and their chemical form, which are governed by physico-chemical and biological characteristics of the environment. Variations and concentration profile of heavy metal content with depth or between mangrove areas are attributed from complex diagenetic processes (Marchand et al., 2006), and this observation can be applicable to present scenario. The anthropogenic input of heavy metals in the study area was found to be negligible since there are no large-scale industries around the sampling locations, which carry out metal processing operations. The higher content of metals in various segments can be attributed to the rapid and efficient removal mechanism by adsorption onto clay minerals, precipitation as well as incorporation into biogenic materials (Alongi et al., 1996; Cho et al.,1999). Fine grained sediments provide higher specific mineral surfaces and stimulate the accumulation of higher concentration of heavy metals (Marchand et al., 2006).

The redox conditions and the decay of organic matter, which is linked with the cycling of Fe and Mn, found to have a control over the concentrations and associations of heavy metals in the study area. It has already been demonstrated that metals can be adsorbed onto the surface of minerals (clay minerals), Fe and/or Mn oxy-hydroxides (Quémerais et al., 1998; Dong et al., 2000). The mobility of heavy metals in sediments is severely limited by strong sorption reaction between metal ions and negatively charged particles of sediment (Stumm, 1987). Under the influence of suboxic conditions, Pb, Ni and Co can be effectively adsorbed on to Mn oxides (Lienemann et al., 1997; Zwolsmann and van Eck, 1999; Dong et al., 2000), which serves as a host phase affecting the distribution pattern and accumulation of trace metals. Higher concentrations of trace metals in various segments of the sediments might also be attributed to

active sulphide co-precipitation which rapidly removes Co, Cu, Ni, Pb and Zn from the dissolved phase to sedimentary phase under anaerobic conditions (Balistrieri et al., 1994; Clark et al., 1998; Schlieker et al., 2001).

In surficial sediments, the variation of metals may take place due to river and/or rain water run-off (Saenger et al., 1991). The stations, S4 and S5 are river influenced during monsoon. The initial distributions of metals can be subsequently modified by seasonal variations in chemical conditions of the sampling sites. The diffusion of metals to a sink located below the sediment - water interface take place whenever the dissolved metal concentrations are higher in water column than in pore-waters (Carignan and Nriagu, 1985; Carignan et al., 1985). This process ultimately results in subsurface peaks in sedimentary metals that could be attributed to variation in metal depositions (Natesan and Seshan, 2010). The subsurface peaks observed for Cu and Ni at S3, Pb at S2, S3 and S4, Co at S1, S2, S3 and S4 might be due to the aforementioned reason. After the deposition of trace metals, they can be mobilized and then can be either relocalised in the sediment phase (Gobeil et al., 1987; Gobeil and Cossa, 1993; Mc Corkle and Klinkhammer, 1993) or diffuse to the water column (Morfett et al., 1998). These processes results in elevated levels of metals at various segments of the core. The physical processes associated with bioturbation operating in the study area (mainly at S2 and S3) govern the accumulation and distribution pattern of heavy metals. The burrowing and feeding activities of benthic organisms in upper layers of sediments ultimately results in mixing which in effect homogenises the concentration of metals in the mixing zone (Mattisoff, 1995). The burrowing crabs were found at S2 and S3, and hence metal concentration gets homogenised in the mixing zone in these stations.

Many authors inferred the fact that heavy metal concentrations in mangrove sediments are usually quite high (Lacerda et al., 1988; Tam and Wong, 2000). Mangrove sediments can act as a long term sink for heavy metals because of their precipitation with sulphides during diagenetic reactions and the relative higher stability of these minerals (Huerta-Diaz and Morse, 1992). Mangrove sediments have the ability to trap materials from water column and their high organic matter content is the major reason for the richness of heavy metals in sediments. The enrichment of heavy metals can also be derived from anthropogenic metal loadings carried by the upstream of tributaries (Marchand et al., 2011). The high concentration of heavy metals in mangrove sediment might be due to anthropogenic activities, proximity to harbour, landfill, industries etc. (Clark et al., 1998; Machado et al., 2002). The variations in the distribution of metals are considered to be due to sediment characteristics like grain size, organic carbon content and presence of mangrove forests which generate physicochemical conditions suitable for the accumulation of the metals in the mangrove ecosystems (Habison, 1986). Distinct trends of metals, from surface to bottom of core, results from the differences in sources and associations of metals in these sediments. The estimated levels of heavy metals were within the comparable range with previous studies in mangrove sediments along Indian Coast; however, concentration of zinc was lower during the present investigation (Sarika and Chandramohanakumar, 2008; Ramanathan et al., 1999; Ratheesh Kumar et al., 2010; Volvoikar and Nayak, 2013).

Organic matter content along with pH is an important parameter controlling heavy metal behaviour in sediments (Natesan and Seshan, 2010). pH exhibited strong correlation with Cu ($r = 0.65$), Co ($r = 0.39$), Fe ($r = 0.38$) and Zn ($r = 0.41$). Significant correlation of total organic carbon (TOC) with

metals reveals the formation of organic complexes with heavy metals by flocculation and subsequently influences their distributions, due to its high specific surface area. Significant correlation between metals with each other indicates their identical behaviour and origin from common source. Toxic trace metals such as Pb and Cd are found to be strongly correlated. The absence of any significant correlation of Cd with granulometric variables indicated its origin from anthropogenic sources. Zn has higher affinity for S and tendency to form sulphide phases (Thornton, 1983; Alloway, 1990). Highly significant positive correlations of Zn with total sulphur ($r = 0.57$) in the present study supports this observation.

The geochemistry of iron and organic matter are found to affect the behaviour of the majority of other trace metals in aquatic environment (Fang and Hong, 1999). Following their release to the environment the heavy metals are efficiently scavenged by newly precipitated Fe and Mn hydroxides (Sarika and Chandramohanakumar, 2008). In the present investigation, Fe exhibited significant association with other heavy metals like Cu, Ni, Co, Mn, and Pb along with TOC, which revealed its key control over the linkage of these metals with organic matrix by association as Fe-oxy-hydroxides. Similar observation was also noticed by Rubio et al., 2000 in the sediments of the Ria de Vigo (NW Spain). The association of Co, Pb and Ni with Mn and Fe suggest that Fe and Mn-oxyhydroxides plays a good role as host phase for these metals. The coagulation-flocculation of metals as colloids with hydrous iron oxide have already been reported (Balachandran et al., 2005).Thus, the redox conditions and decay processes affecting the organic matter control the cycling of Fe and Mn, which in turn control the concentrations and associations of heavy metals (Marchand et al., 2006).

Table 3.2 Correlation matrix of analyzed parameters (n=30)

	pH	Eh	TOC	Sand	Silt	Clay	TN	TS	Cu	Cd	Co	Pb	Ni	Fe	Mn	Zn
pH	1															
Eh	-0.34	1														
TOC	0.68 (**)	-0.61 (**)	1													
Sand	-0.43 (*)	0.40 (*)	-0.67 (**)	1												
Silt	0.19	-0.15	0.35	-0.69 (**)	1											
Clay	0.45 (*)	-0.44 (*)	0.69 (**)	-0.93 (**)	0.37 (*)	1										
TN	0.60 (**)	-0.63 (**)	0.94 (**)	-0.75 (**)	0.44 (*)	0.74 (**)	1									
TS	0.53 (**)	-0.48 (**)	0.70 (**)	-0.47 (**)	0.45 (*)	0.37 (*)	0.72 (**)	1								
Cu	0.65 (**)	-0.55 (**)	0.79 (**)	-0.73 (**)	0.47 (**)	0.69 (**)	0.85 (**)	0.60 (**)	1							
Cd	0.12	0.36 (*)	0.10	-0.21	0.29	0.12	0.17	0.03	0.25	1						
Co	0.39 (*)	-0.27	0.42 (*)	-0.57 (**)	0.52 (**)	0.47 (**)	0.49 (**)	0.41 (*)	0.71 (**)	0.25	1					
Pb	0.34	-0.14	0.50 (**)	-0.55 (**)	0.42 (*)	0.49 (**)	0.48 (**)	0.13	0.66 (**)	0.39 (*)	0.69 (**)	1				
Ni	0.12	-0.07	0.41 (*)	-0.59 (**)	0.51 (**)	0.50 (**)	0.52 (**)	0.19	0.56 (**)	0.36	0.74 (**)	0.68 (**)	1			
Fe	0.38 (*)	-0.25	0.47 (**)	-0.67 (**)	0.65 (**)	0..52 (**)	0.56 (**)	0.42 (*)	0.79 (**)	0.36	0.88 (**)	0.69 (**)	0.75 (**)	1		
Mn	0.03	0.31	-0.11	0.01	0.21	-0.13	-0.05	-0.18	0.17	0.47 (**)	0.63 (**)	0.50 (**)	0.62 (**)	0.54 (**)	1	
Zn	0.41 (*)	-0.51 (**)	0.74 (**)	-0.77 (**)	0.59 (**)	0.68 (**)	0.82 (**)	0.57 (**)	0.91 (**)	0.24	0.77 (**)	0.70 (**)	0.76 (**)	0.87 (**)	0.28	1

*Correlation significant at 0.05 level
** Correlation significant at 0.01 level

3.4 Trace metal contamination

The high concentration of heavy metals in mangrove sediments might be due to anthropogenic activities, land fill, proximity to harbor and industrial areas etc. The degree of pollution in sediments can be estimated by determining the enrichment factor and geoaccumulation index.

3.4.1 Enrichment factor

Enrichment factor estimated as the ratio of metal with that of crustal average, which acts as an efficient tool for regional comparison of trace metals content in sediments (Nolting et al., 1999). Iron was used as normaliser because the geochemistry of iron exhibit close similarity with that of most other trace metals both in oxic and anoxic environments. Furthermore, the natural concentrations of Fe in sediments are observed to be more uniform compared to aluminum and beyond the influence of anthropogenic activities justify its credibility as a normaliser (Daskalakis and O'Connor, 1995). The enrichment factor (EF) was calculated for each metal, using iron as normalising element using the equation,

EF = (metal/ Fe) sediment/ (metal/ Fe) crust.

As per the classification, value of EF < 1.5 suggests that the trace metals may be originated entirely from crustal materials or natural weathering processes (Zhang and Liu, 2002; Feng et al., 2004). However, an EF value >1.5 implies that a significant portion of the trace metal is delivered from non-crustal materials or non-natural weathering (Feng et al., 2004). EF values were interpreted as suggested by Birth, (2003), for metals studied with respect to natural background concentration (Table 3.3)

Table 3.3 Enrichment factor (EF) values as interpreted by Birth, 2003

Enrichment factor	Pollution status
EF <1	No enrichment
EF= 1-3	Minor enrichment
EF= 3-5	Moderate enrichment
EF= 5-10	Moderately severe enrichment
EF = 10-25	Severe enrichment
EF= 25-50	Very severe enrichment
EF> 50	Extremely severe enrichment

The estimation of enrichment factor revealed no enrichment for Cu, Mn and Zn. EFs <1 for these metals in the sediment indicated their origin is predominantly from lithogenous material and suggested the absence of contamination by these metals in the study region. However EF values for Cd reflected no enrichment to moderately severe enrichment. Cobalt exhibited moderate enrichment for all samples. Minor enrichment to moderately severe enrichment was recorded for Pb while Ni showed no enrichment to minor enrichment. The observations pointed out that the mangrove sediments are polluted by Cd, Pb, Co and Ni and acts as a sink for these heavy metals contributed from a multitude of anthropogenic sources.

3.4.2 Geoaccumulation index

Geoaccumulation index (Igeo), put forwarded by Müller (1979), can be utilised for the determination of the extent of heavy metal pollution in sediment and it provides a better estimate of the anthropogenic inputs (Ridgway and Shimmield, 2002).The geoaccumulation Index can be determined according to the equation,

$$I_{geo} = \log_2 (C_n/1.5B_n),$$

where C_n=measured concentration of heavy metal in the mangrove sediment, B_n =geochemical background value in average shale (Wedepohl, 1995) of element n, 1.5 is the background matrix correction in factor due to lithogenic effects. The average shale value is a highly efficient, quick and practical data base for evaluating the enrichments of trace metal in finely grained sediments (Forstner and Wittmann, 1981). According to I_{geo} classification degree of pollution can be classified into six classes (Table 3.4).

Table 3.4 Igeo classification

Igeo class	Igeo value	Degree of pollution
0	Igeo < 0	unpolluted
1	Igeo =0-1	unpolluted to moderately polluted
2	Igeo =1-2	moderately polluted
3	Igeo=2-3	moderately to strongly polluted
4	Igeo=3-4	strongly polluted
5	Igeo=4-5	strongly polluted to very strongly polluted
6	Igeo > 5	very strongly polluted

The I_{geo} analysis revealed that 100% of the samples fall in Class 0 (I_{geo}<0) for the metals Cu, Pb, Ni, Fe, Mn and Zn which indicated that sediment samples are unpolluted with respect to these metals. However in the case of Cd, 27 % of the samples exhibited unpolluted to moderately polluted condition, 10% revealed moderately polluted condition, 3% fall into the class 3 i.e., moderately to strongly polluted condition and the rest of the samples were unpolluted . The I_{geo} value for cobalt also indicated that 13 % of the samples were in class 1(unpolluted to moderately polluted condition) and rest in the class zero. The EF and I_{geo} of heavy metals in the study area is furnished in table 3.5.

Table 3.5 Enrichment factor and Geoaccumulation Index of heavy metals in the study area

Station	Depth (cm)	Cu		Cd		Co		Pb		Ni		Mn		Zn		Fe
		EF	Igeo	EF	Igeo	EF	Igeo	EF	Igeo	EF	Igeo	EF	Igeo	EF	Igeo	Igeo
S1	0-5	0.86	-1.7	0.8	-1.8	1.5	-0.9	1.1	-1.3	1.0	-1.4	0.2	-3.8	0.8	-1.8	-1.5
	5-15	0.74	-2.0	0.8	-1.9	1.8	-0.7	1.8	-0.7	1.1	-1.4	0.2	-3.8	0.8	-2.0	-1.6
	15-25	0.64	-2.2	0.3	-3.2	1.6	-0.9	0.9	-1.8	0.94	-1.7	0.3	-3.3	0.6	-2.3	-1.6
	25-35	0.65	-2.1	4.5	0.7	1.8	-0.7	1.2	-1.2	0.97	-1.6	0.3	-3.2	0.7	-2.1	-1.5
	35-45	0.74	-2.1	5.3	0.8	1.6	-1.0	0.8	-1.8	0.95	-1.6	0.3	-3.5	0.6	-2.3	-1.6
	45-55	0.64	-2.1	4.4	0.7	1.8	-0.6	0.5	-2.3	0.94	-1.6	0.3	-3.0	0.6	-2.1	-1.4
S2	0-5	0.79	-1.2	3.1	0.8	1.5	-0.3	1.3	-0.5	1.2	-0.6	0.2	-2.9	0.9	-0.9	-0.8
	5-15	0.97	-0.9	0.2	-3.2	1.8	-0.1	1.5	-0.2	1.3	-0.5	0.2	-3.1	0.9	-0.9	-0.9
	15-25	0.99	-1.0	0.0	0.0	1.6	-0.4	0.7	-1.5	1.2	-0.8	0.1	-4.2	0.9	-1.1	-1.0
	25-35	0.67	-1.0	3.8	1.5	1.4	0.1	1.0	-0.3	0.9	-0.6	0.2	-3.0	0.8	-0.8	-0.4
	35-45	0.70	-0.9	0.5	-1.4	1.7	0.4	1.0	-0.4	0.9	-0.5	0.2	-2.8	0.7	-0.9	-0.4
	45-55	0.75	-1.1	2.8	0.9	1.8	0.1	1.0	-0.6	1.0	-0.7	0.2	-2.8	0.7	-1.2	-0.7
S3	0-5	0.91	-1.2	8.5	2.0	1.3	-0.7	1.2	-0.7	1.3	-0.6	0.3	-3.0	0.8	-1.4	-1.1
	5-15	0.97	-1.4	0.0	0.0	2.2	-0.2	1.9	-0.4	1.5	-0.7	0.2	-3.5	0.9	-1.5	-1.3
	15-25	0.72	-1.7	0.9	-1.1	2.0	-0.3	1.2	-0.9	1.1	-1.1	0.4	-2.7	0.7	-1.8	-1.3
	25-35	0.67	-2.2	0.0	0.0	2.0	-0.6	0.5	-2.5	1.0	-1.6	0.3	-3.5	0.6	-2.3	-1.6
	35-45	0.60	-2.0	0.0	0.0	1.5	-0.7	0.9	-1.5	0.9	-1.3	0.2	-3.4	0.6	-2.0	-1.3
	45-55	0.53	-2.1	0.0	0.0	1.5	-0.6	1.0	-1.1	0.9	-1.3	0.2	-3.4	0.6	-1.8	-1.2
S4	0-5	0.99	-2.5	2.4	-1.2	2.1	-1.4	3.4	-0.7	1.7	-1.8	0.3	-4.1	0.9	-2.6	-2.5
	5-15	0.92	-2.6	0.0	0.0	2.7	-1.1	0.9	-2.6	1.5	-1.9	0.5	-3.4	0.9	-2.5	-2.5
	15-25	0.78	-2.2	0.0	0.0	2.1	-0.8	1.4	-1.4	1.3	-1.5	0.4	-3.3	0.9	-1.9	-1.9
	25-35	0.42	-2.3	2.2	0.1	1.4	-0.6	1.1	-0.9	0.9	-1.2	0.3	-2.9	0.6	-1.7	-1.0
	35-45	0.39	-2.8	3.4	0.3	1.7	-0.7	1.2	-1.2	1.9	-0.5	0.4	-2.9	0.8	-1.7	-1.5
	45-55	0.30	-3.0	1.5	-0.6	1.4	-0.8	0.9	-1.4	1.7	-0.5	0.3	-2.8	0.7	-1.8	-1.2
S5	0-5	0.72	-0.8	4.2	1.7	1.4	0.1	1.3	-0.1	1.0	-0.4	0.3	-1.9	0.6	-1.0	-0.4
	5-15	0.66	-1.3	0.8	-1.1	1.7	0.0	1.2	-0.4	0.9	-0.8	0.4	-2.1	0.6	-1.3	-0.7
	15-25	0.50	-2.0	1.1	-0.9	1.8	-0.1	1.3	-0.6	1.4	-0.5	0.5	-2.1	0.6	-1.6	-1.0
	25-35	0.52	-1.9	0.5	-1.9	1.9	-0.1	0.8	-1.3	1.4	-0.5	0.4	-2.2	0.7	-1.5	-0.9
	35-45	0.41	-2.5	4.5	1.0	2.1	-0.2	1.2	-0.9	1.1	-1.0	0.4	-2.5	0.5	-2.3	-1.2
	45-55	0.41	-2.2	7.3	2.0	1.7	-0.1	1.4	-0.4	1.2	-0.7	0.5	-2.0	0.5	-1.9	-0.9

3.4.3 Sediment quality guidelines

Numerical Sediment Quality Guidelines (SQGs) have been used to identify heavy metal contaminants which can induce adverse ecological effects in aquatic ecosystems (MacDonald et al., 2000) and found to be useful for initial evaluation of sediment toxicity in the absence of data on direct biological effects (Birch and Taylor, 2002). SQGs (Table 3.6) were applied to this study for the assessment of the eco-toxicological sense of trace element concentrations in sediments with the threshold effect level (TEL), probable effect level (PEL), effects range low (ERL) and effects range median (ERM) guideline values (MacDonald et al., 1996; Long et al., 1998). The TEL denotes chemical concentrations below which adverse biological effects rarely occur, and the PEL represents contaminant concentrations above which adverse biological effects frequently occur. The concentrations below the ERL represent a minimal - effects range while concentrations equal to and above the ERL but below the ERM, represent a probable effects range within which effects would frequently occur (Long et al., 1995). In the present study, there was no or rare biological effects as almost all metals were analysed except Ni. The guidelines for ERL-ERM range (in µg/g) are tabulated (Table 3.6). Pb, Cu and Zn concentrations revealed <ERL class for all the samples, except Cu at S2 (5-15cm, 35-45cm). Most of the samples recorded concentrations below ERL range in the case of Cd (except S2: 25-35cm, S3: 0-5cm, S5: 0-5 and 45-55cm). Estimated Ni content exceeded ERL but were below ERM at S1 and S3, while all samples at S2 and S5 exceeded ERM target value and samples from S3 (0-5 and 5-15cm) and S4 (35-45 and 45-55cm) also recorded levels above ERM and these results suggested that Ni concentrations in the study region may induce serious effects on benthic organisms.

Table 3.6 Screening quick reference for heavy metals in marine sediment

Metal	Threshold Effects Level (TEL)	Probable Effects Level (PEL)	Effects Range Low (ERL)	Effects Range Median (ERM)
Cu	18.7	108.2	34	270
Pb	30.2	112.2	46.7	218
Zn	124	271	150	410
Ni	15.9	42.8	20.9	51.6
Cd	0.68	4.21	1.2	9.6

3.5 Conclusion

Analysis of general sedimentary parameters showed high negative values for Eh, the redox potential, which reflected the anoxic nature of sediments. Surface samples (0-5cm) recorded comparatively higher TOC and TN content. Remarkable down core decrease in TOC was observed which may be due to bacterial mineralisation. Variability in concentration of heavy metals in the sediments, among the mangrove ecosystems can be attributed to the terrestrial inputs, hydrodynamic process and depositional conditions. Heavy metal content generally increased with decreasing particle size of the sediment and the observed strong positive correlation of the metals with Fe, Mn and organic carbon indicated that these constituents play a major role in the vertical distribution. The correlation of most metals with Fe pointed towards the role of Fe-oxy hydroxides as adsorption sites for other metals; since Fe is a major constituent of laterite soil. Estimated enrichment factor revealed that the mangrove sediments were contaminated with Cd, Pb, Co and Ni and acts as a sink for these heavy metals contributed from a multitude of anthropogenic sources, whereas I_{geo} indicated that the sediments from S5 were found to be moderately polluted with respect to Cd. The results of this study would provide a useful aid for assessment of existing environmental conditions and sustainable management of the mangrove forests in the region.

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Chapter 4

BIOGEOORGANICS

4.1 Introduction

Composition of organic matter in marine sediments is usually governed by the processes including in situ production, lateral advection, allochthonous inputs, interaction of organic matter with mineral particles and the prevailing redox conditions (Cowie and Hedges, 1992; Hedges and Keil, 1995; Hartnett et al., 1998). The quantity and quality of organic matter preserved in sediments exhibit wide fluctuations depending on the nature of material transported to the sediment, types of contributing agents to the sediment (e.g., lignins from higher plants are the main sources of aromatic compounds to the sediments, while plankton and bacteria contribute primary aliphatic materials) and on the characteristics of the depositional environment. Inputs of sedimentary organic matter are classified as autochthonous, if they originate at or close to the site of deposition, or allochthonous, if they are transported from another environment. Autochthonous sources in aquatic environments include the remains of phytoplankton, input of organisms that feed directly or indirectly on

phytoplankton, and that of phytoplankton deposited in the upper layers of sediment. Allochthonous organic materials are mostly derived from higher plants, usually transported by water from adjacent areas of land to the deposition site. Both allochthous and autochthonus organic compounds which are resistant to degradation and those which survive diagenesis (the process of organic matter remineralisation) are stored in sedimentary environment depending on redox status.

The organic matter in marine sediments is usually composed of labile and refractory compounds. The labile fraction of organic matter contains simple compounds or biopolymers (which includes carbohydrates, lipids and proteins), representing the bioavailable fraction of organic matter to benthic consumers (Fabiano et al., 1995; Dell'Anno et al., 2002). These are usually referred to as biochemical components. Determinations of biochemical composition have been employed to investigate the origin and parameters controlling diagenetic fate of organic matter in the sediments (Colombo et al., 1996). The assessment of quality and quantity of organic matter, whether labile or refractory, is a crucial step for explaining the diagenetic processes taking place in mangrove ecosystems.

Biogeochemical processes taking place in mangrove forests have been recognised as highly complex, due to the input from allochthonous as well as from autochthonous sources in to the sedimentary organic matter (Joseph et al., 2008). Even though, the biochemical composition of sedimentary organic matter has widely been researched in a number of marine ecosystems (Danovaro et al., 1993; Danovaro et al., 1994; Fabiano and Danovaro, 1994; Fabiano et al., 1995; Pusccedu et al., 1999), in and around Cochin estuary

(Geetha et al., 2008; Joseph et al., 2008; Joseph et al., 2012), there is a noticeable lack of information about concentrations and variability of biochemical components in core sediments of mangrove ecosystems.

This chapter investigates the quality and quantity of organic matter in core sediments of five mangrove ecosystems in terms of the biochemical composition thereby identifying the major biogeochemical pathways. Elemental ratios (C/N) and stable carbon isotopic compositions of sedimentary organic matter were also used to characterise the source and fate of organic matter within marine environments. Simultaneous application of these bulk parameters improves the assurance of identifying the source of organic matter in marine sediments (Yamamuro, 2000; Joseph et al., 2012). Geochemical studies of sediment core profiles label the degree of processes by summarising various amounts of biogenic compounds (including biogenic alkanes, sterols, carbohydrates, protein, hydrocarbons, etc.) and provide useful information on the changes in the quality of the sediments from past period (Karbassi and Shankar, 2005; Al-Juboury, 2009; Ahmad et al., 2010; Chibunda et al., 2010, Akhil et al., 2013).

4.2 Results

The range of vertical variations of biochemical composition, chlorophyll pigments, elemental and stable carbon isotope ratios in the core sediments of mangrove ecosystem are furnished in table 4.1 and in figure 4.1.

Among the evaluated biochemical components, total carbohydrate ranged from 2.46 to 26.98 mg/g with minimum concentration at S1 (5-15cm) and maximum at S3 (0-5cm). Lipid content varied from 0.6 (S1; 25-35cm) to 33.5 mg/g (S3; 0-5cm); whereas the concentration of PRT ranged between

0.06 (S5; 15-25 cm) and 8.23 mg/g (S2; 0-5cm). The concentration of tannin and lignin varied from 0.04 to 11.17 mg/g at S1 (45-55cm) and S3 (0-5cm) respectively. In the case of CHO, stations S1, S4 and S5 exhibited similar vertical profile, i.e., a uniform down core distribution was observed after 15-25cm. The vertical trend of LPD, PRT and tannin and lignin were similar to that of CHO at S1, S4 and S5, while the vertical profile of CHO, LPD and PRT at S3 was entirely different. Comparatively higher CHO, LPD and tannin and lignin concentration was recorded at S3 while maximum content for PRT was recorded at S2. Relatively higher concentrations of biochemical components were recorded in surface sediments.

The sum of the total concentrations of biochemical components (carbohydrate, protein and lipid) has been recognised as labile organic matter (Joseph et al., 2008) and it recorded values ranging from 3.67 to 67.34 mg/g. The ratios of PRT to CHO, LPD to CHO and TOC to TN were estimated and the values varied from 0.02 to 0.47, 0.11 to 1.84 and 11.89 to 24.14 respectively. TOC/TN clearly pointed towards a marine input at S5, which is situated on the confluence of Arabian Sea. Among the chlorophyll pigment; chlorophyll-a recorded concentration between 0.08 and 15.37 µg/g while chlorophyll-b varied from 0.1 to 5.77µg/g and chlorophyll- c recorded values between 0.18 and 5.42 µg/g. The phaeophytin content varied from 1.56 to 21.6 µg/g. Similar to biochemical variables, chlorophyll pigments exhibited their maximum contents at surface sediments (0-5cm) and decreased vertically downwards in all stations. The observed enhanced levels of pigments at S3 indicated the higher productivity at this mangrove forest compared to other stations.

Table 4.1 The range of vertical variations of estimated parameters (Average ± standard deviation)

Parameters	Stations				
	S1	S2	S3	S4	S5
Carbohydrate (mg/g)	2.46 to 3.69 (3.13± 0.40)	3.44 to 24.63 (10.44± 7.76)	15.26 to 26.98 (23.55± 4.43)	3.64 to 11.37 (6.05 ± 3.07)	2.96 to 8.04 (5.03 ± 2.24)
Lipids (mg/g)	0.6 to 6.77 (2.11 ± 2.32)	3.61 to 17.58 (8.55± 5.49)	7.76 to 33.5 (15.37 ± 9.55)	0.49 to 2.47 (1.16± 0.75)	0.62 to 4.85 (2.40 ± 1.41)
Protein (mg/g)	0.44 to 1.74 (0.74 ± 0.50)	1.31 to 8.23 (3.33 ± 2.51)	2.14 to 6.85 (4.03 ± 1.70)	1.1 to 1.94 (1.45±0.38)	0.06 to 0.24 (0.12 ± 0.07)
LOM (mg/g)	4.37 to 12.2 (5.97 ± 3.06)	8.36 to 50.45 (22.32 ± 15.55)	25.53 to 67.34 (42.96 ±14.36)	5.45 to 15.77 (8.65 ± 4.13)	3.67 to13.13 (7.55 ± 3.60)
Tannin and Lignin (mg/g)	0.04 to 0.68 (0.20 ± 0.25)	1.03 to 9.42 (3.21 ± 3.12)	6.98 to 11.17 (8.72 ± 1.54)	0.37 to 1.02 (0.61±0.23)	0.47 to 1.23 (0.73 ± 0.30)
PRT/CHO	0.13 to 0.47 (0.23 ± 0.13)	0.26 to 0.44 (0.33 ± 0.07)	0.1 to 0.25 (0.17 ± 0.05)	0.17 to 0.35 (0.26 ± 0.07)	0.02 to 0.03 (0.02 ± 0.01)
LPD/ CHO	0.18 to 1.84 (0.64±0.61)	0.67 to 1.07 (0.87± 0.19)	0.41 to 1.24 (0.63 ± 0.31)	0.11 to 0.22 (0.18 ± 0.04)	0.21 to 0.6 (0.46 ± 0.15)
TOC/TN	11.40 to 22.22 (19.06 ± 3.86)	19.10 to 23.64 (22.10 ± 1.68)	19.64 to 24.14 (21.85 ± 1.72)	14.52 to 20.40 (16.56 ± 2.39)	11.89 to 20.20 (15.88 ± 3.67)
Chlorophyll a (Chl a, µg/g)	0.08 to 3.82 (0.95± 1.42)	1.38 to 12.48 (4.24 ± 4.12)	3.6 to 11.44 (6.55±2.93)	0.08 to 4.21 (1.04 ± 1.56)	1.26 to 15.37 (4.19±5.57)
Chlorophyll b (Chl b, µg/g)	0.1 to 0.79 (0.44 ± 0.23)	1.07-5.77 (2.08 ± 1.83)	1.47 to 4.37 (2.40 ± 1.06)	0.11 to 0.86 (0.48 ± 0.25)	0.18 to 3.48 (1.07 ± 1.25)
Chlorophyll c (Chl c, µg/g)	0.18 to 1.25 (0.43 ± 0.41)	1.04 to 5.27 (2.20 ± 1.59)	1.54 to 5.42 (3.35 ± 1.52)	0.22 to 1.5 (0.51 ± 0.49)	0.22 to 2.55 (0.78 ± 0.90)
Phaeophytin (phaeo, µg/g)	1.56 to 11.59 (3.76±3.91)	1.91 to 15.71 (6.90±4.94)	8.01 to 15.88 (11.48±3.12)	1.87 to 13.9 (4.51±4.69)	2.03 to 21.6 (6.62±7.58)
Chla/phaeo	0.05 to 0.33 (0.20 ± 0.09)	0.37 to 0.88 (0.61 ± 0.21)	0.45 to 0.72 (0.55±0.10)	0.04 to 0.3 (0.18 ± 0.09)	0.43 to 0.71 (0.57 ± 0.11)
$\delta^{13}C$ (‰)	-28.67 to -25.05 (-26.81 ± 1.45)	-29.19 to -25.55 (-26.96 ± 1.29)	-28.42 to -26.86 (-27.71 ± 0.63)	-27.76 to -25.79 (-26.56 ± 0.66)	-25.43 to -23.87 (-24.80 ± 0.60)

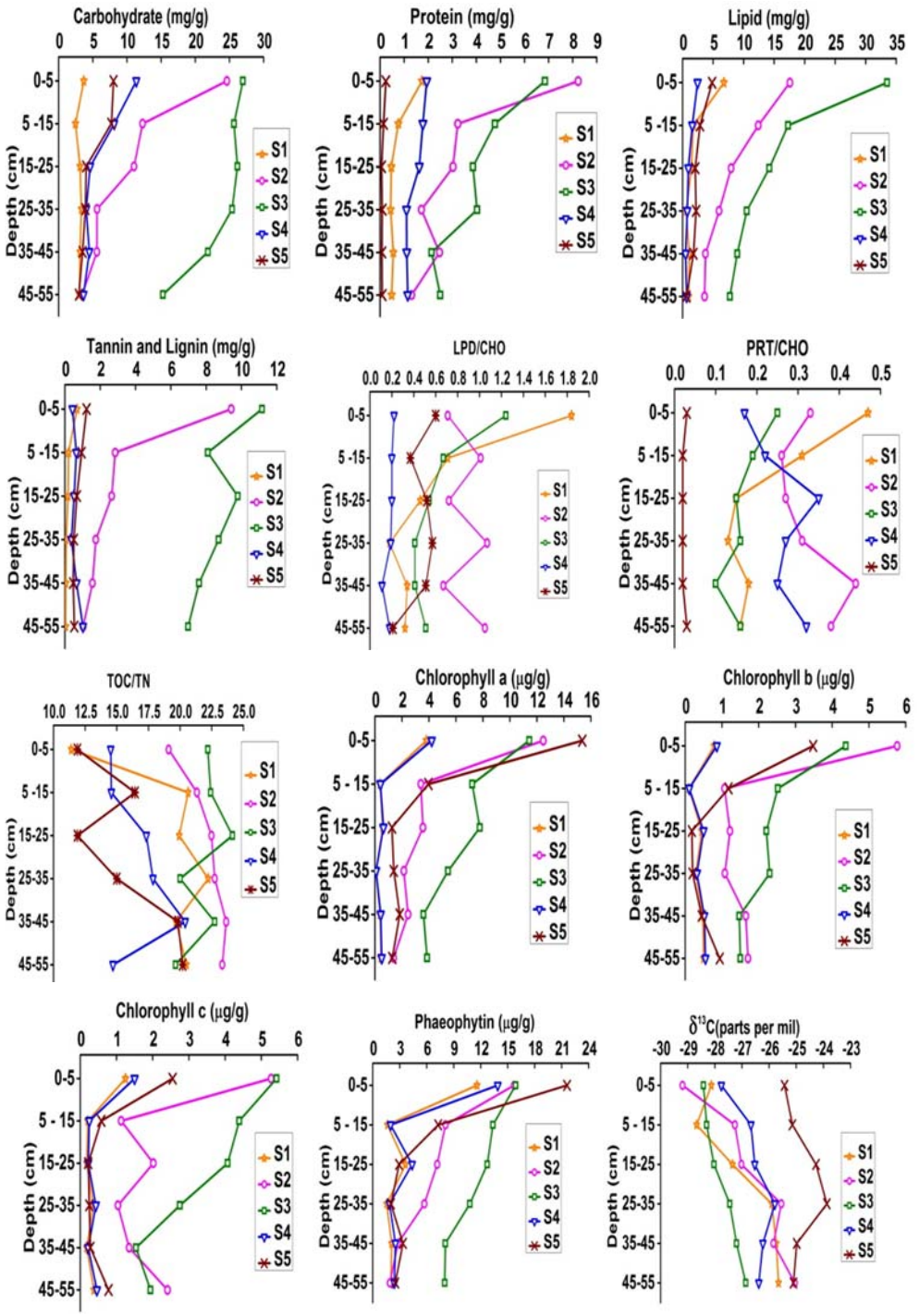

Figure 4.1 Down core variations of analysed parameters

4.3 Discussion

Sediments preserve records of water column processes and act as destination for the final storage of autochthonous and allochthonous organic matter inputs (Fabiano and Danovaro, 1994; Silva et al., 2011). Biogeochemical variables such as the depth of the water column, sedimentation rate, oxygen concentration, primary productivity and bioturbation activities may influence the fundamental processes accounting for the quantity and quality of sedimentary organic matter (Cowie and Hedges, 1992; Danovaro et al., 1999; Fiordelmondo and Pusceddu, 2004). In coastal areas, the sedimentary organic matter is the resultant of primary and secondary production within the ecosystem, inputs of terrestrial material and bacterial production in the sediments . The relative importance of these sources is determined by local factors such as climate, nutrient supply, hydrodynamic conditions of the water column etc. Changes in any of these factors, including anthropogenic involvements, may be reflected in the composition of sedimentary organic matter (Pinturier-Geiss et al., 2002).

A wide variety of organic carbon forms are present in sediments which ranges from freshly deposited litter to highly decomposed forms such as humus. Among them, some are labile and others are refractory. The sum of total carbohydrates, lipids and proteins has been considered as labile organic matter (LOM); which is readily available to benthic community (Fabiano et al., 1995; Dell'Anno et al., 2002) and undergo degradation easily, while refractory compounds such as humic acids are more resistant to degradation than labile ones. Determination of the labile fraction of organic matter is a prerequisite in assessing nutritional quality in benthic ecological studies (Incera et al., 2003).

The biochemical components in the study region recorded a dominance of CHO followed by LPD and PRT. The contribution of carbohydrates, lipids and protein towards LOM in the study region is furnished in tables 4.2 to 4.4 respectively. Prevalence of carbohydrates over proteins in mangroves of Cochin region has already been reported (Geetha et al., 2008). However, Joseph et al., 2008, recorded dominance of lipids followed by proteins and carbohydrates in mangroves of Cochin, which seemed to be quite different from other aquatic systems, where proteins and carbohydrates dominated over lipids. Renjith et al., 2012, observed the dominance of carbohydrates over lipids and proteins in Cochin estuarine system, which indicated the lower nutritive aspect of the organic matter, and their refractory and aged nature of sediment. The shallow water depth and high sedimentation rate in mangrove ecosystems assist the settling of organic matter without significant degradation. Comparatively higher concentrations of carbohydrate, lipid and protein were recorded at S2 and S3. Carbohydrate and lipid found to exhibit lower content at S4 while minimum concentration for protein was recorded at S5. The comparison of biochemical composition among different aquatic system is furnished in table 4.5.

Table 4.2 Percentage contribution of carbohydrate to LOM

Depth (cm)	S1	S2	S3	S4	S5
0-5	30.21	48.83	40.07	72.09	61.25
5 -15	49.40	43.99	53.78	70.73	71.97
15-25	62.12	50.09	59.16	64.17	65.34
25-35	76.21	42.17	63.58	68.34	62.98
35-45	65.77	47.31	66.30	73.70	65.39
45-55	67.48	41.10	59.79	66.78	80.67

Table 4.3 Percentage contribution of lipid to LOM

Depth (cm)	S1	S2	S3	S4	S5
0-5	55.50	34.85	49.75	15.64	36.91
5 -15	35.32	44.45	36.22	13.83	26.69
15-25	28.60	36.14	32.12	13.15	33.67
25-35	13.74	44.92	26.34	13.11	35.62
35-45	22.64	31.79	27.19	8.05	33.21
45-55	21.83	43.18	30.40	12.13	16.93

Table 4.4 Percentage contribution of protein to LOM

Depth (cm)	S1	S2	S3	S4	S5
0-5	14.29	16.32	10.17	12.27	1.84
5 -15	15.28	11.57	10.00	15.45	1.34
15-25	9.28	13.77	8.72	22.67	0.99
25-35	10.05	12.91	10.08	18.55	1.40
35-45	11.59	20.90	6.51	18.24	1.40
45-55	10.69	15.72	9.80	21.09	2.39

Table 4.5 Comparison of biochemical parameters among different aquatic systems

Location	Carbohydrate (mg/g)	Protein (mg/g)	Lipid (mg/g)	References
1. Western Mediterranean Sea	0.76 - 70.53	2.16 - 12.1	0.26- 4.47	Pusceddu et al.,1999
2. Mangalavanam Mangrove	3.31 -14.16	0.54- 32.51	0.88 -5.51	Resmi, 2004
3. Cochin Estuary	0.16 -2.16	0.24- 1.9	0.21 - 0.77	Resmi, 2004
4. Mundaka Estuary	0.2 -5.7	0 -16.70	0.30 -5.00	Cotano and Villate, 2006
5. Eastern Continental Shelf of India	1.28 - 4.43	0.17-0.55	-	Jacob et al.,2008
6. Western Continental Shelf of India	1.08 - 9.88	0.09-1.02	-	Jacob et al.,2008
7. Cochin Estuary	0.25 - 1.23	0.21-1.92	0.31-2.82	Joseph et al.,2008
8. Mangroves, Cochin	0.51- 2.46	0.70-4.61	0.80-6.82	Joseph et al., 2008
9. Mangrove, Cochin	1.36 - 14.82	0.10 - 11.05	-	Nair et al.,2010
10. Cochin Estuary	0.17- 6.34	0.02-2.60	0.04-3.160	Renjith et al.,2012
11. Rio de la Plata estuary	2.24 - 6.50	3.20 - 12.05	1.12 - 6.63	Venturini et al.,2012
12. Mangrove, Kannur and Calicut	2.4- 26.98	0.06- 8.23	0.60- 33.50	Present study

The term carbohydrate (CHO) derives from the fact that many members of this group of compounds have the general formula $C_n(H_2O)_n$. They consist of polyhydroxylated organic compounds ranging in size from 5-6 carbon sugars (ribose, glucose, galactose) to large biopolymers (starch, cellulose) (Cowie and Hedges, 1984). They are versatile molecules which serve as energy storage and structural components of cells. In marine systems, chemical energy is stored in the form of phytoplankton-derived carbohydrates, and this in turn provides energy to non-photosynthesizing organisms through the processes of glycolysis and respiration (Witter and Luther III, 2002). Thus they act as an important energy source for various heterotrophic organisms in the sediment (Decho, 1990; Tibbles et al., 1994). High levels of carbohydrates in sediments have been ascribed to the accumulation of aged organic detritus, and/or to the faster utilisation of protein than carbohydrates by bacteria which is in accordance with Venturini et al., 2012. Prevalence of CHO content in surficial sediments of S3 may be attributed to the greater level of litter addition, anthropogenic input and input resulted by death and decay of aquatic flora and fauna. Bottom sections of the cores showed decrease in the concentration of biochemical components which suggested their utilization by heterotrophic microorganisms.

Proteins (PRT), which are the polymers of α-amino acids, represent a major portion of nitrogen present in organism. Proteins are formed from the 20 different amino acids. Animals cannot synthesise all the amino acids needed for protein formation and hence they have to attain the essential amino acids directly or indirectly from plants. Present study recorded protein content fluctuating between 0.06 and 8.23 mg/g, exhibiting its minimum at S5 and maximum at S3. Protein content in sediments offers useful information on the productivity of a given marine system and it appears to be a suitable indicator of the trophic status of the benthic systems (Danovaro et al., 1999, 2000; Dell'Anno et al., 2002). They have been considered as very

labile and consequently unlikely to survive as high molecular mass components during early diagenesis.

Significantly higher values of total lipids in the study region may be due to its preservation under highly anoxic conditions (Ratheesh Kumar, 2012). Lipids (LPD) are defined as the substances produced by organisms that are insoluble in water but extractable by solvents in which they dissolve. They are one of the major biochemical compound produced by living organisms, constitute an important fraction of dissolved and particulate organic matter (Skoog and Benner, 1997; Borsheim et al., 1999; Burdige et al., 2000). They are consumed by micro heterotrophs in marine ecosystems and contribute to the bacterial production (Rich et al., 1996) and its concentrations have been associated with the most labile fraction of sedimentary organic matter. They are considered as the best descriptor of meiofauna abundance and biomass (Fabiano et al., 1995; Grémare et al., 1997; Grémare et al., 2002). Lipids in sediments are not only derived from aquatic biota but also from wax of higher plants. Similar to proteins, lipids also indicates the productivity of the system (Grémare et al., 1997). Lipids are more resistant to degradation than carbohydrates and proteins. Elevated levels of lipid concentration found at various segments of five cores (figure 4.1) indicated the biological activity associated with the sedimentary environment.

The order of mineralization of biochemical constituents usually follows the trend: LPD>PRT>TN>TOC>CHO (Colombo et al., 1996). In addition, PRT/CHO and LPD/CHO have been used as tools to assess the status of biochemical degradation processes (Galois et al., 2000). The PRT/CHO is used as an index to evaluate the origin of material present in sediments and to determine the age of sedimentary organic matter (Cividanes et al., 2002).This ratio provides information about the trophic state of sedimentary environment (Pusceddu et al., 2003). The PRT/CHO

ratio >1 point out that a major fraction of biopolymeric carbon consists of freshly produced labile organic matter (Pusceddu et al., 2000). A decrease in this ratio reflects the presence of aged organic detritus (Danovaro et al., 1993; Pusceddu et al., 2000) and may be associated with reduced availability of organic matter for consumers (Pusceddu et al., 2005, 2009). PRT/CHO ratio was found to be <1 in the entire study region which implies that mangrove sediments were characterised by a large amount of aged and/or non-living organic matter and confirmed the involvement of heterotrophic microorganisms in the organic carbon dynamics in the study area. Heterotrophic microorganisms play an important role in the ecological and biogeochemical processes in the marine sediments (Fernandes et al., 2014). Heterotrophic activity accounts for most of the organic matter re-mineralisation (Jørgensen, 2000). Irrespective of the selective utilization of the organic matter, bacteria contribute to the sedimentary organic matter pool in the form of bacterial cell walls and other bacterial macromolecules (Veuger et al., 2006; Lomstein et al., 2009). According to Danovaro 1996, the dominance of carbohydrates along with low PRT/CHO ratios suggest a detrital heterotrophic environment prevailing in the study area.

The lipid content and lipid to carbohydrate ratio (LPD/CHO) have been used as good indices to describe the food quality of the organic matter in the sediments (Grémare et al., 1997, 2002; Fabiano and Pusceddu, 1998). Furthermore, the higher lipid concentrations have usually been associated with the most labile fraction of sedimentary organic matter (Grémare et al., 1997, 2002; Cartes et al., 2002). LPD/CHO ratio was found to be <1 for almost all samples with some exceptions (surface samples from S1 and S3 and segments from S2: 5-15cm, 25-35cm and 45-55cm recorded LPD/CHO ratio >1). The deviations might be due to high rate of accumulation of lipids into the sediment or lower degradation rate of carbohydrate.

Bulk geochemical proxies such as C/N and isotopic compositions of sedimentary organic matter have been commonly employed to distinguish the sources of organic matter (Meyers, 1994; Schelskc and Hoddell, 1995; Perdue and Koprivnjak, 2007). Algae and phytoplankton exhibit low C/N ratios (~4-12) because they are characterised by high protein content and the absence of cellulose. On the other hand, terrestrial plants display high C/N ratios (≥20) due to their low protein content and abundance of cellulose (Meyers and Ishiwatari, 1993; Meyers, 1994; Filley et al., 2001). Microphytobenthos and macro algae produce major portions of organic carbon and nitrogen in shallow coastal ecosystems (Barranguet et al., 1996; Lucas et al., 2000). The preferential release of carbon or nitrogen during decomposition of the plants in anoxic sediment could alter the C/N ratios of sedimentary organic matter (Wang et al., 2003). More rapid release of organic carbon than nitrogen during the decomposition of the grasses could reduce the C/N ratios. The microbial immobilisation of N associated with decaying mangrove leaves has been observed in a variety of intertidal environments (Twilley et al., 1986; Benner et al., 1990; Cifuentes et al., 1996) and is believed to influence C/N values. The selective degradation of the different minerals in sediments can also alter the C/N ratios of organic matter (Muller, 1997; Lehmann et al., 2002). Increase in C/N ratio with depth point towards input of high proportion of terrestrial organic matter with age (Guilizzoni et al., 1996). The C/N ratio varied from 11.39 to 24.14 in the study region, recording minimum value at S1 and maximum at S3. The station S5 recorded low C/N ratio throughout the core with a marine signature.

The down core decrease in phytopigments at Kunjimangalam (S1) might be attributed to low adsorbing nature of the sandy sediment. Phytopigment concentrations can be used as a descriptor of the trophic state and productivity of most estuarine and shallow coastal systems (Lucas et al., 2000). Chlorophyll a (Chl-a) occurs in almost all phytoplankton species and

higher plants while chlorophyll b (Chl-b) occurs mainly in green algae and higher plants. Chlorophyll c (Chl-c) is found to exist in diatoms, dinoflagellates and in some brown macro algae (Kowalewska et al., 2004; Volkman et al., 2007). Significantly higher levels of chlorophyll pigments indicated the possibility of higher autochthonous production. Sedimentary plant pigments have been considered as a valuable indicator of paleoecology (Akhil et al., 2013). The highest concentration of phaeophytin (21.6 μg/g) was observed in S5 at 0-5 cm and the concentration was decreased towards the bottom. According to Dell'Anno et al., 2002, the predominance of phaeopigments could have resulted from high turbidity, chemical contamination or other factors affecting photosynthetic potential of the primary producers. Chlorophyll a in sediments are well documented as indicating periods of high productivity/blooms and sediment anoxia/preservation in the past, both for fresh water (Hall et al., 1997; Leavitt and Hodgson, 2001) and marine settings (Louda et al.,2000; Villanueva and Hastings, 2000).The contents of chlorophyll a in sediments depend on primary production, grazing, sedimentation, accumulation rate, and hydrodynamics of water (Baker and Louda, 2002; Reuss et al., 2005; Szymczak-Żyła and Kowalewska, 2009).

Very little information is available on the distribution of chlorophyll in the mangrove sediments of Kerala coast and no report is available on their vertical distribution. Sedimentary Chl-a and phaeophytin (phaeo) contents have not been reported previously from the study area. Different biotic and abiotic factors affect the spatial and depth-wise variations of chlorophyll pigments in the core sediments (Moreno and Niell, 2004). Sedimentary pigment concentrations are dependent on the light availability and oxygen content in the water column (Kowalewska and Szymczak-Żyła, 2001; Kowalewska et al., 2004). The light availability at the sediment surface is

affected by the variability in the hydrodynamic conditions (Moreno and Niell, 2004). Local water column input of Chl-a is clearly a determinant factor of sedimentary Chl-a concentrations (Szymczak-Żyła and Kowalewska, 2007). Phytoplankton productions in water column as well as in the benthic compartments are limited by increased water column turbidity and reduction in sufficient light penetration. A major portion of the primary carbon either settles down or gets transported to the coastal regions during monsoon. Chl-a/Phaeo (Table 4.1) ratios remained <1 throughout the study period indicating the existence of detritus material in the sediment samples.

The high molecular weight polycyclic aromatic compounds like tannins and lignin are widely distributed throughout the plant kingdom (Schnitzer and Khan, 1972; Finar, 1976; Field and Lettinga, 1987). Tannin is an abundant component in mangrove species and it occur in plant leaves, roots, wood, bark, fruits and buds (Kraus et al., 2003) and are estimated to be fourth most abundant compound type (as high as 20% dry weight; Benner et al., 1990) produced by vascular plant tissue, and the first threes are cellulose, hemicellulose and lignins (Hernes and Hedges, 2000). In addition to having a biomarker potential, tannin greatly contributes to bulk organic matter properties including colour, astringency and reactivity (Lin et al., 2006). Leaching, which induces an increase in polymerisation of condensed tannin, is an important mechanism for tannin removal from leaves (Joseph et al., 2008).Tannin and lignin are phenolic compounds and their estimation not only provides information on input of land derived organic detritus in marine sediment but also enable us to determine the relationship between allochthonous and autochthonous organic matter. These compounds are highly resistant to biological degradation. The occurrence of higher tannin and lignin content in the sediments of the study region could be attributed to mangrove input since these are components of higher plants including

mangroves (Ratheesh Kumar, 2012). Tannin and lignin content exhibited its higher content at S3 indicating a major contribution of terrestrial vascular plant debris to the sedimentary organic matter in this mangrove ecosystem. Lignin is a nitrogen free copolymer of various phenyl propenyl alcohols that is present in vascular plants and is usually considered as a specific marker of terrestrial plant remains due to its exclusive association with higher plant. Lignins belong to the class of phenolic compounds occuring exclusively in vascular plants and represent important tracers of terrestrial organic matter (Bianchi et al., 2002). They occur uniquely in vascular plant tissues and are generally associated with cellulose and hemicellulose, forming a material that is collectively referred to as lignocellulose. Refractory organic compounds like tannin and lignin are easily accumulated in marine sediments which contributes a major portion of total organic matter (Middelburg et al., 1999; Zegouagh et al., 1999).

Stable carbon isotope composition is strongly influenced by relative contributions of terrigenous and marine organic matter in the sediments (Summons et al., 1992; Bird et al., 1994; Boreham et al., 2001). Isotope analysis of organic carbon has also been used to evaluate the source and depositional environments of the sediments as marine or non-marine using the bulk $\delta^{13}C$ values of saturated and aromatic fractions (Sofer, 1984; Collister and Wavrek, 1996). Stable carbon isotope signatures ($\delta^{13}C$) of the various carbon inputs are often different, making them powerful source indices to distinguish between allochthonous and autochthonous organic carbon inputs (Middelburg et al., 1997; Bianchi et al., 2002). Enzymatic and diffusional fractionation processes, which helps to discriminate against ^{13}C during photosynthesis, varies between C3, C4, and CAM plants (Brugnoli and Farquhar, 2000). Although terrestrial organic carbon sources transported to the coastal zone fall in two categories, C3 and C4 plant derived matter, each display distinct and

non-overlapping $\delta^{13}C$ range (typically -27 and -13 ‰, respectively), C3 vegetation dominates in most catchment areas (Bouillon et al., 2004). Mangrove plant tissues exhibit $\delta^{13}C$ values ranging from -31.2 to -26.8 ‰ while sediments show values varying from -26.5 to -22.1‰ (Bouillon et al., 2004). Organic matter derived from marine sources typically exhibit $\delta^{13}C$ values between -22 and -20 ‰ and the ~7 ‰ difference between organic matter produced by C3 land plants and marine algae has successfully been used to trace the sources of organic matter in coastal ocean sediments (Gearing et al., 1977).

The $\delta^{13}C$ values obtained in the study region (-29.19 to -23.87‰) suggested a terrestrial origin of organic matter. A down core enrichment in $\delta^{13}C$ with increasing depth was observed in all the cores. Generally, the more enriched values in the low organic carbon sites and more depleted values in organic rich sediments were observed. The sediments from Kadalundi reflected a balance between marine and terrestrial sources. The more depleted $\delta^{13}C$ values reported for the core sediments indicated a major contribution of organic matter from the vascular plants.

Mangroves are characterised as a forests growing at the interface between land and sea and hence the sedimentary organic matter is composed of inputs from both marine and terrestrial sources. The fraction of terrestrial derived organic matter in mangrove sediments (F) could be quantitatively estimated using $\delta^{13}C$ based two end member model proposed by Schultze and Calder, 1976. Taking the marine and terrestrial end members as -20.5 ‰ and -30‰ respectively (Wu et al., 2002; Jia and Peng, 2003; Liu et al., 2006; Zhang et al., 2009), the terrestrial derived organic matter (F) was calculated using the following equation:

$$F\ (\%) = \{(\delta^{13}C_{\ marine} - \delta^{13}C_{\ measured})/\ (\delta^{13}C_{\ marine} - \delta^{13}C_{\ terrestrial})\} \times 100$$

The organic carbon delivered from mangroves is similar in character to that of terrestrial derived organic matter since mangroves are also vascular plants. The contribution of terrestrial derived organic matter in core sediments varied from 35.44 to 91.32 % (Table 4.6). It exhibited spatial as well as depth wise variation ($P<<0.01$). Generally, depth wise decrease in contribution of terrestrial derived organic matter was observed. A significant marine input was evident at Kadalundi as the F value was lower at this site.

Table 4.6 Percentage contribution of terrestrial organic matter

Depth (cm)	S1	S2	S3	S4	S5
0-5	80.35	91.52	83.32	76.43	51.86
5- 15	85.98	71.12	82.08	64.94	48.86
15-25	72.13	68.61	79.30	63.44	39.65
25-35	56.79	53.20	73.14	55.73	35.44
35-45	55.20	56.23	70.54	60.34	47.13
45-55	47.47	47.90	66.96	61.95	48.43

4.3.1 Correlation analysis

Correlation analysis (Table 4.7) revealed strong positive correlation of pH with TOC and TS, implied redox status prevailing in the sedimentary environment. Silt and clay exhibited strong positive correlations with TOC, TS, TN and other biochemical components, which point towards influence of grain size on the distribution of the estimated variables. The observed strong interrelationships existing among the biochemical constituents reflected their origin from common source. The high organic carbon associations which coincided with the high clay contents is attributed to the enhanced adsorption of organic carbon onto the clay minerals (Akhil et al., 2013). Chlorophyll pigments showed distinct variations and also displayed a highly significant positive correlation with clay which is in good agreement with previous reports (Coljin and Dijkema, 1981; Moreno and Niell, 2004).

Table 4.7 Correlation analysis of analysed parameters

	pH	Eh	TOC	Sand	Silt	Clay	CHO	LPD	PRT	Tannin	TN	TS	TP	BPC	Chla	Chlb	Chlc	Phaeo
pH	1																	
Eh	-0.338	1																
	0.678	-0.607																
	(**)	(**)																
TOC	0.678	-0.607	1															
	(**)	(**)																
	-0.430	0.402	-0.675	1														
Sand	(*)	(*)	(**)															
	0.196	-0.149	0.345	-0.691	1													
Silt				(**)														
	0.451	-0.439	0.688	-0.926	0.366	1												
Clay	(*)	(*)	(**)	(**)	(*)													
	0.569	-0.606	0.916	-0.786	0.473	0.765	1											
CHO	(**)	(**)	(**)	(**)	(**)	(**)												
	0.496	-0.601	0.933	-0.564	0.243	0.599	0.846	1										
LPD	(**)	(**)	(**)	(**)		(**)	(**)											
	0.542	-0.514	0.854	-0.615	0.263	0.654	0.846	0.873	1									
PRT	(**)	(**)	(**)	(**)		(**)	(**)	(**)										
	0.514	-0.620	0.889	-0.749	0.466	0.720	.966	0.872	0.852	1								
Tannin	(**)	(**)	(**)	(**)	(**)	(**)	(**)	(**)	(**)									
	0.653	-0.637	0.969	-0.733	0.414	0.727	0.947	0.892	0.788	0.917	1							
TN	(**)	(**)	(**)	(**)		(**)	(**)	(**)	(**)	(**)								
	0.533	-0.481	0.703	-0.469	0.448	0.369	0.709	0.594	0.533	0.747	0.728	1						
TS	(**)	(**)	(**)	(**)	(*)	(*)	(**)	(**)	(**)	(**)	(**)							
	0.316	-0.555	0.608	-0.599	0.540	0.489	0.729	0.551	0.430	0.736	0.702	0.697	1					
TP		(**)	(**)	(**)	(**)	(**)	(**)	(**)	(*)	(**)	(**)	(**)						
	0.549	-0.621	0.960	-0.675	0.339	0.692	0.940	0.976	0.916	0.943	0.941	0.656	0.627	1				
BPC	(**)	(**)	(**)	(**)		(**)	(**)	(**)	(**)	(**)	(**)	(**)	(**)					
	0.528	-0.363	0.734	-0.478	0.311	0.452	0.688	0.717	0.640	0.662	0.740	0.324	0.465	0.731	1			
Chla	(**)	(*)	(**)	(**)		(*)	(**)	(**)	(**)	(**)	(**)		(**)	(**)				
	0.529	-0.397	0.754	-0.546	0.352	0.518	0.739	0.786	0.815	0.761	0.724	0.372	0.444	0.807	0.904	1		
Chlb	(**)	(*)	(**)	(**)		(**)	(**)	(**)	(**)	(**)	(**)	(*)	(*)	(**)	(**)			
	0.550	-0.545	0.868	-0.618	0.436	0.567	0.860	0.886	0.877	0.871	0.857	0.571	0.586	0.915	0.835	0.917	1	
Chlc	(**)	(**)	(**)	(**)	(*)	(**)	(**)	(**)	(**)	(**)	(**)	(**)	(**)	(**)	(**)	(**)		
	0.511	-0.366	0.735	-0.454	0.245	0.456	0.700	0.679	0.606	0.627	0.756	0.321	0.454	0.709	0.938	0.785	0.775	1
Phaeo	(**)	(*)	(**)	(*)		(*)	(**)	(**)	(**)	(**)	(**)		(*)	(**)	(**)	(**)	(**)	

** Correlation is significant at the 0.01 level.
* Correlation is significant at the 0.05 level.

4.3.2 Principal component analysis

Factor analysis is a multivariate statistical technique used to understand the correlation structure of sedimentary data and to identify the most important factors contributing to the data structure and to find associations between parameters so that the number of measured parameters can be reduced. The factors having Eigen values >1 were considered as prominent factors as per the Kaiser criterion (Kaiser, 1960). Principal component analysis (PCA) is a type of treatment which allows us to take into account the relationships (represented by the correlation matrix) that exist among all studied variables. PCA enables the creation of new variables - the principal components (PCs) - that are linear combinations of the original ones. Varimax orthogonal rotation was employed to transform the analysis matrix and to limit the number of variables loaded in each factor (Buckley et al., 1995). The parameters for the PCA were selected in such a way that the component of the analysis can give indication to the significance of processes. The probable biogeochemical processes that can operate in the mangrove environment include; the diagenesis, dissolution and precipitation, input from allochthonous and autochthonous sources, adsorption and desorption along with periodically changing redox condition (Joseph et al., 2008).

A total of 78.88% was described by two factors. First factor explained 47.54% of total variance, which consisted of positive loadings on TOC, CHO, PRT, LPD, TN, tannin lignin, chlorophyll a, b, c and phaeophytin. The absence of significant loadings on grain size parameters in first factor restricts us to reach on the conclusion of sorption/ desorption processes. There exists very weak loadings on the signal of diagenetic process (TS) and these observations lead us to the conclusion that first factor point towards the

common source of biochemical components and chlorophyll components along with TOC. Hence factor 1 point towards the process of litter fall addition. Second factor accounts for 31.34% of total variance. It recorded negative loadings on sand, positive loadings on silt, clay, carbohydrates, lipids, tannin lignin (T&L) and total sulphur. This factor has significant loadings on TS, which is the signal of redox status and hence point towards diagenetic process. Diagenesis is a redox process, largely mediated by sedimentary microorganisms and the suitable indicators to this are the redox element sulphur, organic carbon and nitrogen and it takes place prior to deposition and during the early stages of burial under condition of relatively low temperature and pressure which alters the nature of organic matter in sediment. Biological, chemical and physical processes are the major factors leading to diagenetic transformation. Microbial activity is one of the major agents which alters sedimentary organic matter during early stages of diagenesis near the sediment-water interface where more biochemically labile compounds are consumed, leaving behind the more biochemically stable materials and varieties of alteration products (Ali and Mudge., 2005). These two processes are found to be interdependent since biochemical composition revealed significant loadings on both the principal components (PCs).

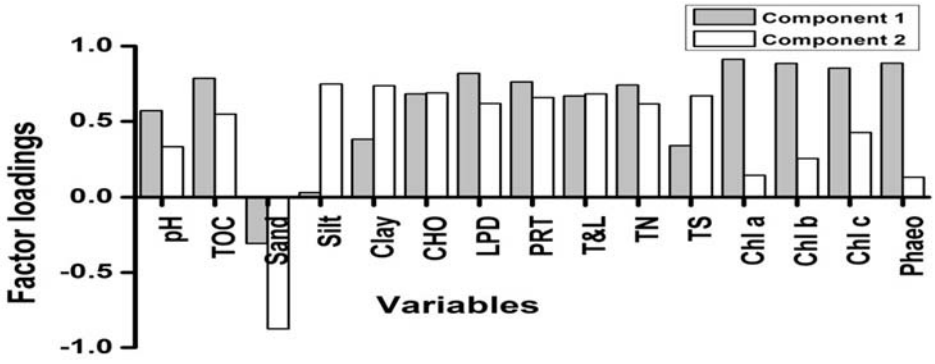

Figure 4.2. Factor loadings of analysed parameters

Table 4.8. Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	10.399	69.330	69.330	10.399	69.330	69.330	7.130	47.536	47.536
2	1.433	9.553	78.882	1.433	9.553	78.882	4.702	31.346	78.882
3	0.953	6.351	85.233						
4	0.766	5.106	90.338						
5	0.647	4.312	94.651						
6	0.378	2.518	97.169						
7	0.155	1.034	98.203						
8	0.108	0.722	98.925						
9	0.065	0.433	99.358						
10	0.046	0.305	99.664						
11	0.021	0.143	99.807						
12	0.013	0.086	99.893						
13	0.009	0.058	99.951						
14	0.007	0.049	100.000						

4.4 Conclusion

Litter fall is considered as the most important primary source of detritus in mangrove environment. The fine grained fraction of sediments contributed to the retention of organic matter. Samples from S1, S4 and S5 showed similar trend in the vertical concentration of carbohydrate, lipid and protein, which remained almost constant after 15cm depth. Among the biochemical components, carbohydrates were the dominant class followed by lipids and then by protein. PRT/CHO ratio was found to be <1 in all core samples which implied that mangrove sediments were characterised by a large amount of aged and/or non-living organic matter and the role of bacteria in influencing the biochemical composition of sediment organic matter. Enhanced anoxia, fine grained sediments and higher concentrations of total organic matter facilitated the preservation of the phytopigments.The occurrence of higher tannin and lignin content in the sediments of the study region could be attributed to mangrove input since these are components of higher plants including mangroves. The more depleted stable carbon isotope ratio ($\delta^{13}C$) values obtained in the study region suggested a major contribution of organic matter from vascular plants. The application of biochemical constituents and bulk organic matter indices like elemental compositions and stable isotopic ratios were quite useful tools for the assessment of total quality and relative contribution of marine and terrestrial derived organic matter in the core sediments, but the source, fate and degradation pathway of the organic matter can only be deduced by molecular biomarker approach.

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Chapter 5

n-ALKANES AND HOPANES AS BIOMARKERS IN CORE SEDIMENTS

5.1 Biomarker potential of n-alkanes

Mangrove forests located along coastal regions and estuarine mouths are rich sources of alkanes. They constitute a significant fraction of sedimentary organic carbon; hence the detection and quantification of these compounds are useful to interpret the nature, sources and biogeochemical processes controlling their distribution. Because of their stability in the natural environment, aliphatic hydrocarbons were selected and used as a measure for indicating possible change of lipids in sediment cores, which would reflect changes in lipid concentration during sedimentation (Jeng, 2007). Marine sediments have been recognised as important reservoir of organic matter including hydrocarbon from a variety of sources (Killops and Killops, 1993, 2005; Yamamoto et al., 2003; Silva et al., 2012). The hydrocarbons in core sediment have widely been used for the source identification and reconstruction of the historical records for environmental studies (Hostettler et al., 1999; Wu et al., 2001; Hu et al., 2011), marine paleoenvironments and

paleoclimates (Meyers, 1997, 2003). The aliphatic hydrocarbons exhibit both low chemical reactivity and bioavailability for microorganisms, due to the lack of functional groups and low water solubility. Microorganisms such as bacteria, fungi and yeast also utilise these components as a source of carbon and energy (van Beilen et al., 2003; Wentzel et al., 2007). In addition, some bacterial species which are highly specialised in degrading hydrocarbons and they play a key role in the removal of hydrocarbons from the polluted environment (Head et al., 2006; Yakimov et al., 2007; Singh et al., 2012).

Even though previous investigations carried out by Ratheesh Kumar (2012) in mangrove system established the efficiency to employ n-alkanes as source tracers in estuarine mangroves; the study was confined only to the surficial sediments of mangroves of Cochin region. A recent study from Cochin estuary (Gireesh Kumar, 2013) was also a significant effort towards the use of n-alkanes as biomarkers. Studies involving the characterisation of sedimentary organic matter using n-alkane biomarkers in core sediments of mangroves along Northern Kerala coast have not been attempted so far. The present chapter elucidates the distribution of n-alkanes in the core sediments of mangrove ecosystems and their source assessment.

5.2. General characteristics of hopanoids

Hopanoids are important class of biological markers whose primary function is to improve plasma membrane fluidity in prokaryotes and are mainly derived from bacteriohopanepolyols which occur especially in bacteria and their presence shows bacterial lipid contributions in geological materials. Hopanoids are marker for specific bacterial populations and environmental condition (Belin, 2009). Different bacterial groups possess recognisable biohopanoid distributions, allowing hopanoids as bacterial markers. Their

occurrence has been noticed in several higher plants, ferns, mosses, fungi, protists, and particularly in bacteria (Orisson et al., 1987). Bacteria are the only known source of C_{35}hopanepolyols (bacterial hopanepolyols; BHPs). The BPHs act as cell membrane rigidifiers in prokaryotes equivalent to sterols in eukaryotes. Hopanoids are receiving intense attention as biomarker with application for geochemical studies of petroleum sources, rocks and oils due to the fact that hopanoid are not easily degraded. Hopanoids are most abundant in aerobic bacteria (methanotrophs, heterotrophs and cyanobacteria), but they also occur in some anaerobic bacteria, but not in Archaea or eukaryotes (Blumenberg et al., 2006). The hopanoids are divided into two groups, biohopanoids such as bacteriohopanetetrol (BHT) and geohopanoids such as hopanols, hopanoic acids and hopanes. It is known that the death of bacteria causes the formation of geohopanoids from biohopanoids by the diagenetic processes modifying the side chain structure (Belin, 2009). Hopanes comes under the category of pentacyclic triterpenoid with 5 membered E ring. Figure 5.1 indicates the standard numbering system of hopane.

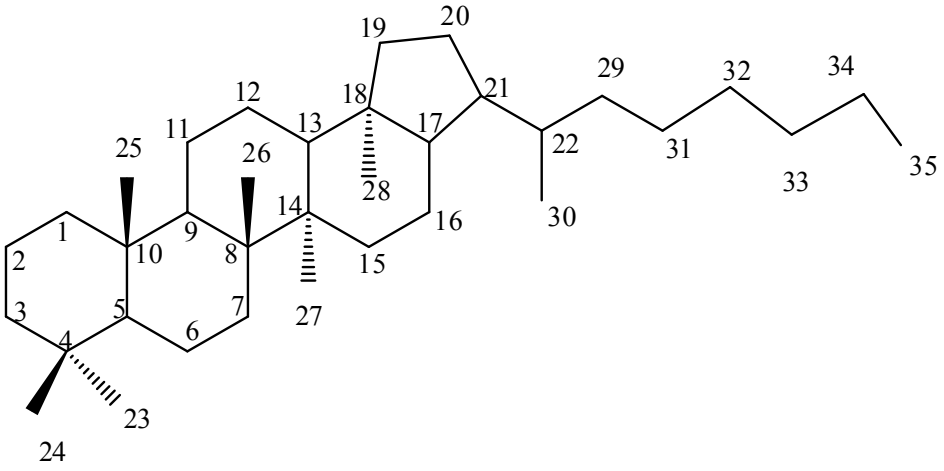


Figure 5.1 The standard numbering convention of pentacyclic triterpenoid, hopane

5.3 Results

5.3.1 Distribution of n-alkanes in sediments

The range of concentration of n- alkanes in the core sediments is furnished in table 5.1. Core sediment samples collected from mangrove forests revealed the presence of n-alkanes ranging from C_{11} to C_{33}. Observations revealed that estimated total concentration of n-alkanes (Σn-alkanes) at S1varied from 12393 to 14998ngg^{-1}. In the case of S1, the maximum concentration of n-alkane (C_{max}) was recorded by C_{29} at 45-55cm (6872ngg^{-1}) while minimum (C_{min}) was exhibited by C_{30} at 25-35cm (10ngg^{-1}). The Σn-alkane at S2 varied from 27813 to 75647ngg^{-1}, the C_{max} was recorded at C_{27} (14683 ngg^{-1}; 45-55cm) and C_{11} exhibited C_{min} (3ngg^{-1}; 0-5cm). S3 was characterized by a C_{max} at C_{29} (19120 ngg^{-1}; 25-35cm) and C_{min} at C_{11} (7ngg^{-1}; 0-5cm) and the Σn-alkane varied from 60182to 81240 ngg^{-1}. Meanwhile S4 recorded a C_{max} at C_{27} (8616ngg^{-1}; 15-25cm) and C_{min} (3ngg^{-1}) at C_{11} (45-55cm), recording Σn-alkane ranging from 34231to 37595ngg^{-1}. Observed total n-alkane concentration at S5 fluctuated between 12453 and 25412ngg^{-1}, the C_{max} of n-alkane at S5 was exhibited by C_{29} (7216ngg^{-1}; 0-5cm) while C_{11} (at 5-15cm) recorded the C_{min} of n-alkane concentration (12 ngg^{-1}).

Table 5.1 The range of n- alkane concentrations in the core sediments (Average± Standard deviation)

Alkanes	Concentration, ngg^{-1}				
	S1	S2	S3	S4	S5
C_{11}	10 to 12 (11.76 ± 0.79)	3 to 109 (24 ± 41)	7 to 21 (14 ± 6)	3 to 18 (7 ± 6)	12 to 36 (23 ± 10)
C_{12}	11 to 96 (39 ± 36)	572 to 1122 (769 ± 216)	650 to 1056 (860 ± 171)	144 to 529 (280 ± 193)	81 to 273 (168 ± 86)
C_{13}	134 to 278 (200 ± 63)	132 to 1215 (650 ± 353)	32 to 661 (320 ± 217)	52 to 768 (251 ± 280)	53 to 417 (199 ± 122)
C_{14}	101 to 556 (288 ± 193)	208 to 1820 (1182 ± 733)	108 to 1689 (889 ± 532)	237 to 766 (364 ± 201)	197 to 1081 (571 ± 393)
C_{15}	217 to 269 (233 ± 20)	262 to 1274 (825 ± 412)	189 to 2651 (1110 ± 897)	135 to 375 (264 ± 79)	415 to 630 (546 ± 75)
C_{16}	121 to 267 (190 ± 60)	372 to 1041 (742 ± 238)	217 to 3081 (1478 ± 984)	184 to 3734 (1002 ± 1351)	438 to 1900 (1056 ± 670)
C_{17}	123 to 325 (230 ± 82.48)	471 to 657 (565 ± 61)	527 to 912 (651 ± 140)	220 to 1126 (480 ± 353)	517 to 819 (657 ± 120)
Pr	15 to 66 (40 ± 20)	201 to 312 (240 ± 39)	206 to 312 (256 ± 39)	28 to 300 (93 ± 103)	157 to 310 (234 ± 65)
C_{18}	166 to 865 (368 ± 263)	392 to 7964 (3017 ± 2925)	1307 to 1725 (1593 ± 157)	326 to 1291 (904 ± 390)	324 to 775 (600 ± 194)
Ph	47 to 192 (101 ± 61)	209 to 1624 (823 ± 596)	420 to 950 (681 ± 202)	150 to 1168 (443 ± 425)	300 to 359 (322 ± 20)
C_{19}	22 to 97 (54 ± 33)	154 to 248 (203 ± 38)	604 to 1590 (1178 ± 381)	282 to 1071 (531 ± 332)	278 to 953 (527 ± 258)
C_{20}	117 to 172 (141 ± 19)	39 to 774 (352 ± 300)	607 to 7094 (2331 ± 2391)	409 to 954 (634 ± 214)	445 to 1174 (799 ± 280)
C_{21}	21 to 315 (111 ± 112)	36 to 387 (170 ± 140)	898 to 2944 (1741 ± 686)	42 to 437 (293 ± 146)	176 to 1301 (591 ± 456)

C_{22}	428 to 1132 (744 ± 231)	125 to 3697 (1171 ± 1471)	154 to 2504 (1318 ± 816)	174 to 2664 (936 ± 1034)	1335 to 7190 (4596 ± 2509)
C_{23}	19 to 100 (46 ± 34)	31 to 1875 (719 ± 698)	113 to 1870 (814 ± 651)	5031 to 7267 (6006 ± 920)	179 to 2766 (791 ± 996)
C_{24}	85 to 820 (429 ± 367)	32 to 2852 (1145±1098)	1372 to 2179 (1771 ± 272)	354 to 1240 (790 ± 371)	188 to 694 (425 ± 202)
C_{25}	10 to 75 (47 ± 26)	2278 to 7547 (4344 ± 1957)	6443 to 10317 (7935 ± 1389)	5278 to 7815 (7078 ± 915)	180 to 389 (276 ± 72)
C_{26}	10 to 81 (56 ± 25)	810 to 10662 (3133 ± 3938)	409 to 1847 (1001 ± 633)	122 to 482 (269 ± 147)	94 to 552 (263 ± 161)
C_{27}	2143 to 3214 (2757 ± 433)	4306 to 14327 (10201 ± 3906)	10369 to 16250 (12838 ± 2278)	7847 to 8616 (8062 ±279)	32 to 102 (56 ± 33)
C_{28}	311 to 381 (330 ± 27)	476 to 7384 (2598 ± 2815)	236 to 370 (312 ± 43)	49 to 89 (63 ± 14)	66 to 300 (155 ±108)
C_{29}	6245 to 6872 (6537 ± 230)	6107 to 13784 (9391 ± 2525)	16022 to 19120 (17611 ± 1308)	3540 to 5723 (4703 ± 775)	4598 to 7216 (5516 ± 1244)
C_{30}	10 to 150 (58 ± 63)	577 to 3135 (1422 ± 1035)	321 to 1593 (1108 ± 456)	527 to 793 (658 ± 93)	154 to 311 (221 ± 67)
C_{31}	198 to 541 (383 ± 120)	1635 to 13648 (5072 ± 4305)	4607 to 8327 (5826 ± 1514)	1386 to 2900 (1958 ± 599)	70 to 112 (97 ± 15)
C_{32}	12 to 135 (77 ±52)	21 to 1042 (385 ± 393)	290 to 1010 (470 ± 268)	173 to 793 (381 ± 189)	55 to 206 (116 ± 61)
C_{33}	17 to 462 (129 ±171)	28 to 4558 (1498 ± 1714)	2899 to 6447 (4745 ± 1429)	77 to 500 (221 ± 148)	81 to 304 (160 ± 81)
$\sum$n-alkane	12393 to 14998 (13600 ±1029)	27813 to 75647 (50644 ± 16821)	60182 to 81240 (68851 ± 8140)	34231 to 37595 (36672 ± 1259)	12453 to 25412 (18964 ± 5643)

The range of C_{17}/pristane ratio varied from 2 to 20.18 while C_{18}/phytane ratio ranged between 1.04 and 5.98. Estimated ratio of pristane (Pr) to phytane (Ph) was from 0.07 to 1.20. Carbon preference index (CPI) was calculated to distinguish sources of organic matter, both for short chain (CPI^a) and long chain alkanes (CPI^b). The CPI^a showed values ranging from 0.22 to 0.88 while CPI^b fluctuated between 2.46 and 22.58. The ratio of short chain carbon and long chain carbon varied from 0.06 to 1.82, while the ratio of C_{17}/C_{29} ranged between 0.02 and 0.23.The estimated variation of average chain length (ACL) was from 26.94 to 29.68, meanwhile, the terrigenous to aquatic ratio (TAR) ranged between 2.70 and 21.60. Two modes of distribution pattern was shown by the samples from study area, i.e., an even over odd carbon predominance was noticed for short chain alkanes while long chain alkanes revealed odd over even carbon predominance (confirmed from CPI^a and CPI^b values).The down core variation of total of short chain n-alkanes, total of long chain n-alkanes and total n-alkanes is furnished in figure 5.2.

5.3.1.1 Vertical distribution of total short chain n-alkanes

The samples from S1 recorded a more or less uniform down core distribution. However, the concentration at S2 increased slightly from 0-5 to 5-15cm and then decreased downwards to 25-35cm followed by an increase in content downwards. A slight increase in concentration was noticed down wards from 0-5 to 5-15cm at S3, which decreased from 5-15 to 25-35cm followed by an increase in content at 35-45cm, which again decreased at 45-55cm. An increase in content was noticed from 0-5 to 15-25cm and then a zig-zag type distribution was displayed down wards at S4. A more or less uniform

distribution of total short chain n-alkane content was recorded down wards from 0-5 to 15-25cm at S5, which then decreased downwards to 35-45cm followed by a slight increase at 45-55cm.

5.3.1.2 Vertical distribution of total long chain n-alkanes

An invariant vertical distribution in total long chain n-alkanes was noticed for samples from S1, S3, S4 and S5. In the case of S2, an increase in concentration was noticed from 0-5 to 5-15cm, which then decreased down the core to 25-35cm and then the concentration increased at 45-55cm.

5.3.1.3 Vertical distribution of total n-alkanes

A more or less uniform vertical distribution was observed for samples from S1and S4. In the case of S2, the concentration increased from 0-5 cm to 5-15cm and then decrease in content was noticed from 15-25 to 25-35cm, followed by an increase in content down the core. The sample segments from S3 revealed a more or less uniform concentration down the core from 0-5 to 25-35cm followed by a slight increase in concentration at 35-45cm, which again decreased down the core. The content at S5 decreased slightly down the core from 0-5 to 35-45cm which then displayed a more or less uniform concentration at 45-55cm.

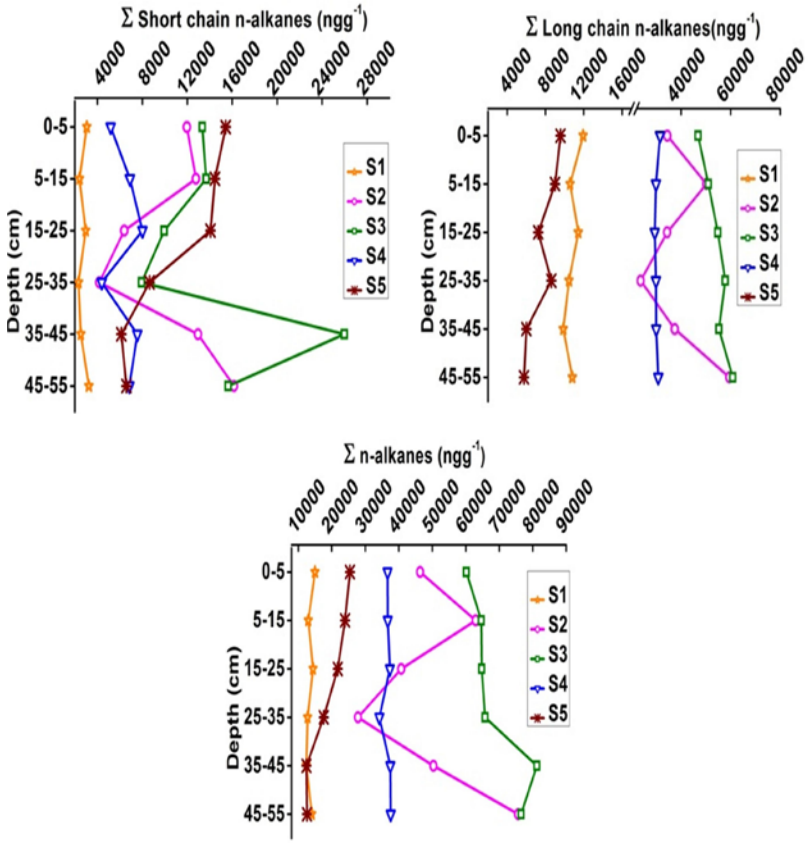


Figure 5.2 Vertical distributions of total short chain n-alkanes, total long chain n-alkanes and total n-alkanes in study area.

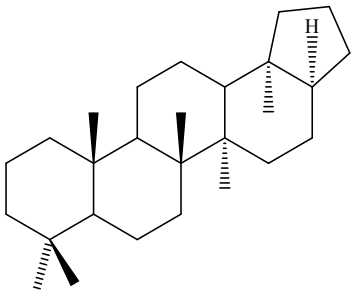
5.3.2 Hopanes identified in the core sediments

The identified hopanes in sediment samples include: 18α-22,29,30-trisnorhopane (Ts), 17α-22,29,30-trisnorhopane (Tm), 17β(H)-22,29,30-trinorhopene (Te), 17α (H) 21β (H)-30-norhopane (C29αβ),17β(H) 21α(H)-30 norhopane (C29βα), 17α (H) 21β (H)-hopane (C30αβ), 17β(H),21α(H)-hopane (C30βα), C31αβ 22 R, C31αβ 22 S, C32αβ 22 R and C32αβ 22 S. Table 5.2 depicts the presence or absence of hopanes in the study area and figure 5.3 depicts the structure of different hopanes.

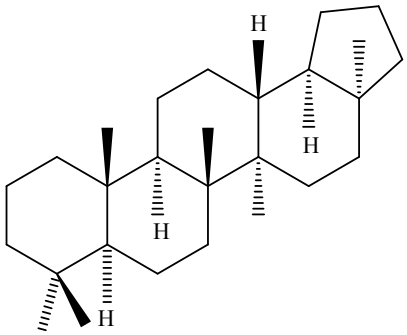
Table 5.2 The presence/absence of different types of hopanes in core sediment samples from study area

Station	Depth (cm)	Ts	Te	Tm	C29 αβ	C29 βα	C30 αβ	C30 βα	C31 αβ 22S	C31 αβ 22 R	C32 αβ 22 S	C32 αβ 22 R
	0-5	+	+	-	+	+	+	+	+	+	+	+
	5-15	+	+	-	+	+	+	+	+	-	-	+
	15-25	+	+	-	+	-	-	+	+	+	+	+
	25-35	+	+	-	+	+	-	-	-	-	-	-
	35-45	-	+	-	+	-	-	-	-	+	+	+
S1	45-55	-	+	-	+	+	+	+	+	-	-	+
	0-5	+	+	-	+	+	+	-	+	+	+	+
	5-15	+	+	-	+	-	-	-	+	+	+	-
	15-25	-	+	-	+	+	-	-	+	-	-	-
	25-35	+	+	-	+	+	+	-	+	-	-	-
	35-45	-	+	-	+	-	+	-	+	+	+	-
S2	45-55	-	+	-	+	+	+	-	+	+	+	-
	0-5	-	+	-	+	-	-	-	+	+	-	-
	5-15	-	+	-	+	-	-	-	+	+	-	-
	15-25	-	+	-	+	-	-	-	+	+	-	-
	25-35	-	+	-	+	-	-	-	+	+	-	-
	35-45	-	+	-	+	-	-	-	+	+	-	-
S3	45-55	-	+	-	+	-	-	-	+	+	-	-
	0-5	-	+	-	+	-	-	-	+	+	+	+
	5-15	-	+	-	+	-	+	-	-	+	-	-
	15-25	-	+	-	+	+	-	+	-	+	-	+
	25-35	+	+	-	+	+	+	-	+	+	-	+
	35-45	+	-	-	+	-	-	+	+	+	+	+
S4	45-55	-	+	-	+	+	+	+	-	+	+	+
	0-5	+	+	+	+	-	+	+	-	+	-	+
	5-15	+	-	-	+	+	-	-	+	+	-	+
	15-25	+	+	+	+	-	-	+	+	+	-	+
	25-35	+	-	+	-	+	+	+	+	+	+	-
	35-45	+	-	-	+	+	-	-	-	-	+	+
S5	45-55	+	-	-	+	+	-	-	+	-	+	-

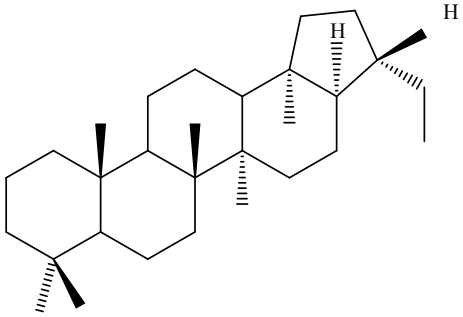
+denotes present
-denotes absent



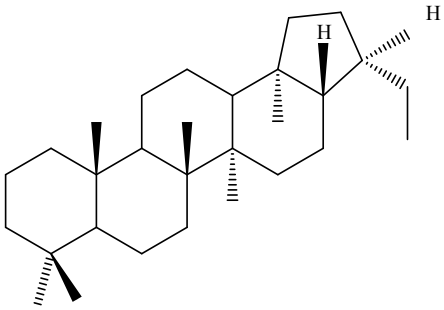
17α (H)-22, 29, 30-Trisnorhopane (Tm)



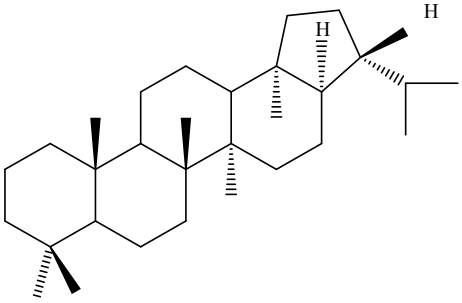
18α (H)-22, 29, 30- Trisnorhopane (Ts)



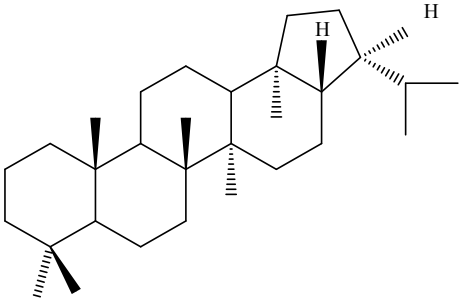
17α (H), 21β (H)-30- Norhopane (29αβ)



17β (H), 21 α (H)-30-Norhopane (29βα)



17α (H), 21β (H) - hopane (30αβ)



17β (H), 21α (H) - hopane (30βα)

Figure 5.3 The structure of different hopanes

5.4 Discussion

5.4.1 n- Alkanes

Organic geochemical data can be used to evaluate the total mass of certain compounds in the sediments and to interpret down core environmental changes as indicated by the abundance and distribution of some organic compounds occurring in cores (Jeng, 2007). Among the organic compounds, n-alkanes are class of organic compounds which are easy to analyse and exhibit source specificity and therefore are widely utilised to trace out the sources of organic matter in aqueous phase, suspended particulate matter and sediments from different aquatic environments (Harji et al., 2008; Kameyama et al., 2009; Maioli et al., 2011). n-Alkanes have been established as efficient biomarkers for evaluating sources, transport processes and contribution of terrestrial organic matter to aquatic ecosystems (Prahl et al., 1994; Mead et al., 2005; Seki et al., 2006; Seki et al., 2010). They are readily adsorbed onto suspended particulate matter and will ultimately sink to bottom sediments. Hence bottom sediments may act as source of these particular classes of organic compounds (Medeiros et al., 2005). These compounds exhibit distinct well defined sources, such as terrestrial plant waxes, marine phytoplankton, bacteria, biomass combustion as well as other anthropogenic input (Meyers, 2003; Maioli et al., 2010).

Odd number carbon chains tend to dominate in biological materials. A clear indication of a strong biogenic input is demonstrated by the odd numbered carbon preference from C_{23} to C_{33} while short chain alkanes ($C \leq 22$) recorded even carbon predominance. According to Ficken et al., 2007, short chained n-alkanes (C_{15}-C_{21}) with no distinct odd-over-even predominance are derived from algae and bacteria, while the long chain n-alkanes (C_{22}-C_{33}) are mainly from higher plant wax. Epicuticular wax of higher land plants seems to contain long-chain

odd numbered n-alkanes (Hu et al., 2013). The strong odd to even carbon predominance of high molecular weight n-alkanes (>C_{22}) in core sediments revealed the prominent terrigeneous contribution from higher vascular plant wax (Aboul-Kassim and Simoneit, 1996; Hu et al., 2013). Relatively low values (<1.0) of short chain/long chain ratio was established for marine animals, sedimentary bacteria and higher plants show while algae and plankton produces >1.0 (Clarck and Blumer, 1967; Gao et al., 2007).

In the present study, the short to long chain n-alkane ratio varied between 0.14 (S3; 25-35cm) and 1.82 (S5; 15-25cm) and were < 1 in most of the samples except at S5 (0-5cm, 5-15cm, 15-25cm and 45-55cm). The low ratio noted for short chain to long chain n- alkanes point towards the input from vascular plants. The higher values for short chain to long chain ratio could be due to the major input from algae and plankton which exceeded terrestrial input or else the degradation of fatty acids might have resulted in the formation of short chain alkanes (Dastillung and Corbet, 1978). The content of TOC is a major proxy for classifying the input of organic matter from autochthonous (phytoplankton, bacteria, aquatic macrophytes) and allochthonous sources (terrestrial plant debris, pollen) (Ficken et al., 1998; Meyers, 2003). The highest total n-alkane concentrations were found in those sediments with high TOC, which was in confirmation with previous studies (Ficken et al., 2007; Wang et al., 2010). Increased sedimentation rate can retard the degradation of organic matter which contributes to higher levels of TOC relative to others (Gaskell et al., 1975). This process can leave an imprint at any sediment depth, including surface. More rapid sedimentation rates are accompanied by high TOC levels, implying greater preservation of organic matter due to quicker establishment of anoxic post-depositional environment in sediments (Stevenson and Cheng, 1972; Gaskell et al., 1975).The stations

S2 and S3, which were characterized by large quantities of leaf litter and comparatively high TOC, recorded maximum content of total n-alkanes.

There exist difference in assemblage of n-alkane found in marine biota and that of terrestrial biota (Punyu et al., 2013), i.e., the predominance of short chain odd carbon n- alkanes such as C_{15}, C_{17} and C_{19} are due to input from marine planktons while long chain odd numbered n-alkanes (>C_{22}) are markers of land and terrestrial plants (Pearson and Eglinton, 2000; Zhao et al., 2003; Jeng and Huh, 2008). The cyanobacteria and red, green and brown algae generally produce the C_{15}, C_{17} and C_{19} n-alkanes with predominant compound being species dependent (Clark and Blumer, 1967; Gogou et al., 2000) while even carbon n-alkanes in the C_{12}-C_{22} range originate from diatoms (Elias et al., 2000). Bacteria, algae and fungi are supposed to produce mainly short chain even n-alkanes (C_{14}-C_{22}; Grimalt and Albaigés, 1987), while n-C_{17} in particular is considered to be a biomarker for algae and photosynthetic bacteria (Meyers, 2003). Indices such as carbon preference index (CPI), pristane/phytane ratio, n-C_{17}/pristine ratio and n-C_{18}/phytane ratio have been established to be useful to identify n-alkane sources (Volkman et al., 1992; Commendatore and Esteves, 2004; Zaghden et al., 2005; Hu et al., 2009). In the present study, short chain, even numbered carbon chain n-alkanes (C_{12}-C_{22}) were predominant (confirmed from CPI^a values) and this might be due to the input from diatoms, bacteria, algae and fungi. The feature of predominance of even to odd carbon in the short chain homologues has also been observed in marine and freshwater sediments with various ages, depositional conditions and biological sources including plankton (Elias et al., 1997; Volkman et al., 1998; Ekpo et al., 2005; Harji et al., 2008). The microbial reworking of algal detritus and recent biogenesis of lipid materials (Hu et al., 2013) also contribute to the predominance of even to odd carbon in the short chain homologues. The even carbon preference of the C_{12}-C_{22} n-alkanes may be due to the direct biogenic contribution from bacteria, fungi and yeast species (Gireesh

Kumar et al., 2015). Additionally, the even predominance is also suggested to be formed by the reduction of fatty acids under anoxic environments (Dastillung and Corbet, 1978). As the n-alkanes has low susceptibility to degradation and hence higher proportions of these compounds reflect the periods of time when organic matter enriched with lipid content was deposited or bulk organic matter was subjected to greater amounts of degradation (Meyers and Benson, 1988). The n-alkane content in the present study region is found to be lower than those detected in Hauraki Gulf, New Zealand (table 5.3).

Table 5.3 Concentration of total n-alkanes in various environments

Sl.No	Location	Concentration (µg/g dry weight)	Reference
1	Changjiang estuary, China	2.20 to 11.82	Bouloubassi et al., 2001
2	Fraser River Basin, Canada	1.60 to 20.60	Yunker et al., 2003
3	Sao Sebastiao, Brazil	0.03 to 4.77	Medeiros and Bícego, 2004
4	Patos lagoon estuary, Brazil	0.20 to 7.50	Medeiros et al., 2005
5	Jiaozhou Bay, China	0.54 to 8.12	Wang et al., 2006
6	Pearl River estuary, USA	3.43 to 8.46	Gao et al., 2007
7	Southern Okinawa Through,	1.31 to 4.6	Jeng, 2007
8	Gulf of Fos, France	7.80 to 180	Mille et al., 2007
9	Sfax coastal zone, Tunisia	2.18 to 429.5	Zaghden et al., 2007
10	Mandovi estuary, India	0.80 to 3.20	Harji et al., 2008
11	Marmugoaharbour, India	1.60 to 10.70	Harji et al., 2008
12	Bohai Sea, China	0.39 to 4.94	Hu et al., 2009
13	Hauraki Gulf, New Zealand	326 to 819	Sikes et al., 2009
14	Mundaú–Manguaba estuarine–lagoon system, Brazil	0.39 to 43.38	Maioli et al., 2010
15	Sergipe River estuarine system, Brazil	9.9 to 30.8	Lima et al., 2012
16	Coastal marine sediments off China	0.12 to 1.68	Liu et al., 2012
17	Mundaú–Manguaba estuarine–lagoon system, Brazil	27.8 to 139.5	Silva et al., 2012
18	Guanabara Bay, Rio de Janeiro, Brazil.	7.66 to 57.22	Wangener et al., 2012
19	Cochin estuary, India	6.03 to 43.23	Gireesh Kumar, 2013.
20	Visakhapatnam Harbour, India	0.2 to 31	Punyu et al., 2013
21	Mundaú–Manguaba estuarine-lagoon system, Brazil	27.8 to 139.5	Silva et al., 2013
22	Hecate Strait, Canada	0.35 to 1.88	Yunker et al.,2014
23	Mangrove core sediment, India	12.39 to 81.24	Present study

The assessment of the possible sources of n-alkanes in the core sediments of the study area was calculated by employing carbon preference index as a tool. CPI for n-alkanes is defined as a summation of odd carbon number homologues over a range divided by the summation of even carbon number homologues over the same range (Elias et al., 2000; Gao et al., 2007) and is routinely used as a source indicator in marine sediments. The CPI for the short chain n-alkanes is designated as CPI^a and that of long chain is regarded as CPI^b. The CPI^b values of 1 or near 1 indicate inputs from petroleum products, whereas, CPI^b <1 suggest input from microorganisms including bacteria and diatioms (Clark and Blumer, 1967; Garg and Bhosle, 2004). In organic geochemistry, CPI is used to indicate the degree of diagenesis of straight-chain geolipids, and is a numerical representation of how much of the original biological chain length specificity is preserved in geological lipids (Meyers and Ishiwatari, 1995). The trend in CPI values may be caused by plants exhibiting different n-alkane CPI values. The most likely cause for the trend in CPI values is the extent of degradation taking place after the decay of plants and/or their wax-containing parts (Vogts et al., 2012). Epicuticular leaf waxes of higher plants generally have a higher carbon preference index =4-40; (Collister et al., 1994) than sediments in which these terrestrial products are presumed to be the dominant wax input (Tissot and Welte, 1984).

$$CPI^a = \frac{(C_{11} + C_{13} + C_{15} + C_{17} + C_{19} + C_{21})}{(C_{12} + C_{14} + C_{16} + C_{18} + C_{20} + C_{22})}$$

$$CPI^b = \frac{(C_{23} + C_{25} + C_{27} + C_{29} + C_{31} + C_{33})}{(C_{24} + C_{26} + C_{28} + C_{30} + C_{32})}$$

In the present investigation, CPI^b was > 1, pointing towards the predominance of odd carbon numbered long chain n-alkanes, which were

mostly derived from terrestrial sources. The CPI^a was < 1 for all the samples i.e., short chain n-alkanes recorded even carbon number predominance. The CPI^a varied from 0.22 (S2; 0-5cm) and 0.88 (S3; 25-35cm). The even over odd predominance for n-alkanes for short chain n-alkanes might be attributed to biochemical degradation processes. There are microorganisms which are active, capable of producing n-alkanes without odd carbon number predominance during the decay process (Gelencsér et al., 1998). Furthermore, it has been found that the odd carbon number predominance of n-alkanes diminishes during the decay of organic matter (Tissot and Welte, 1984). Higher CPI^b values found in sediment or soil show greater contribution from vascular plants (Rieley et al., 1991; Hedges and Prahl, 1993). In the present investigation, CPI^b ranged from 2.46 (S2; 5-15cm) to 22.58 (S4; 35-45cm).

The total content of $C_{27}+C_{29}+C_{31}$ n-alkanes have been used as terrestrial organic matter source indicator, while the total content of $C_{15}+C_{17}+C_{19}$ n-alkanes is a representative of marine organic matter indicator (Xing et al., 2011). The long chain, odd carbon n-alkanes are of terrestrial origin and can be found in waxes of higher plants (Brassell et al., 1978; Rieley et al., 1991), Plankton generally produces a simple mixture of hydrocarbons dominated by short chain odd carbon n-C_{15}, n-C_{17} and n-C_{19} (Goutx and Saliot, 1980; Gogou et al., 2000) and hence the ratio of $C_{27}+C_{29}+C_{31}$ to $C_{15}+C_{17}+C_{19}$ is valuable for determining changes in relative contributions of organic matter from land and aquatic flora although it may over-represent the absolute amounts from terrigenous sources (Meyers, 1997). However, the ratio overestimate of the terrigenous input due to the preferential preservation of terrestrial hydrocarbons compared to planktonic counterparts (Volkman et al., 1987). The terrigenous to aquatic ratio (TAR) was calculated using the equation,

$$TAR = \frac{C_{27} + C_{29} + C_{31}}{C_{15} + C_{17} + C_{19}}$$

All mangrove sites exhibited TAR values > 1, however comparatively lower values were recorded at S5, which may be due to high marine input, which should have diluted terrestrial input since the station S5 is situated along the confluence of Arabian Sea. The TAR varied between 2.70 (S5; 45-55cm) and 21.60 (S1; 35-45cm).

Average chain length (ACL) is an another parameter that can be used to delineate n-alkanes sources which describes the weight average number of carbon atoms per molecule based on the abundance of the odd-numbered higher plant-derived alkanes (Poynter and Eglinton, 1990; Boot et al., 2006; Jeng, 2006). The distribution of ACL has been linked to the geographical distribution of fluvial and eolian inputs and source regions (Poynter and Eglinton, 1990). The average chain length (ACL) is a parameter that can be used to identify n-alkyl lipids from different vegetation (Ternois et al., 2001; Boot et al., 2006; Jeng, 2006). Vegetation types seem to have main influence on chain length of terrigenous leaf lipids. For example, leaf lipids derived from grasslands may have longer chain lengths on average than leaf lipids from plants in forests (Cranwell, 1973).

$$ACL = \frac{\left[\left(25*C_{25}\right)+\left(27*C_{27}\right)+\left(29*C_{29}\right)+\left(31*C_{31}\right)+\left(33*C_{33}\right)\right]}{\left(C_{25}+C_{27}+C_{29}+C_{31}+C_{33}\right)}$$

The values should remain with limited changes within the environment and different in various ecosystems (Jeng, 2006). The values showed slightly significant variations along the entire cores, with values varying from 26.94 (S4; 45-55cm) to 28.98 (S2; 45-55cm) which pointed towards stronger terrestrial influence (Sikes et al., 2009). According to Sarkari et al., 2012, various values over time suggest change in environment due to environmental disturbances. In the present study, fluctuating values over time were recorded which indicated environmental disturbances occurred in the study area.

A number of indices such as the ratios of short chain/long chain n-alkanes, n-C_{17}/Pr and n-C18/Ph, Pr/Ph also have been used to identify the sources of n-alkanes in environmental samples (Bouloubassi et al., 2001; Ou et al., 2004; Gao et al., 2007). Different indices were evaluated to unfold the source characterisation potential of n-alkane in the study area. The value of different indices is given in table 5.4.

Table 5.4 Different indices in the study area

Station	Depth (cm)	C_{17}/Pr	C_{18}/Ph	Pr/Ph	CPI [a]	CPI[b]	SLR	ACL	TAR	C_{17}/C_{29}
S1	0-5	3.74	2.60	0.78	0.40	7.15	0.26	28.75	18.04	0.03
	5-15	2.96	2.45	0.25	0.48	6.75	0.23	28.65	20.39	0.02
	15-25	4.93	5.43	0.94	0.79	8.91	0.26	28.45	15.26	0.05
	25-35	20.87	2.94	0.27	0.60	21.98	0.22	28.42	17.78	0.05
	35-45	6.37	3.99	0.51	0.44	16.63	0.26	28.59	21.60	0.02
	45-55	7.00	4.51	0.17	0.28	14.30	0.30	28.46	21.04	0.03
S2	0-5	2.87	2.61	0.46	0.22	3.33	0.35	28.31	6.14	0.25
	5-15	2.56	3.48	0.27	0.27	2.46	0.25	28.22	6.25	0.12
	15-25	2.17	1.87	1.20	0.69	15.29	0.19	27.82	5.52	0.12
	25-35	2.45	2.32	0.62	0.47	9.18	0.18	27.89	4.13	0.24
	35-45	2.16	3.30	0.15	0.32	2.90	0.35	28.13	5.85	0.06
	45-55	2.11	4.90	0.19	0.37	2.80	0.27	28.98	8.72	0.15
S3	0-5	3.11	4.11	0.49	0.56	10.30	0.28	28.30	8.15	0.10
	5-15	4.07	3.40	0.49	0.62	8.34	0.27	28.33	7.64	0.13
	15-25	2.00	2.29	0.35	0.60	10.29	0.18	28.33	12.45	0.06
	25-35	2.20	2.10	0.33	0.88	12.25	0.14	28.44	21.58	0.07
	35-45	2.13	1.38	0.30	0.50	12.33	0.47	28.65	5.60	0.07
	45-55	2.16	2.22	0.41	0.65	11.16	0.26	28.62	8.58	0.07
S4	0-5	4.30	1.57	0.07	0.37	15.57	0.16	27.30	14.71	0.06
	5-15	3.75	1.11	0.26	0.67	11.87	0.23	27.10	8.99	0.23
	15-25	7.46	2.17	0.58	0.42	9.83	0.27	27.14	10.76	0.13
	25-35	7.98	5.21	0.12	0.41	11.94	0.15	27.03	16.02	0.04
	35-45	6.95	2.63	0.23	0.41	22.58	0.25	27.13	9.23	0.06
	45-55	7.33	5.98	0.28	0.42	11.49	0.22	26.94	8.86	0.09
S5	0-5	2.69	2.07	0.60	0.26	4.42	1.54	28.95	3.64	0.07
	5-15	3.67	2.37	0.52	0.24	6.58	1.52	28.93	4.22	0.08
	15-25	4.01	2.38	0.55	0.33	5.71	1.82	28.96	3.12	0.14
	25-35	2.41	2.32	0.97	0.29	7.14	0.97	28.94	3.10	0.16
	35-45	2.85	1.08	0.80	0.64	5.37	0.97	28.94	2.81	0.18
	45-55	2.02	1.04	0.90	0.55	7.05	1.10	28.90	2.70	0.12

Pristane (2, 6, 10, 14 - tetramethylpentadecane) and phytane (2, 6, 10, 14 - tetramethylhexadecane) are products of geological alteration of phytol and other isoprenoid natural products, and are not primary constituents of most terrestrial biota (Didyk et al., 1978; Li et al., 1995; Gao et al., 2007). However, pristine (Pr) in the marine environment can be contributed by zooplankton and other higher marine animals while phytane (Ph) is normal component of oil but also can be synthesised by the methanogenic and photosynthetic bacteria (Steinhauer and Boehm, 1992; Sakata et al., 1997). In immature sediments, pristane and phytane are commonly produced from the phytyl side chain of chlorophyll a and b (Ragan and Chapman, 1978) and therefore can indicate algal source in marine sediments. Ratios of Pr/Ph can be used to assess relative contributions from petrogenic hydrocarbons in sediments. Low (<1) values for n-C_{17}/Pr ratio and n-C_{18}/Ph ratio revealed the presence of degraded petroleum hydrocarbons while higher values (>1) for these ratio which implies presence of less degraded or fresh input of hydrocarbons (Harji et al., 2008). High C_{17}/Pr ratios (i.e., $\gg$2) are thought to reflect significant contributions from algae (Readman et al., 2002) ; whereas low C_{17}/Pr ratios (<1) are indicative of highly weathered oil (Wang et al., 1995). The Pr/Ph ratio is also considered to be an indicator of depositional condition of uncontaminated sediment. The value <1 represents anoxic condition and >1 reflects oxic condition (Didyk et al., 1978; Lü and Zhai, 2006). The C_{17}/Pr and C_{18}/Ph were >1 in all most all the samples while Pr/Ph exhibited values were < 1 in all sediment samples. The existence of anoxic condition in the study region can be confirmed from low Pr/Ph ratio.

The sources of hydrocarbons are different in land and marine sources (Sarkari et al., 2012). The ratio of n-C_{17}/n-C_{29} can also be employed as a parameter to establish marine versus terrigenous input of n-alkanes

(Venkatesan et al., 1987; Jeng et al., 2003). In the present study, the ratio was < 1 for all samples. The low n-C_{17} to n-C_{29} ratio can probably be attributed to the predominance of the terrestrial n-alkane contribution to the coastal marine sediments and/or preferential degradation of marine-derived n-alkanes relative to terrigenous n-alkanes (Prahl et al., 1980; Meyers et al., 1984; Jeng et al., 2003).

5.4.2 Hopanes

Hopanoids have been isolated from a wide range of bacteria and their taxonomic distribution has been reviewed by Ourisson et al., 1987 and Rohmer et al., 1992. Bacteriohopanoids have been detected in some, but not all, cyanobacteria, purple nonsulphur bacteria, gram-negative and gram-positive bacteria, methylotrophs and acetic acid bacteria. Hopanoids appear to be absent from the green and the purple sulpur bacteria and from all anaerobic symbiotic and parasitic forms (Brocks et al., 2003). Although hopanoid biosynthesis does not require oxygen, it is of some interest that they are generally not present in obligate anaerobes (Rohmer et al., 1984). The most abundant hopanoids in bacterial membranes are C_{35}-bacteriohopanepolyols that carry an extended polyhydroxylated or otherwise functionalised side chain. All bacteria that synthesize C_{35}-bacteriohopanepolyols also contain lower concentrations of the C_{30}-hopanoids (diploptene and diplopterol). Archaea do not produce hopanoids (Ourisson et al., 1987) mean while they are present in some Eucarya (Rohmer et al., 1992) such as cryptogams, ferns, mosses, lichens, filamentous fungi in very low concentrations. The rare eukaryotic hopanoids possess only 30 carbon atoms and do not carry the diagnostic polyhydroxy side-chains, so C_{35}-hopanoids have the quality to become biomarkers for bacteria (Rohmer et al., 1992).

Hopanes readily isomerise at asymmetric carbon atoms, C_{17} and C_{21}, and hence have four possible stereoisomers: 17β, 21β (H)-hopane (ββ-hopane), 17β, 21α (H)-hopane (βα-moretane), 17α, 21β (H)-hopane (α β-hopane) and 17α, 21α (H)-hopane (αα-hopane), where α and β denote whether the hydrogen is below or above the plane of the ring system respectively. The ββ-hopanoids are the commonly observed biological configuration and are found in bacterial cultures and immature organic material whereas αα-hopanes were not reported in sediments. The ββ configuration is nearly planar, which enables the molecule to fit into the membrane lipid bilayer (Peters et al., 2005). Among the hopane stereoisomeric series, the ββ-hopane is the least thermodynamically stable (Seifert and Moldowan, 1980; Kolaczkowska et al., 1990; Peters et al., 2005). During diagenesis and catagenesis, ββ-hopane is removed by thermal degradation or interconversion to the more thermodynamically stable βα-moretane and αβ-hopane. The αα-hopane is less thermodynamically stable than either 17β, 21α (H)-moretane or 17α, 21β (H)-hopane, and it is largely undetected in petroleum and mature petroleum source rocks (Bauer et al., 1983; Kolaczkowska et al., 1990). 18α (H)-22, 29, 30-trisnorneohopane (Ts) comes under the category of modified hopane. The presence of hopanes in the mangrove sediment samples point out the contribution of bacteria towards organic matter.

5.5 Conclusion

The source characterization of organic matter in core sediments could be explained to some extent by analyzing n-alkane biomarkers.The long chain n-alkanes predominated over shorter ones (with some exceptions), indicating predominance of higher plant input to the sedimentary organic matter. The dominance of terrestrial input was confirmed from high TAR values (>1) in the study region. The short chain n-alkanes recorded even over odd carbon

number predominance while long chain n-alkanes showed odd over even carbon chain predominance. The even over odd predominance for short chain n-alkanes might be attributed to biochemical degradation processes by microorganisms while the predominance of odd over even long chain n-alkanes point towards the input from vascular plants. The average chain length (varied from 26.94 to 28.98) along with low C_{17}/ C_{29} ratio further confirmed the terrestrial input to sedimentary organic matter. The existence of anoxic condition in the study region can be confirmed from low Pr/Ph ratio. The presence of hopanes in the study area reflects the bacterial contribution towards the sedimentary organic matter.

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Chapter 6

FATTY ACIDS AS BIOMARKERS IN CORE SEDIMENTS

6.1 Introduction

Lipids are recognised as the densest form of energy in marine ecosystems. Among the lipid class of organic compounds, fatty acids (FAs) are considered to be important determinants of ecosystem health and stability (Parrish, 2013) and are major constituents of lipid pool in living and dead organic material. Their source specificity and greater stability compared to amino acids and carbohydrates make them ideal as biomarkers. Previous investigations clearly illustrated that fatty acid biomarkers can be effectively used to trace the origin, transport and diagenetic changes of organic material in water columns and sediments (Harvey, 1994; Niggemann and Schubert, 2006). These characteristic groups of organic compounds have specificity for particular organisms together with the different labilities depending on their chemical structure (Canuel and Martens, 1996; Camacho-Ibar et al., 2003; Lü et al., 2010). These properties highlight them as efficient tool to investigate

quality and sources of sedimentary organic matter. Source-specific information about autochthonous and allochthonous inputs of organic matter within coastal ecosystems can be provided by the application of fatty acid compounds, groups and ratios (Mc Callister et al., 2006). Furthermore, fatty acid biomarkers have been used as geochemical indicators of early diagenetic processes (Haddad et al., 1992). These biomarkers can be used to trace the origin and trajectory of organic matter in the ecosystem. Major differences in the FA composition of source organisms allow an assignment of predominating sources by distinguishing the relative contribution of primary producers (diatoms, dinoflagellates), secondary producers (zooplankton, bacteria) and terrestrial inputs (Volkman et al., 1989; Budge and Parrish, 1998; Zimmerman and Canuel, 2001). The studies of FAs in sedimentary records from coastal areas enable us to understand the influence of recent natural and anthropogenic processes on the distribution of organic matter from different sources (Canuel, 2001). The vast available literature data in different aquatic systems indicated the fact that source signatures provided by fatty acids will be useful for the tracing the organic matter input in marine sediments (Camacho-Ibar et al., 2003; Joseph, 2009; Bourgeois et al., 2011). Mangroves are highly complex environment, which receives both allochthonous and autochthonous input. The n-alkane biomarkers alone could not effectively characterise organic matter sources due to the fact that many n-alkanes can originate from different sources. Therefore an attempt is also made to identify the sources of organic matter and to unfold the major biogeochemical pathways in core sediments of mangrove ecosystems using fatty class of organic compounds.

6.2 Results

Twenty seven to thirty four individual fatty acids were identified representing a multitude of organic matter inputs into the core sediments of the study region. For the sake of easier interpretation, FAs are broadly categorised into five classes which represent distinct specific sources (Zimmerman and Canuel, 2001; Venturini et al., 2012). Briefly, the classes include: (1) short chain (C<22:0) saturated fatty acids (SCSFAs) = non-specific marine markers (2) monounsaturated fatty acids (MUFAs)= algae and zooplankton (3) polyunsaturated fatty acids (PUFAs)= plankton and recently produced organic matter (4) long chain (C≥22:0) saturated fatty acids (LCSFAs)= terrestrial markers (5) branched (iso(i) and anteiso(a)) odd-chain fatty acids and the 18:1n7 (BAFAs) = bacterial markers. The distribution of fatty acid throughout the core as the sum of the concentrations of the fatty acids assigned above to each source is shown in figure 6.1.The range of fatty acid concentration in different sampling sites is given in table 6.1.

C_8, C_{10}, C_{12}, C_{14}, iC_{15}, aC_{15}, C_{15}, C_{16}, iC_{17}, aC_{17}, C_{17}, C_{18}, and C_{20} were the SCSFAs identified in the core sediments from all stations, whereas C_{11}, C_{13} and C_{21} were identified only at S1, S2, S3 and S5. The total short chain saturated fatty acids (∑SCSFAs) ranged between 0.65 and 23.03 $\mu g g^{-1}$. The vertical profile of ∑SCSFAs at S1 decreased downwards from 0-5 to 25-35cm and then increased at 35-45cm followed by a remarkable decrease at 45-55cm. In the case of S2, content of ∑SCSFAs also declined downwards from 0-5 to 15-25cm, then increased from 15-25 to 35-45cm and then decreased at 45-55cm. The vertical profile of ∑SCSFAs at S3 was similar to that of S1. The core sediment samples from S4 recorded a decrease in ∑SCSFAs content from 0-5 to 25-35cm, which then increased down the core from 25-35 to 45-55cm. The concentration of ∑SCSFAs depleted from 0-5 to 5-15cm, which then

increased at 15-25cm followed by a decrease in content from 15-25cm to 45-55cm. ∑SCSFAs are the major contributors to TFAs except at S2 (0-5cm, 5-15cm and 15-25cm) and at S3.

$C_{14:1}$, $C_{16:1n7}$, $C_{18:1n9}$, $C_{18:1n7}$, $C_{20:1n9}$, $C_{22:1n9}$ and $C_{24:1}$ were the MUFAs identified in the study region. Among these MUFAs, $C_{16:1n7}$, $C_{18:1n9}$, $C_{20:1n9}$ and $C_{22:1n9}$ were present at all stations. The total MUFAs (∑MUFAs) varied from 0.08 to 17.29 $\mu g g^{-1}$ and recorded a comparatively higher content at S3. A decrease in ∑MUFAs was observed down the core at S1. In the case of samples from S2, decrease in concentration was noticed from 0-5 to 15-25cm and then displayed a zig- zag manner of vertical distribution. Similarly, decrease in content of ∑MUFAs was also recorded at S3 from 0-5 to 15-25cm, after this depth, even though the content showed an increase at 35-45cm, again a decrease in concentration was noticed at 45-55cm. Unlike other stations, an increase in concentration was displayed by sample segment from 0-5 to 5-15cm; however a sharp decline was noticed down the core. Meanwhile S5 recorded a decrease in ∑MUFAs content from 0-5 to 5-15cm which then increased sharply at 15-25cm followed by a decrease in concentration. The contribution of ∑MUFAs towards TFAs varied from 0.69 (S2; 35-45cm) to 33.39 % (S3; 25-35cm).

The PUFAs, $C_{18:2n6}$, $C_{20:5n3}$ and $C_{22:6n3}$ were present at all stations, while $C_{18:3n3}$ was identified at S1, S2, S3 and S4. However, the PUFA $C_{18:3n6}$ was present only at S2 and S3. The concentration of ∑PUFAs was comparatively higher at S4. A decrease in content of ∑PUFAs was noticed down the core at all stations. The concentration of ∑PUFAs varied from 0.03 (S5; 45-55cm) to1.24 $\mu g g^{-1}$ (S4; 0-5cm).

The BAFAs, iC_{15}, aC_{15}, C_{15}, iC_{17}, aC_{17} and C_{17} were identified at all stations, while $C_{18:1n7}$ was present only at S1, S2 and S3. The ∑BAFAs in the

study region ranged between 0.07 (S5; 25-35cm) and 2.72 μgg^{-1} (S4; 0-5cm). The contribution of ∑BAFAs towards TFAs was from 0.43 (S2, 35-45cm) to 13.02 % (S4; 0-5cm). Comparatively higher contribution of ∑BAFAs towards TFAs was recorded at S4.The ∑BAFAs content decreased downwards at S1, while decrease in content was also noticed at S2 from 0-5 to 35-45cm followed by a slight increase at 45-55cm. Meanwhile a zig-zag pattern of vertical distribution was recorded at S3. The concentration of ∑BAFAs was noted to be decreasing from 0-5 to 25-35cm at S4, which then increased down the core. Even though, a decrease in concentration of ∑BAFAs from 0-5 to 5-15cm was recorded at S5, the content increased at 15-25cm followed by a decrease in concentration down the core.

The LCSFAs, C_{22}, C_{24}, C_{26}, C_{28} and C_{30} were detected in all stations, while the presence of C23 was noticed at S1, S2, S3 and S5. ∑LCSFAs varied from 0.21 (S2; 35-45cm) to 66.69 μgg^{-1} (S3; 0-5cm). Comparatively higher values were noted at S3, while S2 at 0-5cm, 5-15cm and 15-25cm also recorded comparatively higher values. The vertical profile of ∑LCSFAs at S1 showed a slight increase in concentration from 0-5 to 5-15cm, then decreased at 15-25cm and thereafter a more or less uniform concentration was recorded down the core. The content of ∑LCSFAs was uniform at 0-5 and 5-15cm for sample segment from S2, which decreased at 15-25cm and then showed a uniform concentration at 25-35cm, which decreased sharply at 35-45cm followed by an increase in content at 45-55cm. A decrease in concentration was noticed from 0-5 to 15-25cm at S3, which increased down the core. Similarly, a decrease in content was observed for samples from S4 from 0-5 to 25-35cm, which then increased slightly at 35-45cm followed by a decrease at 45-55cm. A more or less uniform concentration down the core from 0-5 to 25-35cm was noticed at S5 which then decreased down the core.

The concentration of TFAs decreased down the core at S1. However, at S2, a decrease from 0-5 to 15-25cm then increased up to 25-35cm, which then decreased down the core. The station S3 also displayed similar distribution pattern. At S4, a decrease in concentration was noticed down the core from 0-5 to 25-35cm, and then the content increased downwards the core. The content of TFAs declined from 0-5 to 5-15cm and then increased at 15-25cm, which thereafter decreased down the core. The concentration of TFA ranged between 1.42 (S4; 25-35cm) and 76.92 μgg^{-1} (S3; 0-5cm).

Total short chained saturated fatty acids were the predominating FAs at S1, S2 (25-35cm, 35-45cm and 45-55cm), S4 and S5 (Figure 6.2). ∑LCSFAs were the second most contributors towards TFAs at S1, S4 and S5. At S1, ∑MUFAs were the third most contributing FAs at 0-5cm, 5-15cm and 15-25 cm followed by ∑BAFAs from 25-35cm to 45-55cm. At S2, ∑LCSFAs was the major contributing FAs towards TFAs from 0-5 to 15-25cm down the core. ∑MUFAs followed by ∑BAFA were the third and fourth most contributing FAs towards TFAs respectively at S2. ∑LCSFAs followed by ∑MUFAs were the major contributing FAs towards TFAs at S3. ∑LCSFAs were the second most contributors towards TFAs at S4, while ∑BAFAs were the third most contributing FAs at 0-5cm and ∑PUFAS became third most contributing FAs from 5-15 to 25-35cm down the core then ∑BAFAs again dominated over ∑PUFAS from 35-45 to 45-55cm. At S5, ∑SCSFAs followed by ∑LCSFAs were the major contributing FAs towards TFAs. ∑MUFAs and ∑BAFAs became third and fourth most contributing FAs respectively towards TFAs. At S2 and S3, high vegetation mass (leaf litter) and limited tidal rhythm might be attributed to the accumulation and preservation of long chain fatty acid. Higher contribution of SAFAs towards TFAs are indicative of older partially degraded materials in the surface sediments (Dunn et al., 2008), since

the SAFAs are comparatively less susceptible of microbial degradation (Gong and Hollander, 1997). Along with terrestrial contribution, significant bacterial, zooplankton and algal input were also noticed.

Table 6.1 Range of fatty acids in the study area (Average ± Standard deviation)

Fatty acid	Concentration, μgg^{-1}				
	S1	S2	S3	S4	S5
C8	0.01 to 0.13	0.01 to 0.33	ND to 0.49	0.005 to 0.32	ND to 0.30
C10	0.04 to 0.10	0.01 to 0.19	ND to 0.85	0.01 to 0.17	ND to 0.27
C11	ND to 0.03	ND to 0.02	ND to 0.29	ND	ND to 0.01
C12	0.72 to 1.13	0.22 to 1.85	0.19 to 1.00	0.13 to 1.59	0.40 to 2.69
C13	0.003 to 0.03	ND to 0.07	ND to 0.13	ND	0.005 to 0.02
C14:1	ND to 0.09	ND to 0.28	ND to 0.14	ND	ND to 0.03
C14	0.03 to 0.81	0.25 to 2.38	0.10 to 0.89	0.05 to 1.07	0.24 to 1.53
iC15	0.01 to 0.05	0.01 to 0.08	0.06 to 0.34	0.03 to 1.16	0.01 to 0.21
ac15	0.01 to 0.05	0.01 to 0.04	0.07 to 0.27	0.02 to 0.47	0.01 to 0.12
C15	0.05 to 0.11	0.05 to 1.25	0.05 to 0.98	0.01 to 0.49	0.02 to 0.26
C16:1n7	0.06 to 0.31	0.01 to 0.22	0.03 to 0.10	ND to 2.19	0.02 to 0.20
C16	2.37 to 7.87	2.73 to 12.42	1.02 to 2.78	0.23 to 4.42	1.48 to 6.66
iC17	0.01 to 0.12	ND to 0.07	0.07 to 0.11	0.01 to 0.17	0.002 to 0.11
aC17	0.01 to 0.14	ND to 0.01	0.01 to 0.07	0.01 to 0.20	0.002 to 0.08
C17	0.05 to 0.20	ND to 0.54	0.02 to 0.09	0.004 to 0.23	0.02 to 0.28
C18:3n6	ND	0.005 to 0.03	0.03 to 0.12	ND	ND
C18:2n6	0.04 to 0.23	0.01 to 0.05	0.02 to 0.12	0.01 to 0.55	0.01 to 0.10
C18:3n3	0.005 to 0.46	ND to 0.04	0.03 to 0.11	0.11 to 0.56	ND
C18:1n9	0.02 to 0.38	0.02 to 0.93	0.05 to 0.46	0.05 to 0.99	0.09 to 1.04
C18:1n7	0.01 to 0.54	0.004 to 0.19	0.05 to 0.52	ND	ND
C18	0.69 to 0.85	0.82 to 3.71	0.14 to 0.73	0.06 to 1.24	0.26 to 5.22
C20:5n3	0.01 to 0.04	0.005 to 0.14	0.04 to 0.61	0.002 to 0.23	0.002 to 0.05
C20:1n9	0.003 to 0.01	0.004 to 0.05	0.01 to 0.35	0.003 to 0.05	0.003 to 0.02
C20	0.04 to 0.11	0.02 to 0.99	0.10 to 0.83	0.01 to 0.33	0.02 to 0.43
C21	ND to 0.02	0.005 to 0.89	0.03 to 0.45	ND	0.01 to 1.34
C22:6n3	0.01 to 0.05	0.004 to 0.38	0.03 to 0.12	0.003 to 0.15	0.01 to 0.03
C22:1n9	ND to 0.05	0.01 to 3.36	0.10 to 0.56	0.003 to 0.20	0.01 to 0.02
C22	0.10 to 0.16	0.01 to 3.36	0.28 to 16.52	0.005 to 0.80	0.04 to 0.97
C23	0.01 to 0.12	0.04 to 0.90	0.46 to 1.08	ND	0.01 to 0.27
C24:1	ND	0.004 to 1.08	0.08 to 0.27	0.005 to 0.19	ND to 0.05
C24	0.10 to 0.18	0.01 to 8.68	1.61 to 10.16	0.08 to 1.88	0.04 to 0.61
C26	0.15 to 0.52	0.01 to 6.97	1.70 to 10.16	0.07 to 0.97	0.03 to 0.38
C28	0.15 to 0.34	0.04 to 13.00	3.79 to 12.26	0.10 to 1.40	0.05 to 0.38
C30	0.24 to 0.56	0.02 to 10.83	4.37 to 16.05	0.15 to 1.99	0.05 to 0.53

ND denotes not detected

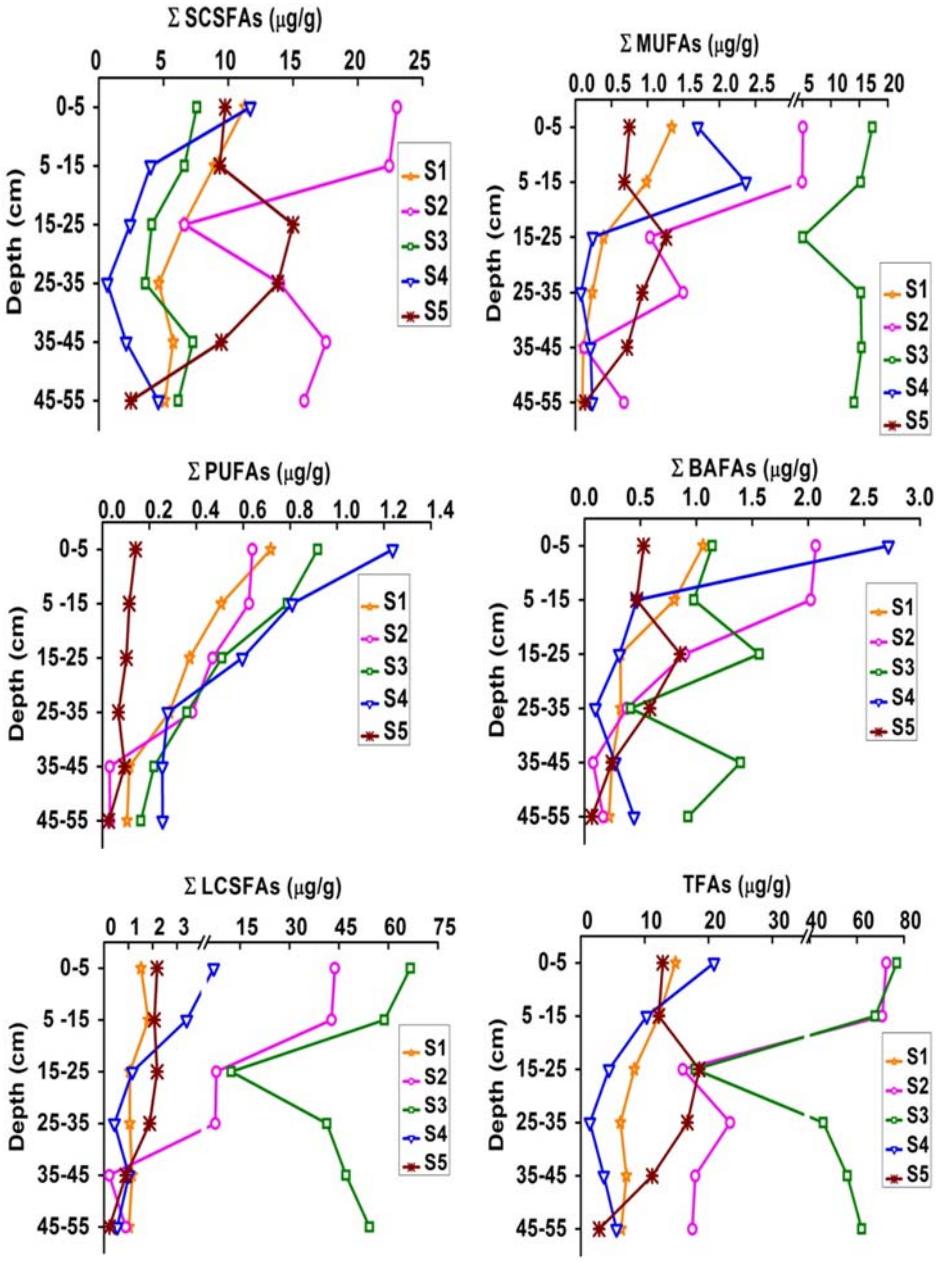

Figure 6.1 Vertical profiles of various classes of fatty acids

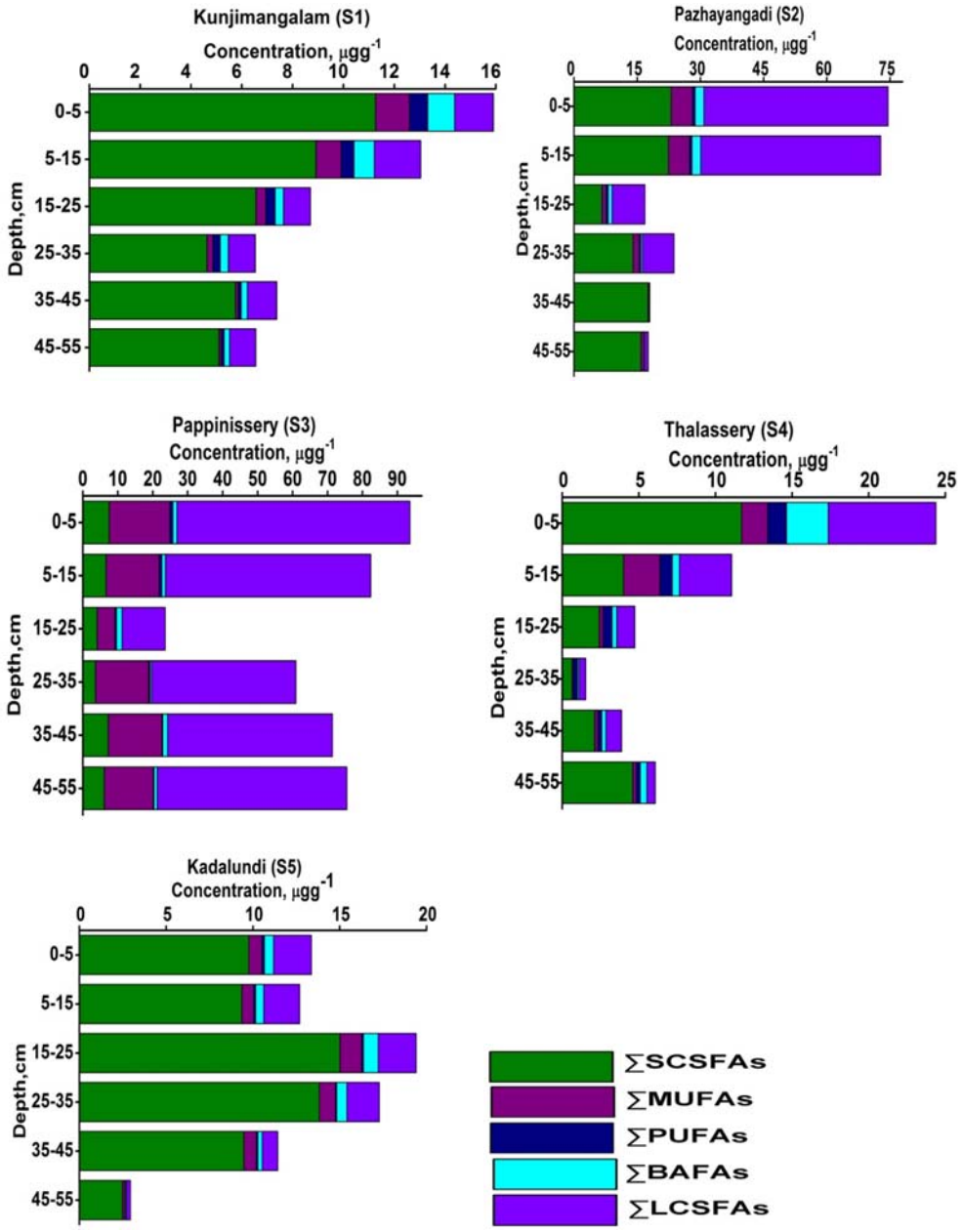

Figure 6.2 Distributional trends of different fatty acids at different sampling sites

6.3 Discussion

Fatty acids are widely used as a tool for the source characterisation of organic matter in marine sediments (Laureillard et al., 1997a, b; Budge and Parrish, 1998; Mudge et al., 1998; Fahl and Stein, 1999). There are many studies available which describes the relative distributions of the different sources of fatty acids in different aquatic sediments (Colombo et al., 1996; Gong and Hollander, 1997; Laureillard et al., 1997a; Stefanova and Disnar, 2000). However, the utility of fatty acids as quantitative tracers of the different organic carbon sources is complicated by many factors. Uncertainty in source are common (Harvey and Macko, 1997a; Wakeham, 1999), and the susceptibility to diagenetic processes of individual fatty acids usually varies during particle settlement through the water column (Wakeham and Canuel, 1990; Meyers and Eadie, 1993; Harvey and Macko, 1997b; Budge and Parrish, 1998) and after deposition (Sun and Wakeham, 1994; Canuel and Martens, 1996; Sun et al., 1997). The detection in changes of the source contribution is important for the reconstruction of environmental changes based on the sedimentary organic matter compositions. Changes in organic matter input also govern the vertical profile of fatty acids.

The prevailing environmental condition of sedimentary system (anoxic/suboxic/oxic) is another factor which determines the distribution of fatty acids in the sediments, since they determine the mode of microbial utilisation of sedimentary organic matter. In general oxygen- depleted (suboxic) or oxygen free (anoxic) conditions increase the preservation potential of organic matter (Holtvoeth et al., 2010). Efforts to link the

sedimentary FA composition and the availability of oxygen revealed that individual FAs undergo selective enrichment under oxygen limited conditions (Niggemann and Schubert, 2006). Gong and Hollander (1997) also established a greater contribution of bacterial FAs in sediments from the anoxic depocentre than in oxic sediments, in an investigation from Santa Monica Basin. Another example of enriched levels of bacterial and terrestrial FAs were reported in sediments from the Arabian Sea within the oxygen minimum zone (OMZ, <0.5 ml O_2/L), whereas the concentrations of other FAs showed no relation to the OMZ (Schulte et al., 2000).

Diagenesis modifies both the absolute concentration and the relative contribution of individual FAs. The fatty acids which escape degradation processes may accumulate or preserve under anoxic condition in the sediment layer. Preservation of organic compounds under anoxic condition plays a more important role in mangrove ecosystems. However, the source specific compounds have different preservation abilities.The differences in reactivity of FAs have mostly been associated with different sources; planktonic FAs are more reactive than terrestrial FAs (Canuel and Martens, 1996; Camacho-Ibar et al., 2003) and unsaturated FAs degrade faster than saturated FAs (Haddad et al., 1992; Sun and Wakeham, 1994). The unsaturated fatty acids are hard to preserve in their original contents in marine sediments because of their labile characteristics, resulting in loss via bacterial actitvity and/or zooplankton grazing (Carrie et al., 1998).

Association with protective matrices has been suggested to interpret for the greater stability of terrestrial FAs (Haddad et al., 1992; Canuel and

Martens, 1996). PUFAs and SCFAs are degraded more rapidly over time (e.g., with depth in the sediment core), while LCSFAs are more stable. The trend of decreasing concentration of ∑SCSFAs with depth is most likely due to preferential degradation of SCSFAs over time (Haddad et al., 1992; Canuel and Martens, 1996). Throughout early digenesis, FAs are preferentially degraded over the bulk organic carbon pool (Wakeham et al., 1997a, b). The reactivity of organic matter decreases with depth as more labile compounds are preferentially consumed (Canuel and Martens, 1996).

Bioturbation process can be recognised as one of the important reason for the variability of fatty acid concentration down the core (Allison et al., 2000). Even though bioturbation seems to occur at the surface samples, which may alter the redox state, promote the vertical transport of particles and stimulate microbial degradation, thereby having a greater impact on the diagenesis of sedimentary lipids than physical mixing alone (Aller et al., 2001; Kristensen and Holmer, 2001). Bioturbation supports degradation both directly by active consumption of sedimentary organic material and indirectly by stimulating microbial activity (Aller, 1982), and thus might effectively increase degradation rates (Niggemann and Schubert, 2006). Furthermore, subsurface deposit feeder organisms which live in deep sediment layers, enhance bioturbation rates (Dauwe et al., 1998). The activity of subsurface deposit feeder organisms thus represents one of the factors responsible for the degradation and vertical distribution of FAs in the sediments.

6.3.1 Biomarker Approach

6.3.1.1 Short chain saturated fatty acids (SCSFAs):

The SCSFAs include saturated fatty acids with C<22.The saturated fatty acids $C_{16:0}$ and $C_{18:0}$ are ubiquitous in the marine environment and are used as a measure of total community biomass and as biomarkers of plankton in the marine environment (Parkes, 1987) while $C_{14:0}$ fatty acid occurs in phytoplankton, especially in diatoms (Reitan et al., 1994) and to a lesser extent in dinoflagellates (Napolitano et al., 1995). The marine phytoplankton and settling particles in marine environments exhibit characteristic fatty acid composition in the range of $C_{14\text{-}22}$ (Claustre et al., 1989; Reemtsma et al., 1990; Colombo et al., 1996). $\sum C_{16}/\sum C_{18} > 1$, could be considered to be an indicator of benthic phytoplankton since $C_{16:0}$ is mainly found in phytoplankton; whereas zooplankton contains more $C_{18:0}$ (Sargent, 1976; Wakeham, 1995). $\sum C_{16}/\sum C_{18} > 1$ was recorded at all core sediment samples, which point towards the contribution of diatom (Parrish et al. 2000, Sanil Kumar and Nair, 2015). $C_{16:0}$ is the most abundant fatty acid in mangrove leaves (Sassen, 1977; Mfilinge et al., 2003, 2005; Hall et al., 2006) and was the major contributing fatty acid towards SCSFAs confirming the fact that litter addition is the most predominant source of organic matter in mangrove sediments.

6.3.1.2 Monounsaturated fatty acids (MUFAs)

MUFAs are commonly found in algae, zooplankton, bacteria and benthic fauna (Zimmerman and Canuel, 2001; Venturini et al., 2012). MUFAs such as, $C_{16:1n5}$, $C_{16:1n7}$ and $C_{16:1n9}$ act as signals for diatom derived organic matter (Berge et al., 1995; Suzuki and Matsuyama, 1995; Carrie et al., 1998).

Marine animals such as zooplankton and fish contain $C_{20:1}$ fatty acids (Ota et al., 1995; Albers et al., 1996). Although synthesised by various phytoplanktonic species (Zhukova and Aizdaicher, 1995; Volkman et al., 1998) and by zooplankton (Albers et al., 1996; Kattner and Hagen, 1998), the presence of 18:1n7 may reflect the bacterial contribution to the TFA pool (Thoumelin et al., 1997; Mudge et al., 1998). $C_{16:1}$ fatty acid is relatively common in marine algal species (Reitan et al., 1994; Berge et al., 1995). The input of diatom and dinoflagellate could be distinguished by the ratio of $C_{16:1}/C_{16:0.}$ The ratio >1.6 has been regarded as diatom origin (Budge and Parrish, 1998). However due to the higher exposure of unsaturated fatty acids to the biological and chemical degradation during the sedimentation (Birgel et al., 2004), the ratio could not be considered as a reliable one. This ratio recorded values <1 throughout the present investigation. MUFAs such as, $C_{20:1}$ and $C_{24:1}$ have been considered as zooplanktonic in origin (Wakeham et al., 1997a; Falk-Petersen et al., 1999; Sañé et al., 2011) , while $C_{15:1}$ is considered as signal of bacterial input. $C_{18:1n9}$ was also detected at all the five stations and this MUFA has been reported as a biomarker for brown algae (Jamieson and Reid, 1972; Johns et al., 1979). It is also related to the presence of dinoflagellates in primary producer's communities and zooplankton (Carrie et al., 1998). Mangrove ecosystems are complex environment for phytoplankton due to the combination of periodic variations and extremes of its physico-chemical parameters that could affect the zooplankton biomass in mangroves.

6.3.1.3 Polyunsaturated fatty acids (PUFAs)

$C_{16\text{-}22}$ PUFAs represent labile organic matter primarily of algal origin (Volkman et al., 1989; Carrie et al., 1998; Sushchik et al., 2013). The occurrence of PUFA, $C_{20:5n3}$ was noticed at all segments of the sedimentary extract. These PUFA classes of compounds have commonly been detected in diatoms (Pond et al., 1998), and have been used as diatom marker in marine environments (Currie and Johns, 1988; Colombo et al., 1996). Diatoms are one of the most common types of phytoplankton and are a major group of eukaryotic microalgae. Microalgae are a major source of fatty acids in most mangrove ecosystems. The detection of $C_{22:6n3}$ has been considered as dinoflagellate marker (Carrie et al., 1998). This PUFA also was present at all stations. The observations confirmed that diatoms and dinoflagellates are colonised in the sedimentary environment which is enriched with mangrove detrirus. The PUFAs, $C_{18:2n6}$, $C_{18:3n\ 3}$ and $C_{18:3n\ 6}$ have been employed as indicator of green algae (Dunstan et al., 1992; Kharlamenko et al., 1995; Napolitano et al., 1997; Meziane and Tsuchiya, 2000). The PUFA, $C_{18:2n6}$ was noted at all stations and $C_{18:3n3}$ except at S5, while $C_{18:3n6}$ was detected only at S2 and S3. Fatty acid analyses in recent studies revealed that $C_{18:2n6}$ and $C_{18:3n3}$ are also dominant in mangrove leaves (Hall et al., 2006; Meziane et al., 2007) and hence the polyunsaturated FAs: $C_{18:2n6}$ and $C_{18:3n3}$ can also be used as markers of terrestrial inputs in coastal environment (Napolitano et al., 1997; Budge and Parrish, 1998) and also as useful biomarkers of mangrove leaves in estuarine food web (Hall et al., 2006; Meziane et al., 2007).

In general, PUFAs are labile, highly abundant in fresh plankton and are rapidly lost during degradation in water column and sediment (Wakeham et al., 1997a; Budge and Parrish, 1998) by bacterial degradation and/or via zooplankton grazing and hence most of the originally produced PUFAs were lost before the particles reached the sediment. (Niggemann and Schubert, 2006). Thus, these PUFAs associated with phytoplankton would not necessarily be expected to be preserved in their original amounts, which may partially explain the absence of several diagnostic PUFAs in the sediments (Carrie et al., 1998). Therefore, the use of PUFAs alone could not be able to explain phytoplankton structure in sediments (Carrie et al., 1998; Hu et al., 2006).Those PUFAs, which escaped from diagenesis, may have preserved in the mangrove sediment samples under anoxic condition.

6.3.1.4 Long chain saturated fatty acids (LCSFAs)

Long chain saturated fatty acids principally (LCSFAs) are used as markers of terrestrial inputs in coastal environment (Napolitano et al., 1997; Budge and Parrish 1998; Meziane et al., 2006). Long chain even carbon number fatty acids from $C_{22:0}$ to $C_{30:0}$ are generally associated with the waxy leaf coatings of higher plants and are thus considered as indicative of higher plant inputs (Kolattukudy, 1970; Scribe et al., 1991; Colombo et al., 1996; Meyers, 1997). LCFAs were also found in high concentrations in mangrove leaves (Wannigama et al., 1981; Meziane and Tsuchiya, 2000; Alfaro et al., 2006). Five higher plant biomarkers, $C_{22:0}$, $C_{24:0,}$ $C_{26:0}$, $C_{28:0}$ and $C_{30:0}$ were characterised in this study. ∑LCSFAs contributed more towards TFAs at S2 (at 0-5cm, 5-15cm and 15-25cm) and S3.The high vegetation mass and limited tidal rhythm

favor the retention of organic matter which might be cause of higher concentration of LCFAs in these stations. LCSFAs are linked with the waxy leaf coatings of higher plants (Wannigama et al., 1981) and have been recognized as an indicator of terrestrial organic matter input (Nichols et al., 1982; Reiley et al., 1991) including mangroves (Meziane and Tsuchiya, 2000).

6.3.1.5 Bacterial fatty acids (BAFAs)

Bacteria are typically the dominant sources of odd and branched-chain acids, especially the iso- (i) and anteiso- (a) acids, i.e., $iC_{15:0}$, $iC_{17:0}$, $aC_{15:0}$ and $aC_{17:0}$ (Volkman et al., 1980; Kaneda, 1991; Haddad et al., 1992; Harvey, 1994; Gong and Hollander, 1997; Rajendran et al., 1997; Budge and Parrish, 1998; Carrie et al., 1998; Volkman et al., 1998; Palomo and Canuel, 2010). They are well-known biomarkers of gram-positive bacteria, gram-negative anaerobes and sulphate reducing bacteria (Wakeham et al., 1984; Rütters et al., 2002; Harvey et al., 2006; Dunn et al., 2008; Widenfalk et al., 2008; Gireeshkumar et al., 2015). Odd-numbered branched fatty acids (Br-FAs), are commonly synthesised by gram-positive microorganisms (Sushchik et al., 2013), and its presence in core sediment samples indicated marked bacterial contribution in sediments of study region. Bacteria contain the most distinct fatty acid compositions of all marine taxa, with high proportions of C_{13} to C_{21} odd-numbered fatty acids, often branched and with at most one unsaturation (Claustre et al., 1989). Fatty acid $C_{18:1n7}$ has also been used as a bacterial biomarker (Volkman et al., 1980; Claustre et al., 1989; Sañé et al., 2011). Hu et al., 2006, defined the sum of odd carbon-numbered (C_{13}-C_{19}) and all branched-chain fatty acids as bacterial indicator. Branched FAs were absent in fresh mangrove leaves, but detected during decomposition of leaf

and this might be due to the growth of microbes that were rich in branched FAs (Alikunhi et al., 2010).

6.4 Principal component analysis

Principal component analysis (PCA) has been used as a tool to determine factors which regulates the fatty acid composition in the study region and also reveals factors which could be attributed to different sources (Reentsma and Ittekot, 1992; Niggemann and Schubert, 2006) and environmental processes (Canuel, 2001). It provides the opportunity for identifying individual components as well as groups of components which gives explanations for the largest part of total variance in data set. This method is based on comparison of relative differences between contents of individual components of in different samples. This method has the advantage of revealing changes in minor components which might play a significant role in the identification of the state of degradation (Niggemann and Schubert, 2006).

A total of 85 % is explained by 6 factors out of which first two factors explained 46% of total variance (Table 6.2). Factor 1 accounted for 30% of total variance. This component consist of positive loadings for all LCSFAs (C_{22}, C_{24}, C_{26}, C_{28} and C_{30}), most of SCSFAs (C_8, C_{14}, C_{15}, C_{16}, C_{17}, C_{18} and C_{20}), and PUFAs ($C_{18:2n6}$, $C_{20:5n3}$ and $C_{22:6n3}$). The rotated component matrix is depicted in figure 6.2. According to the distribution, factor 1 reflects the diagenetic transformations which are characterised by the preferential accumulation of saturated fatty acids. PUFAs are mainly assigned to phytoplankton sources i.e., $C_{20:5n3}$ is considered as an indicator of diatoms, while presence of $C_{22:6n3}$ reflects the input from dinoflagellates. C18:2n6 is

found to be a component of mangrove leaves. Positive loadings on LCSFAs are the indication of terrestrial inputs. Factor 2 accounted 16% of total variance and consists of positive loading on iC_{15}, aC_{15}, iC_{17}, aC_{17} and $C_{18:1n7}$. These are bacterial biomarkers and hence factor 2 point towards bacterial reworking taking place in the mangrove sediments. Traditionally, long chain FAs are assigned to terrestrial sources. However, Gong and Hollander (1997) established that part of the long chain FAs are in situ products of bacterial reworking. Naraoka and Ishiwatari (2000) suggest that long chain FAs in sediments from the open Pacific derive from marine rather than from terrestrial sources. In the present study, the factor loading analysis showed that LCFAs and BAFAs form separate group, hence it can be concluded that the input of LCFAs was from higher plants.

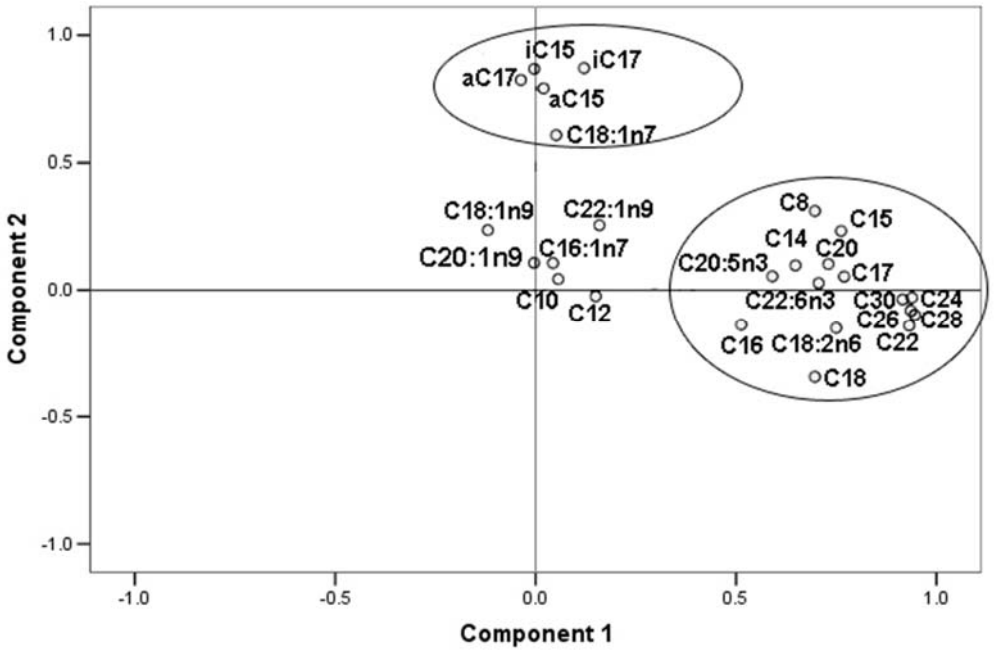

Figure 6.2 Component plot in rotated space

Table 6.2 Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	9.00	36.02	36.02	9.00	36.02	36.02	7.51	30.03	30.03
2	4.62	18.51	54.53	4.62	18.51	54.53	3.92	15.66	45.69
3	3.06	12.24	66.77	3.06	12.24	66.77	3.81	15.24	60.93
4	1.86	7.47	74.24	1.86	7.47	74.24	2.99	11.98	72.91
5	1.78	7.12	81.36	1.78	7.12	81.36	2.06	8.24	81.15
6	1.01	4.04	85.40	1.01	4.04	85.40	1.07	4.25	85.40
7	0.89	3.59	88.99						
8	0.76	3.06	92.05						
9	0.55	2.22	94.27						
10	0.38	1.51	95.78						
11	0.34	1.39	97.17						
12	0.33	1.32	98.49						
13	0.12	0.49	98.98						
14	0.10	0.40	99.38						
15	0.06	0.24	99.62						
16	0.04	0.18	99.80						
17	0.02	0.08	99.88						
18	0.01	0.04	99.92						
19	0.007	0.03	99.95						
20	0.002	0.01	99.96						
21	0.002	0.006	99.966						
22	0.001	0.004	99.97						
23	0.001	0.003	100.00						
24	6.44E-006	2.58E-005	100.00						
25	2.90E-007	1.16E-006	100.00						

6.5 Conclusion

Although most of the fatty acids are non-specific, the present study and studies in mangrove sediments from Cochin (Joseph et al., 2012) and those from Cochin estuarine sediments (Gireeshkumar, 2013) suggest that some of the fatty acids or fatty acid groups can be assigned to dominant sources. Plankton (phytoplankton and zooplankton) is probably the most important source of the monounsaturated acid $C_{16:1n7}$, and the polyunsaturated acids with 20 and 22 carbons (Zhukova and Aizdaicher, 1995; Volkman et al., 1998; Zimmerman and Canuel, 2001). Bacteria are typically the dominant sources of odd and branched-chain acids, especially the iso- (i) and anteiso- (a) acids $iC_{15:0}$, $iC_{17:0}$, $aC_{15:0}$ and $aC_{17:0}$ (Kaneda, 1991; Gong and Hollander, 1997; Harvey and Macko, 1997a). Long-chain fatty acids ($C_{24:0}$, $C_{26:0}$, $C_{28:0}$ and $C_{30:0}$) in marine sediments are typically associated with terrestrial inputs of organic matter from higher plants (Meyers, 1997). From the study, fatty acid biomarkers have established to be highly effective to evaluate the sources of organic matter in the different mangrove ecosystems under investigation. However, due to the fact that mangroves and terrestrial plants share common fatty acid markers, it is difficult to distinguish between mangrove and terrestrial plant organic matter inputs through the long chain fatty acids. Multi proxy biomarker approach should be employed as a more effective tool to differentiate the terrestrial higher plant sources from the mangrove litter.

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SUMMARY

Mangroves are highly productive ecosystems. They have well developed adaptation capability to cope with special environmental situation in tidal areas, characterised by anaerobic sediments and high salinity. An important function of mangroves is the stabilization of coastline by increased sedimentation rate and reduced erosion. They accumulate large amount of nutrients from ocean and land. The high macrophytic production generates much detritus, which is a major source of organic carbon to sediments. The material exchange between mangrove zones and adjacent coastal habitats influences the richness of organisms to inhabit in these environments. Primary production has a major role in the generation of large amounts of organic carbon in these transitional systems.

Defining the sources and composition of organic matter within mangrove sediments is crucial to understand the carbon dynamics in these ecosystems. Mangroves are valuable ecosystems with high biodiversity and valuable biological resources as well as they are the critical areas, being threatened due to human interventions like land reclamation, construction of ports and industrial operations. These ecosystems are disappearing at a faster rate with little public attention. Therefore the knowledge on the biogeochemical characteristics of these ecosystems is a prerequisite for the conservation and management of the existing mangrove vegetation cover.

The major portion of the mangrove forests of the state is located in the Kannur and Kozhikkode districts. A reconnaissance survey was conducted to

find out the true mangrove ecosystems in northern coast of Kerala and five sampling sites were identified, the selected stations were: Kunjimangalam (S1), Pazhayangadi (S2), Pappinissery (S3), Thalassery (S4) and Kadalundi (S5).

To study the general environmental condition, surface water samples were collected from these five ecosystems and water quality parameters were analysed seasonally. The core sediment samples were also collected from each station and analyzed for sedimentary variables like texture, total organic carbon, total nitrogen, total sulfur and heavy metals. Trace metal study established that Fe and Mn-oxyhydroxides plays a good role as host phase for trace metals and hence have a control on the distribution of heavy metals in the sediments. The complexation with organic matter also acts as significant mechanism for their dispersal pattern. Pollution indices such as enrichment factor, geoaccumulation index were employed to evaluate the historical record of contamination status of the core sediments, which indicated that the mangrove forests are under the threat of heavy metal accumulation. Numerical sediment quality guidelines were applied to assess the adverse biological effects of these metals and the study suggests that occasional biological effect may occur due to Ni.

The biochemical components (CHO, PRT, and LPD) along with chlorophyll pigments and phaeophytin were analysed to understand the quality and source characterisation of organic matter in sediments. The biochemical composition of sedimentary organic matter in the study region is quite different from other coastal systems and showed a dominance of carbohydrate over lipids and then by proteins. Significantly higher values of LPD in the study region might be due to its preservation under highly anoxic conditions. Higher concentrations of CHO point towards the possibility of higher input of vascular plant materials, especially mangrove litter. PRT/CHO ratio was found

to be <1 at all core samples which implied that mangrove sediments were characterized by a large amount of aged and/or non-living organic matter. The relatively lower LPD/CHO ratio in the sediments indicates the low nutritional quality of labile organic matter. Bulk elemental approach (C, H, N and S) was also employed to understand the environmental setting and source characterisation of the organic matter. The TOC/TN ratios were intermediate to that of autochthonous and terrestrial inputs of organic matter, signaling to a mixed origin. Stable carbon isotope ratio ($\delta^{13}C$) analysis showed values ranging from -29.19 to -23.87‰, suggesting vascular plant input into the sediment organic matter. The geochemical process like litter addition and diagenesis were found to be the major process controlling the biogeochemistry of the mangrove systems under study, which is established from the principal component analysis.

n-Alkanes are recognised as a significant fraction of sedimentary organic carbon and hence the detection and quantification of these compounds is useful to interpret the nature, sources and biogeochemical processes controlling their distribution in sediments. The characterisation of sources of organic matter in sedimentary environment was achieved through the analysis of composition of n-alkane in the core sediments from study area. The long chain n-alkanes predominated over short chain n-alkanes (except Kadalundi) indicating higher input of vascular plants to the sedimentary organic matter. The different indices analysed (CPI^a, CPI^b, TAR, ACL, C_{17}/Pr, C_{18}/Ph, Pr/Ph) confirmed the preservation of organic compounds in core sediments under anoxic condition. The presence of hopanes in the study region indicated bacterial input.

Fatty acids are ubiquitous in living organisms and due to their biological specificity, they can act as biomarkers for prokaryotes, fungi,

diatoms, dinoflagellates or vascular plants. They are useful tracers of the origin and flow of mangrove-derived organic carbon. Fatty acid biomarker analysis is highly useful for the source characterisation of organic matter since they are very source specific and easier to trace the origin of organic matter. The estimated fatty acids in the present investigation were classified into short chained saturated fatty acids, monounsaturated fatty acids, polyunsaturated fatty acids, bacterial fatty acid, each having well defined source signature. The fatty acid composition of the core sediments in mangrove sediments revealed significant quantities of highly potential source indicating compounds, provided clues on planktonic, bacterial and terrestrial contribution to sedimentary organic matter of the study region. The study using core sediments was helpful to reconstruct the historical events which were recorded in the sediment samples.

Scope and social benefit

Mangroves are highly productive but extremely sensitive and fragile ecosystems. They are of rich biodiversity, have highly significant role in the sustainability of seafood species, shoreline stability, economic standing and the survival of selected communities. But they are under the threat of reclamation and other human encroachment. Conservation of mangrove vegetation is a prerequisite in the context of predicted scenarios of global warming and sea level rise. The organic matter in mangroves is composed of substances from various sources and in different states of decomposition. The source characterisation of organic matter in sediments is important to understand about the biogeochemical cycles. Study of specific organic compounds in modern sediments isolated from different depths can provide information about the changes in organic matter sources and about post-depositional alterations of the organic matter itself.

Future scope of the work

The present study clearly indicates the complexity of the mangrove ecosystems. A better characterisation of source of organic matter can be achieved through multi proxy biomarker approach involving quantification of wide classes of lipid biomarkers like n-alkanols, sterols, fatty alcohols and pentacyclic triterpenoids along with the alkanes, hopanes and fatty acids. An efficient and reliable arrangement and facilities for survey, identification of sources of organic matter to sediments, quantification of these biomarker proxies, long term monitoring of biogeochemical characteristics of the sediments and implementation of proper sustainable management strategy can prevent further ecological degradation of these vulnerable ecosystems.

APPENDICES

Table 2.1 Spatial and seasonal variation of hydrographical parameters in the study area

Season	Stations	pH	Salinity	DO (mg/L)	Alkalinity, (mg $CaCO_3$/L)	Nitrite (µmol/L)	Nitrate (µmol/L)	Ammonia (µmol/L)	Phosphate (µmol/L)	TP (µmol/L)	Chl-a (µg/L)	Chl-b (µg/L)	Chl-c (µg/L)	Phaeophytin (µg/L)
Post monsoon	S1	7.20	8.21	3.84	49.50	0.15	1.37	4.73	0.59	2.96	17.29	0.09	4.34	31.01
	S2	7.40	7.67	4.90	79.20	0.28	3.65	10.24	0.83	4.31	3.85	0.17	1.29	24.59
	S3	7.10	4.26	2.86	44.55	0.22	1.94	22.85	0.59	8.61	0.77	0.38	0.31	4.28
	S4	7.30	9.25	5.31	49.50	0.22	2.79	27.95	0.93	5.92	1.19	ND	ND	4.01
	S5	7.20	4.26	6.41	54.45	0.55	8.43	25.21	1.37	7.54	6.01	1.61	1.93	25.93
Pre monsoon	S1	8.00	35.97	9.34	138.23	0.59	0.29	7.88	3.57	3.67	40.86	3.65	13.80	22.27
	S2	7.90	33.97	2.38	128.53	0.29	0.85	0.79	3.13	3.56	18.91	2.43	6.21	10.52
	S3	7.20	29.31	0.51	167.33	0.61	1.31	98.09	6.56	6.65	3.23	1.99	3.37	1.98
	S4	8.00	34.30	5.09	121.25	0.70	4.33	5.12	2.89	2.95	2.18	1.12	1.70	1.01
	S5	8.00	34.70	5.26	123.68	0.99	2.34	0.00	1.32	1.53	15.19	6.00	7.43	7.64
Monsoon	S1	7.81	0.73	3.76	43.65	0.42	3.14	5.52	11.11	21.96	3.09	1.39	0.05	3.31
	S2	8.03	0.71	6.86	25.22	0.33	11.68	48.45	14.92	21.43	2.81	1.71	2.44	23.20
	S3	8.05	0.24	5.22	37.83	0.46	15.67	80.36	14.39	21.15	1.11	1.71	0.87	1.23
	S4	7.82	11.14	5.88	83.42	0.99	16.81	69.33	9.98	10.04	ND	ND	ND	ND
	S5	7.89	26.64	7.35	22.31	0.31	20.79	7.09	15.07	22.88	0.36	ND	ND	0.19

ND denotes not detected

Table 3.1 Concentration of estimated parameters at Kunjimangalam (S1)

Parameters	0-5 cm	5-15 cm	15-25 cm	25-35 cm	35-45 cm	45-55 cm
pH	6.18± 0.02	6.15± 0.03	6.1± 0.01	5.82± 0.02	5.8 ±0.01	5.7± 0.02
Eh	-361±3	-372±2	-374±5	-365±3	-355±4	-345±3
Sand (%)	85.35± 5.8	89.72± 5.7	77.41± 4.9	55.24± 2.56	52.76± 3.76	48.76± 5.72
Silt (%)	4.62± 2.2	1.08± 0.63	8.36± 0.59	27.34± 2.03	25.79± 4.32	22.18± 3.06
Clay (%)	10.02± 3.56	9.2± 5.07	14.23± 4.31	17.42± 3.32	21.45± 4.6	29.06± 5.94
TOC (%)	1.76± 0.03	0.52± 0.01	0.57± 0.01	0.4± 0.01	0.48± 0.02	0.41± 0.01
TN (%)	0.15± 0.02	0.03± 0.001	0.03± 0.001	0.02± 0.004	0.02± 0.006	0.02± 0.003
TS (%)	0.13± 0.01	0.04± 0.01	0.03± 0.005	0.01± 0.001	0.01± 0.003	0.01± 0.003
Cd (mg/kg)	0.19± 0.05	ND	ND	0.47± 0.02	0.56± 0.03	0.29± 0.01
Co (mg/kg)	10.70± 1.23	13.44± 2.35	16.47± 1.79	18.92± 1.82	17.52± 1.79	16.88± 2.24
Cu (mg/kg)	11.97± 3.31	11.01± 1.23	14.39± 1.45	13.84± 1.26	9.66± 1.95	8.55± 1.19
Fe (%)	1.25± 0.05	1.25± 0.03	1.93± 0.06	3.44± 1.03	2.57± 1.15	3.00± 1.79
Mn (mg/kg)	72.58± 4.39	121.66± 5.52	127.12± 4.13	169.19± 3.39	175.06± 3.16	182.05± 2.23
Ni (mg/kg)	29.92± 1.17	26.65± 1.23	37.03± 1.19	45.27± 1.57	71.95± 1.63	72.99± 2.33
Pb (mg/kg)	18.24± 1.54	5.06± 1.01	11.46± 1.07	16.04± 3.53	13.24± 0.04	11.65± 1.67
Zn (mg/kg)	23.01± 0.97	24.75± 1.12	38.36± 3.25	45.11± 1.29	43.14± 1.31	40.22± 1.79

Table 3.II Concentration of estimated parameters at Pazhayangadi (S2)

Parameters	0-5 cm	5-15 cm	15-25 cm	25-35 cm	35-45 cm	45-55 cm
pH	7.12± 0.03	6.99± 0.02	6.92± 0.03	6.87± 0.04	6.82± 0.02	6.79± 0.03
Eh	-365±3	-369±4	-365±2	-371±4	-370±3	-368±4
Sand (%)	1.22± 0.26	10.87± 1.23	52.53± 1.56	57.78± 0.75	51.24± 1.22	48.79± 1.79
Silt (%)	27.42± 1.22	20.71± 1.11	20.5± 1.23	19.94± 1.24	22.63± 1.27	25.97± 2.34
Clay (%)	71.36± 2.12	68.43± 2.56	26.96± 1.13	22.28± 1.24	26.13± 1.54	25.24± 1.11
TOC (%)	4.31± 1.1	3.84± 0.98	3.21± 0.79	1.91± 0.59	2.18± 1.24	1.12± 0.78
TN (%)	0.23± 0.03	0.18± 0.02	0.14± 0.02	0.08± 0.02	0.09± 0.01	0.05± 0.03
TS (%)	0.42± 0.01	0.3± 0.01	1.2± 0.04	1.15± 0.19	1.32± 0.17	0.57± 0.21
Cu (mg/kg)	29.42± 4.23	25.82± 3.21	20.07± 2.22	14.96± 3.12	16.85± 2.25	16.01± 3.11
Co (mg/kg)	17.93± 3.42	24.43± 4.43	23.86± 3.18	18.34± 2.28	17.75± 2.76	19.19± 1.32
Cd (mg/kg)	1.84± 0.02	ND	0.21± 0.11	ND	ND	ND
Fe (%)	3.39± 1.12	2.78± 1.19	2.93± 1.35	2.32± 1.23	2.92± 1.35	3.15± 1.65
Mn (mg/kg)	162.30± 4.67	115.76± 4.56	198.27± 3.38	110.09± 4.53	122.57± 2.96	120.55± 4.73
Ni (mg/kg)	65.43± 5.42	61.34± 2.23	48.41± 5.27	34.77± 3.26	40.22± 2.23	40.68± 3.36
Pb (mg/kg)	18.13± 1.65	23.02± 2.14	15.53± 2.12	5.35± 1.54	10.69± 1.23	14.04± 1.17
Zn(mg/kg)	55.10± 4.56	51.72± 4.32	41.63± 3.37	29.66± 2.25	35.39± 3.35	40.18± 4.15

Table 3.III Concentration of estimated parameters at Pappinissery (S3)

Parameters	0-5 cm	5-15 cm	15-25 cm	25-35 cm	35-45 cm	45-55 cm
pH	7.03± 0.03	6.98± 0.03	6.89± 0.02	6.85± 0.04	6.79± 0.03	6.76± 0.02
Eh	-375±5	-381±3	-378±2	-372±3	-372±4	-368±5
Sand (%)	33.92± 1.25	1.66± 0.65	15.46± 1.15	7.1± 0.78	4.62± 0.69	7.45± 1.12
Silt (%)	24.7± 1.24	41.69± 1.36	28.39± 1.65	33.62± 1.38	30.74± 1.25	39.93± 2.15
Clay (%)	41.39± 1.26	56.65± 2.59	56.15± 2.11	59.28± 1.45	64.63± 1.64	52.62± 1.34
TOC (%)	6.88± 1.12	5.65± 0.79	4.2± 0.32	3.4± 0.59	3.91± 0.29	2.97± 1.23
TN (%)	0.31± 0.09	0.25± 0.03	0.17± 0.01	0.17± 0.02	0.17± 0.03	0.15± 0.07
TS (%)	2.73± 1.13	2.71± 1.03	2.72± 0.94	2.18± 0.76	1.92± 0.63	2.02± 0.19
Cu (mg/kg)	29.81± 2.57	35.99± 3.36	33.55± 1.98	34.09± 2.24	36.05± 1.97	32.29± 1.76
Co (mg/kg)	23.03± 2.12	28.22± 1.56	22.05± 1.79	30.42± 3.11	36.94± 3.56	31.56± 2.59
Cd (mg/kg)	0.77± 0.27	0.05± 0.01	ND	1.30± 0.23	0.17± 0.13	0.82± 0.05
Fe (%)	3.93± 0.45	3.89± 0.36	3.43± 0.25	5.34± 1.02	5.40± 0.86	4.49± 0.83
Mn (mg/kg)	173.01± 4.56	147.18± 3.76	71.45± 4.56	160.74± 5.34	189.12± 5.25	179.32± 5.56
Ni (mg/kg)	68.68± 2.35	72.71± 1.17	57.33± 1.23	67.50± 2.16	71.40± 3.12	63.89± 1.29
Pb (mg/kg)	21.49± 2.19	25.83± 1.76	10.57± 1.27	23.73± 1.59	23.06± 3.12	19.86± 1.88
Zn(mg/kg)	75.33± 1.34	78.42± 1.42	67.23± 2.59	82.21± 1.79	76.49± 1.45	63.94± 2.14

Table 3.IV Concentration of estimated parameters at Thalassery (S4)

Parameters	0-5 cm	5-15 cm	15-25 cm	25-35 cm	35-45 cm	45-55 cm
pH	6.92± 0.03	6.89± 0.02	6.78± 0.03	6.64± 0.04	6.65± 0.03	6.59± 0.02
Eh	-355±3	-358±4	-360±3	-354±2	-352±3	-352±4
Sand (%)	44.94± 1.23	36.2± 1.15	65.3± 1.46	60.87± 1.72	71.73± 1.97	66.96± 1.23
Silt (%)	22.54± 1.55	29.65± 1.14	13.79± 1.35	18.24± 1.41	12.24± 1.11	15.03± 0.96
Clay (%)	32.51± 1.11	34.15± 1.32	20.91± 1.78	20.88± 2.11	16.04± 2.41	18.02± 1.66
TOC (%)	2.13± 0.76	2.04± 0.78	1.56± 0.37	1.25± 0.15	1.02± 0.58	1.22± 0.36
TN (%)	0.15± 0.01	0.14± 0.01	0.09± 0.02	0.07± 0.01	0.05± 0.02	0.08± 0.01
TS (%)	0.36± 0.11	0.73± 0.13	1.19± 0.53	1.47± 0.29	1.32± 0.56	1.48± 0.34
Cu (mg/kg)	20.55± 1.45	16.98± 1.13	14.32± 1.34	15.49± 1.12	16.23± 1.43	15.87± 1.24
Co (mg/kg)	14.87± 1.14	17.11± 1.32	15.00± 1.45	17.44± 1.84	14.37± 1.23	18.52± 1.78
Cd (mg/kg)	0.13± 0.03	0.12± 0.1	0.05± 0.06	0.71± 0.53	0.77± 0.33	0.73± 0.42
Fe (%)	2.50± 0.56	2.39± 0.23	2.34± 0.18	2.48± 0.21	2.31± 0.26	2.61± 0.76
Mn (mg/kg)	91.89± 3.65	89.15± 2.21	126.40± 2.57	137.30± 2.18	115.70± 1.37	159.96± 1.38
Ni (mg/kg)	37.63± 1.15	38.78± 1.12	32.28± 1.35	34.50± 2.33	33.40± 1.78	32.79± 1.89
Pb (mg/kg)	12.32± 1.73	18.95± 1.45	8.88± 0.92	13.30± 1.56	8.38± 0.79	6.09± 0.32
Zn (mg/kg)	39.88± 1.56	36.63± 1.52	29.87± 1.76	32.53± 1.58	29.34± 2.12	33.49± 1.46

Table 3.V Concentration of estimated parameters at Kadalundi (S5)

Parameters	0-5 cm	5-15 cm	15-25 cm	25-35 cm	35-45 cm	45-55 cm
pH	6.9± 0.02	6.83± 0.03	6.79± 0.04	6.61± 0.03	6.59± 0.04	6.57± 0.02
Eh	-359±3	-366±4	-356±3	-364±5	-356±3	-346±4
Sand (%)	44.65± 2.35	65.78± 3.26	43.87± 1.75	59.22± 2.25	48.4± 1.17	60.46± 2.25
Silt (%)	28.94± 1.23	13.32± 1.15	23.27± 1.28	20.64± 2.11	25.79± 2.16	24.04± 2.11
Clay (%)	26.41± 1.17	20.9± 1.54	32.86± 2.32	20.14± 1.75	25.81± 1.99	15.5± 1.76
TOC (%)	2.53± 0.17	1.95± 0.24	1.07± 0.15	1.2± 0.13	1.19± 0.16	1.01± 0.05
TN (%)	0.21± 0.07	0.12± 0.01	0.09± 0.03	0.08± 0.01	0.06± 0.01	0.05± 0.01
TS (%)	0.4± 0.03	0.34± 0.4	0.17± 0.02	1.11± 0.03	0.76± 0.12	0.58± 0.15
Cu (mg/kg)	38.17± 3.49	27.16± 2.79	17.43± 2.13	18.13± 1.34	12.03± 1.57	14.72± 1.75
Co (mg/kg)	30.72± 1.98	28.59± 2.13	26.05± 3.14	28.29± 3.23	25.49± 3.11	26.10± 1.33
Cd (mg/kg)	1.48± 0.35	0.22± 0.02	0.25± 0.15	0.12± 0.03	0.89± 0.32	1.78± 0.76
Fe (%)	5.53± 2.45	4.29± 2.11	3.61± 1.11	3.67± 1.15	3.06± 1.23	3.78± 1.36
Mn (mg/kg)	341.55± 5.78	293.10± 4.96	304.79± 3.37	272.77± 5.59	224.47± 2.55	315.61± 3.56
Ni (mg/kg)	78.02± 3.87	58.95± 4.56	70.80± 3.67	73.03± 4.38	50.26± 5.44	64.67± 5.97
Pb (mg/kg)	29.93± 1.72	22.74± 2.43	19.94± 1.89	12.36± 3.11	16.26± 2.43	22.18± 3.11
Zn (mg/kg)	71.66± 2.13	55.97± 1.43	46.46± 2.34	50.02± 4.22	29.69± 3.28	38.92± 3.95

Table 4.1 Distribution of various parameters at Kunjimangalam (S1)

Parameters	0-5cm	5-15cm	15-25cm	25-35cm	35-45cm	45-55cm
Carbohydrates, mg/g	3.69± 0.13	2.46± 0.6	3.13± 0.18	3.33± 0.02	3.13± 0.78	3.03± 1.01
Lipid, mg/g	6.77± 0.40	1.76± 0.24	1.44± 0.72	0.60± 0.05	1.08± 0.16	0.98± 0.52
Protein, mg/g	1.74± 0.45	0.76± 0.17	0.47± 0.04	0.44± 0.02	0.55± 0.16	0.48± 0.32
Tannin & lignin, mg/g	0.68± 0.15	0.21± 0.08	0.17± 0.06	0.07± 0.02	0.05± 0.001	0.35± 0.06
PRT/CHO	0.47	0.31	0.15	0.13	0.18	0.16
LPD/CHO	1.84	0.71	0.46	0.18	0.34	0.32
Chlorophyll a, µg/kg	3.82± 0.22	0.38± 0.12	0.58± 0.13	0.08± 0.005	0.39± 0.02	0.45± 0.06
Chlorophyll b, µg/kg	0.79± 0.03	0.10± 0.02	0.45± 0.11	0.29± 0.03	0.48± 0.06	0.50± 0.07
Chlorophyll c, µg/kg	1.25± 0.15	0.21± 0.03	0.18± 0.03	0.36± 0.02	0.18± 0.015	0.38± 0.17
Phaeophytin, µg/kg	11.59± 0.21	1.65± 0.13	3.65± 0.21	0.56± 0.06	2.11± 0.25	2.01± 0.23
$\delta^{13}C$, ‰	-27.76± 0.01	-26.67± 0.01	-26.53 ± 0.01	-25.79 ± 0.01	-26.23± 0.01	-26.38± 0.01
TOC/TN ratio	11.40	20.64	19.93	22.22	19.67	20.50

Table 4.II Distribution of various parameters at Pazhayangadi (S2)

Parameters	0 -5 cm	5 -15 cm	15 - 25 cm	25 -35 cm	35-45 cm	45- 55 cm
Carbohydrate, mg/g	24.63± 1.11	12.28± 1.14	11.04± 0.54	5.62± 1.10	5.60± 0.89	3.44± 0.77
Lipid, mg/g	17.58± 1.14	12.41± 1.11	7.96± 0.59	5.99± 0.38	3.76± 0.27	3.61± 0.31
Protein, mg/g	8.23± 0.55	3.23± 0.48	3.03± 0.77	1.72± 0.51	2.47± 0.68	1.31± 0.25
Tannin & Lignin, mg/g	9.42± 1.27	2.85± 0.76	2.65± 0.78	1.75± 0.65	1.56± 0.72	1.03± 0.67
PRT/CHO	0.33	0.26	0.27	0.31	0.44	0.38
LPD/CHO	0.71	1.01	0.72	1.07	0.67	1.05
Chlorophyll a, µg/kg	12.48± 1.14	3.40± 0.58	3.56± 0.74	2.14± 0.52	2.46± 0.56	1.38± 0.75
Chlorophyll b, µg/kg	5.77± 1.1	1.07± 0.32	1.22± 0.15	1.08± 0.24	1.65± 0.15	1.71± 0.21
Chlorophyll c, µg/kg	5.27± 1.24	1.13± 0.24	2.02± 0.25	1.04± 0.72	1.35± 0.62	2.41± 0.37
Phaeophytin, µg/kg	15.71± 1.22	8.09± 0.59	7.17± 1.24	5.74± 0.57	2.80± 0.65	0.91± 0.12
$\delta^{13}C$, ‰	-28.42 ± 0.01	-28.30± 0.01	-28.03± 0.01	-27.45± 0.01	-27.20± 0.01	-26.86± 0.01
TOC/TN ratio	19.10	21.33	22.48	22.74	23.64	23.33

Table 4.III Distribution of various parameters at Pappinissery (S3)

Parameters	0-5 cm	5 – 15 cm	15-25 cm	25-35 cm	35-45 cm	45-55 cm
Carbohydrate, mg/g	26.98± 1.62	25.66± 1.54	26.17± 0.68	25.40± 1.12	21.85± 1.21	15.26± 0.78
Lipid, mg/g	33.50± 1.65	17.28± 1.12	14.21± 1.24	10.52± 1.41	8.96± 0.78	7.76± 0.24
Protein, mg/g	6.85± 0.75	4.77± 0.98	3.86± 0.76	4.03± 0.68	2.14± 0.75	2.50± 0.48
Tannin &Lignin, mg/g	11.17± 1.24	8.10± 0.98	9.79± 0.59	8.71± 0.79	7.60± 0.45	6.98± 0.57
PRT/CHO	0.25	0.19	0.15	0.16	0.10	0.16
LPD/CHO	1.24	0.67	0.54	0.41	0.41	0.51
Chlorophyll a, µg/kg	11.44± 1.1	7.21± 0.79	7.77± 0.82	5.42± 0.78	3.60± 0.87	3.87± 0.64
Chlorophyll b, µg/kg	4.37± 1.23	2.52± 0.56	2.21± 0.58	2.30± 0.79	1.47± 0.39	1.50± 0.59
Chlorophyll c, µg/kg	5.42± 1.06	4.39± 0.89	4.07± 0.57	2.75± 0.58	1.54± 0.89	1.94± 0.28
Phaeophytin, µg/kg	15.88± 1.2	17.36± 1.05	12.73± 1.14	10.80± 1.24	8.07± 0.79	8.01± 0.97
$\delta^{13}C$, ‰	-29.19 ±0.01	-26.90± 0.01	-27.26 ± 0.01	-27.02 ± 0.01	-25.55 ± 0.01	-25.84± 0.01
TOC/TN ratio	22.19	22.42	24.14	20.00	22.73	19.64

Table 4.IV Distribution of various parameters at Thalassery (S4)

Parameters	0-5 cm	5-15 cm	15-25 cm	25-35 cm	35-45 cm	45-55cm
Carbohydrate, mg/g	11.37± 1.75	8.13± 1.21	4.62± 0.75	4.03± 0.54	4.49± 0.46	3.64± 0.96
Protein, mg/g	1.94± 0.25	1.78± 0.34	1.63± 0.24	1.10± 0.16	1.11± 0.21	1.15± 0.11
Lipid, mg/g	2.47± 0.45	1.59± 0.13	0.95± 0.09	0.77± 0.11	0.49± 0.07	0.66± 0.12
Tannin& lignin, mg/g	0.43± 0.23	0.60± 0.32	0.52± 0.21	0.37± 0.62	0.65± 0.32	1.01± 0.35
PRT/CHO	0.17	0.22	0.35	0.27	0.25	0.32
LPD/CHO	0.22	0.20	0.20	0.19	0.11	0.18
Chlorophyll a, µg/kg	4.21± 1.21	0.41± 0.12	0.63± 0.23	0.08± 0.02	0.43± 0.04	0.50± 0.05
Chlorophyll b, µg/kg	0.86± 0.19	0.11± 0.05	0.50± 0.12	0.32± 0.25	0.52± 0.34	0.55± 0.44
Chlorophyll c, µg/kg	1.50± 0.59	0.25± 0.12	0.22± 0.25	0.43± 0.32	0.22± 0.15	0.46± 0.32
Phaeophytin, µg/kg	13.90± 5.63	1.98 ± 0.75	4.38± 0.67	1.87± 0.87	2.53± 0.76	2.41± 0.57
$\delta^{13}C$, ‰	-28.13± 0.01	-25.05 ± 0.01	-28.67± 0.01	-27.35± 0.01	-25.90 ± 0.01	-25.74 ±0.01
TOC/TN ratio	14.52	14.57	17.33	17.86	20.40	14.70

Table 4.V Distribution of various parameters at Kadalundi (S5)

Parameters	0-5 cm	5 -15cm	15-25cm	25-35cm	35-45cm	45-55cm
Carbohydrate, mg/g	8.04± 0.78	7.72± 1.11	4.03± 0.63	3.92± 0.95	3.51± 1.02	2.96± 0.68
Lipid, mg/g	4.85± 0.26	2.86± 0.56	2.08± 0.65	2.22± 0.73	1.79± 0.65	0.62± 0.06
Protein, mg/kg	241.94± 7.3	143.98± 5.2	61.36± 3.5	86.96± 3.25	75.23± 2.57	87.88± 3.62
Tannin & Lignin, mg/g	1.23± 0.9	0.95± 0.58	0.67± 0.5	0.50± 0.3	0.47± 0.15	0.53± 0.53
PRT/CHO	0.03	0.02	0.02	0.02	0.02	0.03
LPD/CHO	0.60	0.37	0.52	0.57	0.51	0.21
Chlorophyll a, µg/g	15.37± 1.29	3.96± 0.69	1.26± 0.37	1.40± 0.25	1.84± 0.65	1.29± 0.28
Chlorophyll b, µg/g	3.48± 0.56	1.18± 0.23	0.18± 0.09	0.20± 0.02	0.45± 0.01	0.94± 0.03
Chlorophyll c, µg/g	2.55± 0.15	0.58± 0.03	0.22± 0.03	0.25± 0.01	0.28± 0.02	0.78± 0.02
Phaeophytin, µg/g	21.60± 1.25	7.28± 0.65	2.93± 0.23	2.03± 0.06	3.36± 0.23	2.51± 0.12
$\delta^{13}C$, ‰	-25.43± 0.01	-25.14± 0.01	-24.27± 0.01	-23.87± 0.01	-24.98± 0.01	-25.10 ± 0.01
TOC/TN ratio	11.89	16.45	11.89	15.00	19.83	20.20

Table 5.I The concentration of n - alkanes in Kunjimangalam (S1)

Alkanes	Concentration, ngg^{-1} (Average±Standard Deviation)					
	0-5 cm	5-15 cm	15-25 cm	25-35 cm	35-45 cm	45-55 cm
C_{11}	10±1.15	12±1.15	12±2.31	12±1.13	12±1.05	12 ±1.11
C_{12}	11±0.98	14±1.11	16±1.03	26±1.12	96±1.21	73±2.93
C_{13}	147+5.34	134±1.23	252±2.32	243±2.18	278±1.13	153± 2.02
C_{14}	462+ 3.12	116±1.12	101±1.10	156±1.21	556±1.17	339±1.23
C_{15}	269±1.24	222±1.21	247±1.32	217±1.17	231±1.78	218±1.15
C_{16}	130±1.23	183± 1.15	252±1.21	121±1.41	267±1.18	185±1.34
C_{17}	233±1.17	123±1.27	325± 1.51	318±1.94	153±1.41	229±1.32
Pr	62±0.23	42±0.32	66±0.12	15±0.33	24±0.24	33±1.15
C_{18}	207±1.12	405±1.45	379±1.32	166±1.18	189±1.15	865±0.78
Ph	80±0.22	165±0.87	70±1.01	56±0.23	47±0.92	192±0.34
C_{19}	44±0.11	94±0.25	97±0.31	22±0.23	39±0.05	29±0.17
C_{20}	142±1.21	141±1.11	117±1.02	126±1.15	172±0.67	147±0.77
C_{21}	135± 0.84	129± 1.11	315±1.23	29± 0.15	36±0.12	21±0.12
C_{22}	1132±7.35	633±1.96	714±2.12	811±1.13	428±1.15	748±2.22
C_{23}	100±1.11	28±0.21	19±0.13	78±0.28	34±0.15	20±0.32
C_{24}	820±1.15	750±1.42	720±1.65	111±1.17	85±0.98	92±0.04
C_{25}	75±1.13	70±1.12	29±0.34	10±0.31	41±0.15	24±0.23
C_{26}	50±0.13	54±0.18	66±0.15	10±0.24	73±0.15	81±0.33
C_{27}	2601±2.97	2143±8.76	3199±7.34	3214±3.06	2444±3.13	2944±3.42
C_{28}	313±1.13	336±1.31	326±1.03	312±0.93	311±0.78	381±1.10
C_{29}	6693±2.31	6431±2.22	6607±1.15	6375±1.32	6245±1.36	6872±1.19
C_{30}	150±0.25	127±0.37	13±0.12	10±0.11	30±1.22	19±0.12
C_{31}	541±1.25	382±1.21	399±1.14	311±1.16	469±0.11	198±0.56
C_{32}	131±1.21	97± 0.21	29±0.11	12±0.06	60±0.77	135±0.63
C_{33}	462±0.17	155±0.14	25±0.05	17±0.02	72±0.05	42±0.06
Total	14998±17	12985±21	14395±28	12779±87	12393±95	14050±76

Table 5.II The concentration of n - alkanes in Pazhayangadi (S2)

Alkanes	Concentration, ngg^{-1} (Average± Standard Deviation)					
	0-5 cm	5-15 cm	15-25 cm	25-35 cm	35-45 cm	45-55 cm
C_{11}	3 ±0.02	10±0.19	14±0.11	6±0.06	5±0.02	109±1.12
C_{12}	824±0.15	1122±1.19	583±1.01	629±0.23	882±0.14	572±0.15
C_{13}	493±1.17	669±1.25	644±1.11	132±1.03	748±1.17	1215±1.15
C_{14}	1820±9.2	1710±8.7	1447±3.49	292±0.12	1614±1.43	208±1.14
C_{15}	432±1.13	811±1.23	947±1.32	262± 1.59	1274±1.34	1224±1.12
C_{16}	1041±1.25	578±0.79	741±0.67	372±0.54	865±0.17	858±0.22
C_{17}	576±0.17	592±0.15	547±0.19	549±0.15	471±0.23	657±1.17
Pr	201±1.23	231±1.11	252±1.31	224±1.37	218±1.86	312±1.17
C_{18}	1149±4.43	2972±1.76	392±1.23	834±1.19	4792±1.25	7964±1.44
Ph	441±1.53	853±1.37	209±1.45	360±1.34	1453±2.27	1624±1.22
C_{19}	248±0.54	180±0.31	178±0.13	154±1.21	218±1.16	240±1.31
C_{20}	774±1.31	590±1.12	228±1.16	45±0.04	39±0.08	436±1.18
C_{21}	264±1.02	205±1.54	85±0.44	44±0.18	36±1.65	387±1.32
C_{22}	3697±8.37	2248±9.76	125±1.67	274±1.54	334±1.66	348±2.31
C_{23}	1875±2.11	1158±2.16	93±0.22	31±0.08	574±1.12	584±0.65
C_{24}	2852±2.65	1738±3.45	104±1.34	32±1.12	606±1.56	1539±2.25
C_{25}	2278±8.79	4996±7.66	4658±4.34	2321±3.69	7547±4.48	4267±3.27
C_{26}	1643±2.19	10662±2.31	850±1.01	546±0.98	810±0.39	4289±4.38
C_{27}	8612±8.82	10435±9.31	14327±7.11	8844±6.62	4306±7.12	14683±9.58
C_{28}	1166±7.89	707±1.75	476±1.28	1145±1.18	4712±6.73	7384±8.12
C_{29}	9554±3.37	13784±4.56	8570±4.44	8456±3.56	9874±8.76	6107±4.34
C_{30}	1236±5.59	749±1.05	637±1.16	577±1.32	3135±3.27	2201±2.63
C_{31}	3564±2.35	3741±3.15	4476±2.37	1635±2.11	3368±1.19	13648±10.21
C_{32}	1042±1.23	637±0.76	41±0.18	21±0.98	334±1.17	233±1.21
C_{33}	585±1.12	1583±1.27	106±0.76	28±0.07	2127±1.98	4558±1.56
Total	46370±12	62961±29	40732±31	27813±28	50342±25	75647±18

Table 5.III The concentration of n - alkanes in Pappinissery (S3)

Alkanes	Concentration, ngg^{-1} (Average± Standard Deviation)					
	0-5 cm	5-15 cm	15-25 cm	25-35 cm	35-45 cm	45-55 cm
C_{11}	7± 0.28	13±0.35	8±0.04	18±0.27	19±0.18	21±0.13
C_{12}	840±8.34	1052±5.98	696±5.45	1056±3.65	869±1.54	650±1.59
C_{13}	242±0.34	392±0.67	186±0.87	32±0.22	661±1.05	407±1.54
C_{14}	938±1.35	1002±1.32	541±1.34	108±0.34	1689±7.43	1057±2.88
C_{15}	645±2.11	675±1.45	830±2.32	189±0.86	2651±1.56	1671±2.27
C_{16}	1063±1.29	1620±1.69	947±2.11	217±0.34	3081±0.79	1940±0.85
C_{17}	641±1.21	912 ±1.25	527±3.43	539±2.19	610±2.97	676±2.18
Pr	206±0.97	224±1.12	263±0.47	245±1.35	286±0.23	312±0.65
C_{18}	1725±6.74	1564±7.13	1707±7.34	1565±5.31	1307±4.83	1689 ±6.11
Ph	420±0.45	459±0.24	746±1.86	747±3.65	950±2.13	763±1.16
C_{19}	1590±1.65	1544±3.46	917±1.11	604±1.32	1312±1.56	1103±2.11
C_{20}	1839±2.14	1562±1.75	939±1.47	607±0.97	7094±1.16	1942±1.27
C_{21}	1458±2.11	1440±2.05	898±0.76	1866±1.23	2944±1.26	1842±2.46
C_{22}	1724±4.36	1217±2.35	745±3.12	154±1.11	2504±2.54	1563±1.53
C_{23}	246±1.45	915±3.14	574±1.28	113±2.35	1870±3.41	1166±2.23
C_{24}	1593±2.65	1372±2.34	1776±3.12	1875±2.24	1829±2.47	2179±2.94
C_{25}	6443±4.28	6865±2.78	8449±2.54	7395±4.23	8143±4.66	10317±5.23
C_{26}	1497±2.32	1847±2.33	1327±3.14	431±1.02	409±1.12	494±1.32
C_{27}	12407±8.97	12197±2.41	14851±3.41	16250±2.31	10369±4.56	10952±5.86
C_{28}	323±3.26	318±0.79	236±0.87	312±0.95	317±1.84	370±1.22
C_{29}	16095±6.75	17564±1.23	16022±2.57	19120±4.65	18201±5.64	18661±2.13
C_{30}	321±0.69	907±1.17	1117±1.56	1457±2.13	1251±2.34	1593±4.46
C_{31}	4607±2.35	4861±4.41	5004±2.25	5081±1.92	7075±4.64	8327±1.89
C_{32}	412±2.31	1010±2.45	399±2.87	290±1.13	341±1.44	371±1.28
C_{33}	2899±12.45	3098±10.45	5067±6.79	5500±2.25	5460±2.45	6447±2.65
Total	60182±21	64630±32	64771±41	65769±35	81240±41	76512±12

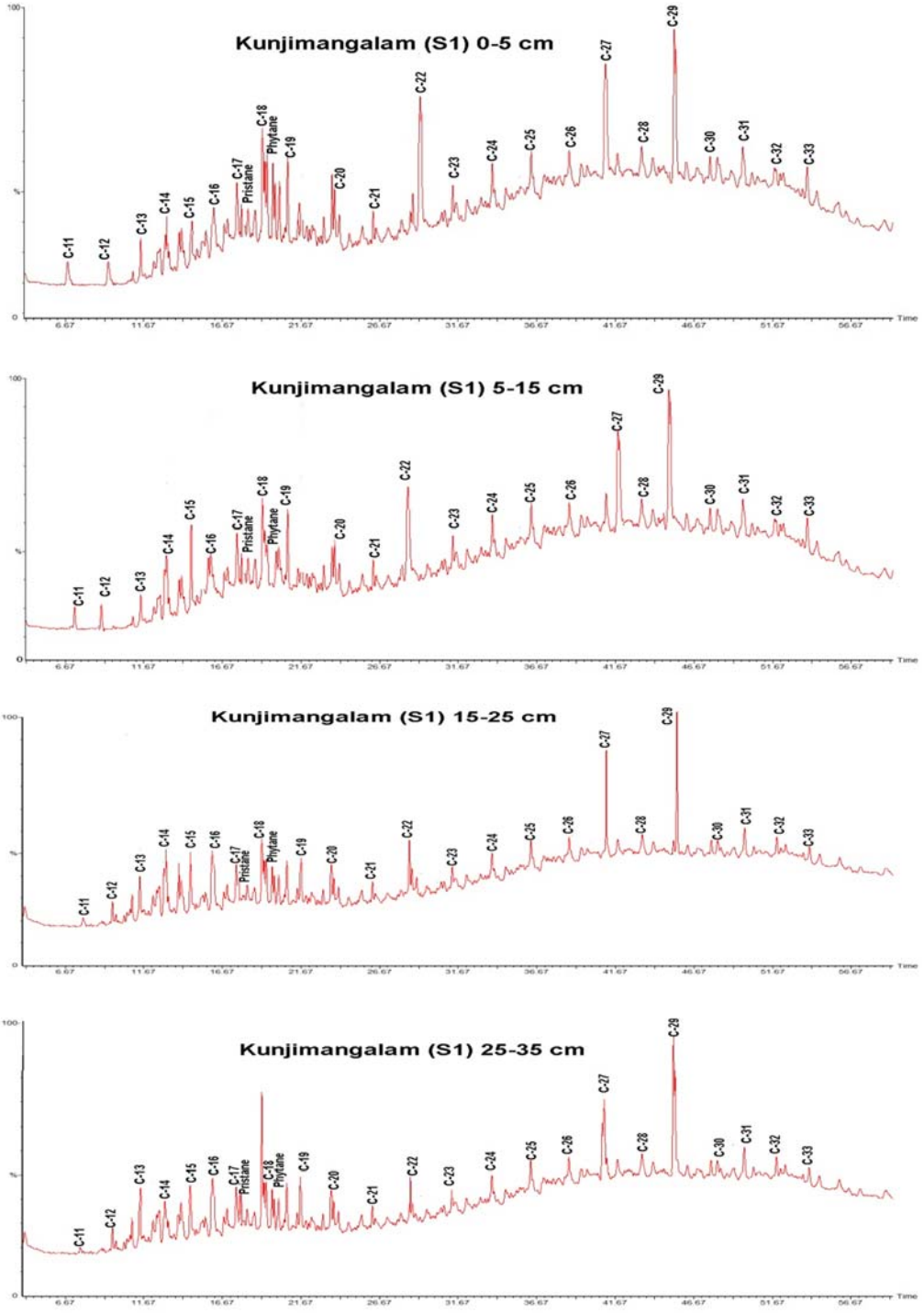
Table 5.IV The concentration of *n*- alkanes in Thalassery (S4)

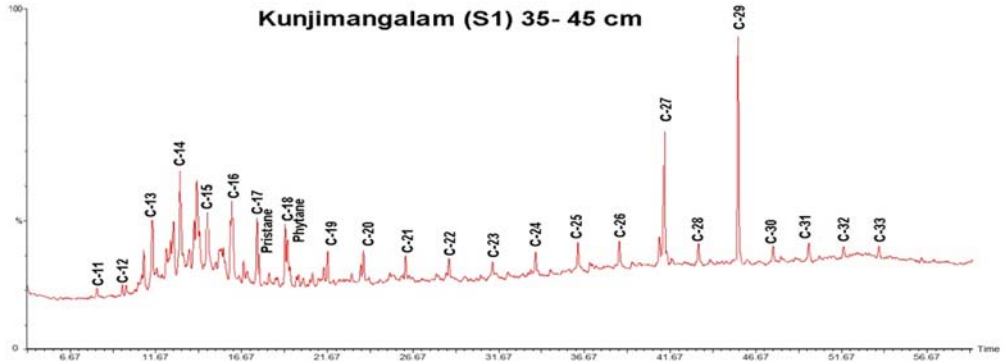
Alkanes	Concentration, ngg^{-1} (Average± Standard Deviation)					
	0-5 cm	5-15 cm	15-25 cm	25-35 cm	35-45 cm	45-55 cm
C_{11}	5±0.28	9±0.35	6±0.21	3±0.05	18±0.81	3±0.28
C_{12}	529±1.16	144±2.33	526±1.45	147±1.28	154±1.93	177±1.89
C_{13}	166±1.16	373±2.13	768±1.67	52±1.21	75±1.45	75±1.22
C_{14}	237±1.46	766±1.04	267±2.13	257±1.72	318±2.17	338±1.34
C_{15}	375±1.65	135±1.46	252±1.57	271±1.56	248±2.25	305±1.13
C_{16}	184±1.34	308±2.23	3734±3.11	584±2.28	541±2.27	662±2.68
C_{17}	243±1.49	1126±1.78	650±2.33	220±1.02	321±0.87	318±0.56
Pr	56±0.67	300±0.87	87±0.23	28±0.21	46±0.19	43±0.15
C_{18}	1193±7.72	1291±6.73	326±1.67	1151±2.13	540±0.95	921±0.77
Ph	760±1.97	1168±1.56	150±2.31	221±2.15	205±3.11	154±1.04
C_{19}	361±1.45	323±2.98	282±1.77	327±1.04	1071±2.43	822±2.67
C_{20}	574±1.78	578±1.66	409±1.54	460±1.15	954±1.49	832±1.52
C_{21}	42±0.45	207±0.32	332±0.21	341±0.27	402±0.59	437±0.96
C_{22}	465±1.15	174±1.55	222±1.47	330±1.46	2664±8.75	1761±6.72
C_{23}	6704±6.39	5031±1.69	5195±1.59	6435±1.77	5408±1.59	7267±1.32
C_{24}	363±1.67	754±1.78	1092±2.19	1240±2.23	354±0.93	937±0.31
C_{25}	7435±7.83	7401±8.79	5278±8.15	6805±7.95	7815±5.86	7732±6.34
C_{26}	482±3.26	297±1.21	394±2.27	154±1.56	122±1.55	162±1.12
C_{27}	7958±9.76	8056±8.85	8616±8.33	7847±8.93	7936±7.98	7960±6.89
C_{28}	58±0.89	66±0.24	89±0.34	49±0.37	57±0.54	60±0.27
C_{29}	4065±6.57	4978±3.87	4993±7.33	4919±2.54	5723±4.69	3540±2.44
C_{30}	628±2.54	793±2.84	710±2.56	691±3.45	527±2.18	599±1.32
C_{31}	2900±4.87	1867±3.97	2467±3.89	1386±2.26	1595±2.19	1533±6.32
C_{32}	368±0.33	408±0.28	423±0.47	173±0.21	210±0.28	703±0.73
C_{33}	500±0.98	174±0.13	77±0.23	141±0.15	181±0.45	253±0.21
Total	36651±12	36727±23	37345±34	34231±31	37484±23	37595±43

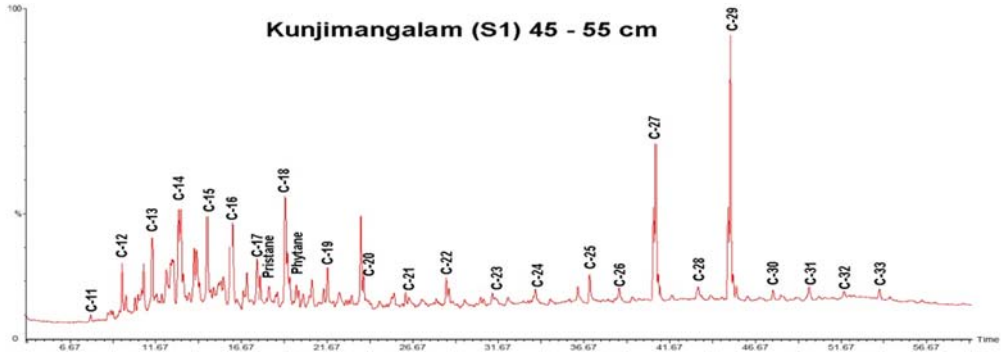
Table 5.V The concentration of n - alkanes in Kadalundi (S5)

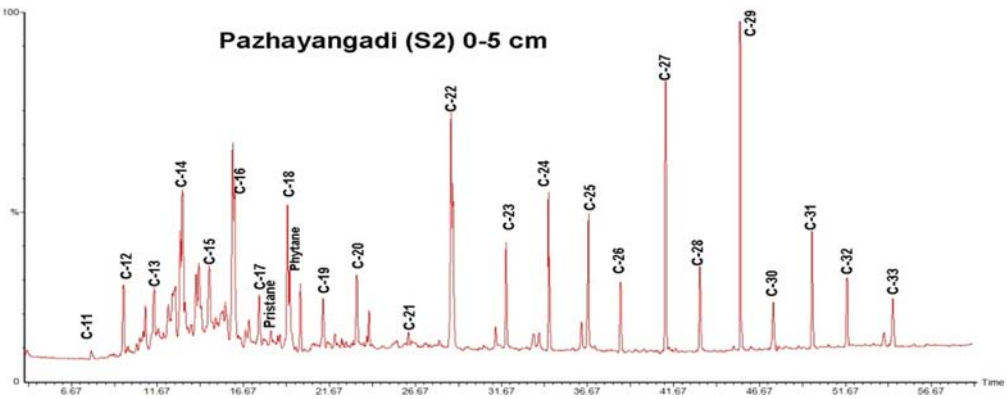
Alkanes	Concentration, ngg^{-1} (Average± Standard Deviation)					
	0-5 cm	5-15 cm	15-25 cm	25-35 cm	35-45 cm	45-55 cm
C_{11}	33±0.43	12±0.56	36±0.78	24±0.08	17±0.18	16±0.76
C_{12}	271±0.23	81±0.45	273±0.84	90±0.67	156±0.83	134±0.57
C_{13}	175±0.76	208±1.11	417±1.01	53±0.98	211±0.67	133±0.56
C_{14}	1032±0.45	1081±0.79	197±0.23	226±0.35	507±0.75	381±0.87
C_{15}	568± 0.45	585±0.65	630±0.49	415±1.63	568±0.78	509±1.12
C_{16}	1470±2.43	1592±2.54	1900±2.31	493±0.78	438±0.84	446±0.34
C_{17}	517±0.37	578±1.28	716±0.76	746±0.47	819±1.98	565±0.24
Pr	192±1.56	157±0.74	179±0.55	310±0.89	288±0.55	280±1.01
C_{18}	663±2.12	711±1.05	775±1.16	742±0.56	387±1.17	324±1.17
Ph	320±0.54	300±1.15	326±1.76	320±1.95	359±1.98	310±1.29
C_{19}	953±0.99	549±1.43	278±1.53	390±2.25	310±1.16	679±1.65
C_{20}	1174±3.82	940±1.75	965±1.54	746±1.19	522±1.68	445±1.45
C_{21}	866±1.15	746±1.02	1301±0.85	176±1.21	223±1.03	232±1.33
C_{22}	7190±8.65	6920±6.79	6076±7.45	3922±5.63	1335±6.17	2135±7.87
C_{23}	289±0.45	519±1.03	797±1.32	2766±2.67	179±0.76	195±3.45
C_{24}	694±0.65	408±1.02	558±0.56	502±0.78	199±1.05	188±1.13
C_{25}	276±2.21	322±1.15	389±2.65	180±1.96	243±0.97	245±1.93
C_{26}	552±2.48	182±2.26	207±1.58	208±1.69	332±1.17	94±0.49
C_{27}	93±2.25	102±1.62	32±0.95	36±0.19	36±1.12	37±1.43
C_{28}	300±6.63	288±1.25	85±2.16	66±1.92	98±1.54	93±2.15
C_{29}	7216±8.72	7008±4.96	4941±6.69	4694±2.34	4640±1.19	4598±4.39
C_{30}	158±0.87	169±0.89	244±1.69	164±2.19	282±2.25	311±1.50
C_{31}	108±2.21	112±1.05	99±0.76	70±1.89	90±1.12	102±1.48
C_{32}	141±1.19	206±1.59	55±0.64	157±0.58	80±0.69	61±1.12
C_{33}	164±2.80	184±2.88	304±3.1	81±0.52	136±0.77	90±1.54
Total	25412±32	23960±35	21778±27	17575±36	12453±22	12604±30

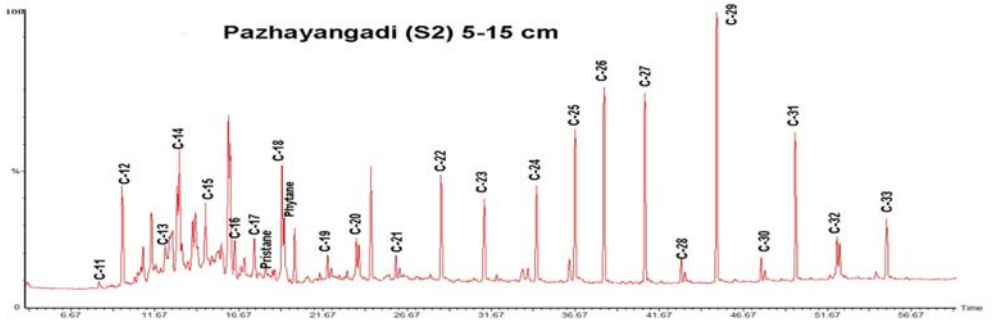
Total ion chromatogram of n-alkanes in the study area

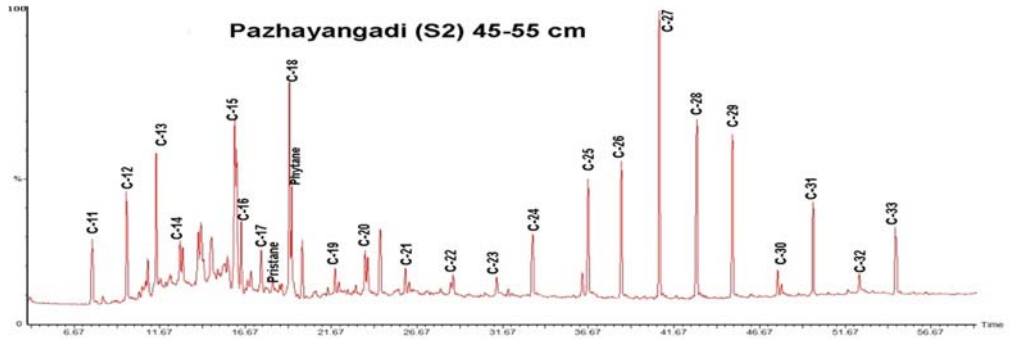


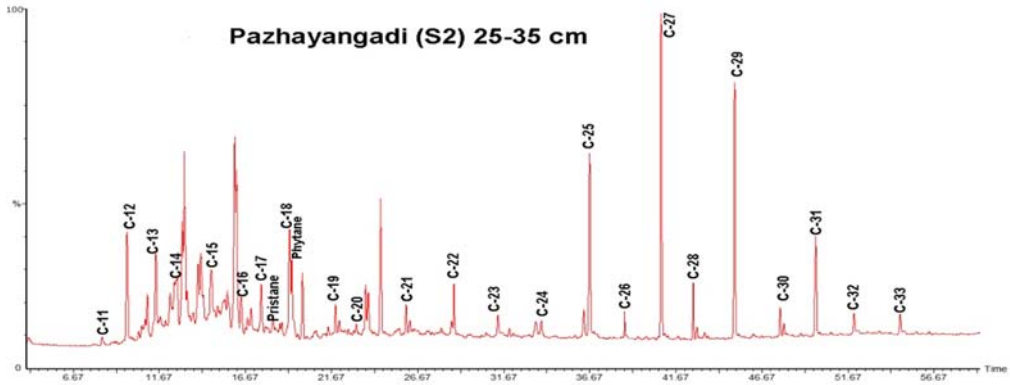

Kunjimangalam (S1) 35- 45 cm
C-11
C-12
C-13
C-14
C-15
C-16
C-17
Pristane
C-18
Phytane
C-19
C-20
C-21
C-22
C-23
C-24
C-25
C-26
C-27
C-28
C-29
C-30
C-31
C-32
C-33
Time

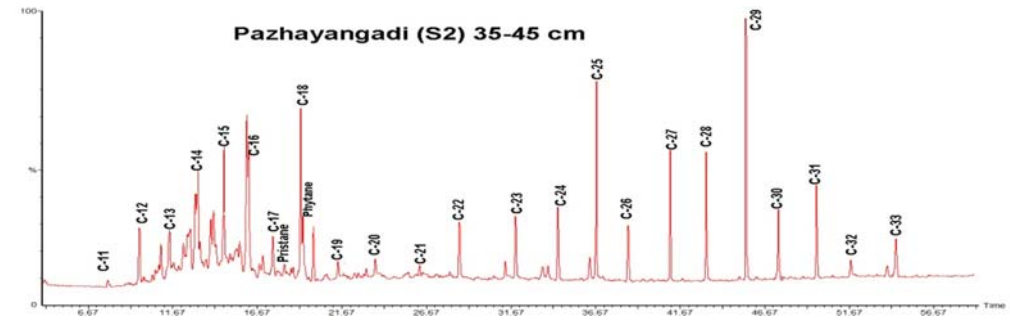

Kunjimangalam (S1) 45 - 55 cm
C-11
C-12
C-13
C-14
C-15
C-16
C-17
Pristane
C-18
Phytane
C-19
C-20
C-21
C-22
C-23
C-24
C-25
C-26
C-27
C-28
C-29
C-30
C-31
C-32
C-33
Time

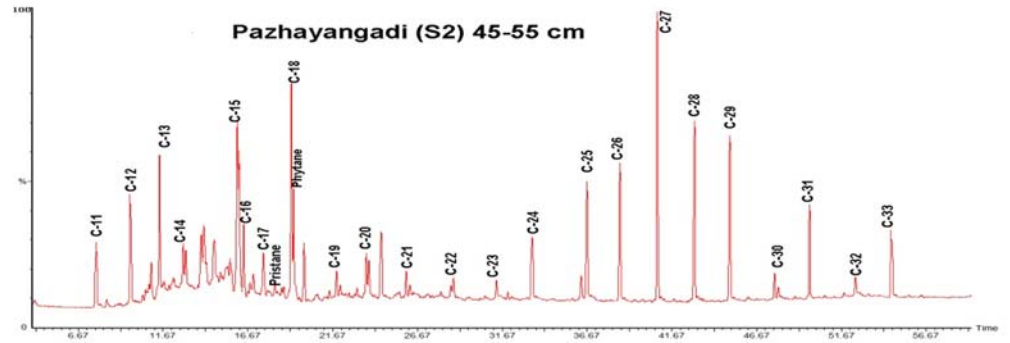

Pazhayangadi (S2) 0-5 cm
C-11
C-12
C-13
C-14
C-15
C-16
C-17
Pristane
C-18
Phytane
C-19
C-20
C-21
C-22
C-23
C-24
C-25
C-26
C-27
C-28
C-29
C-30
C-31
C-32
C-33
Time

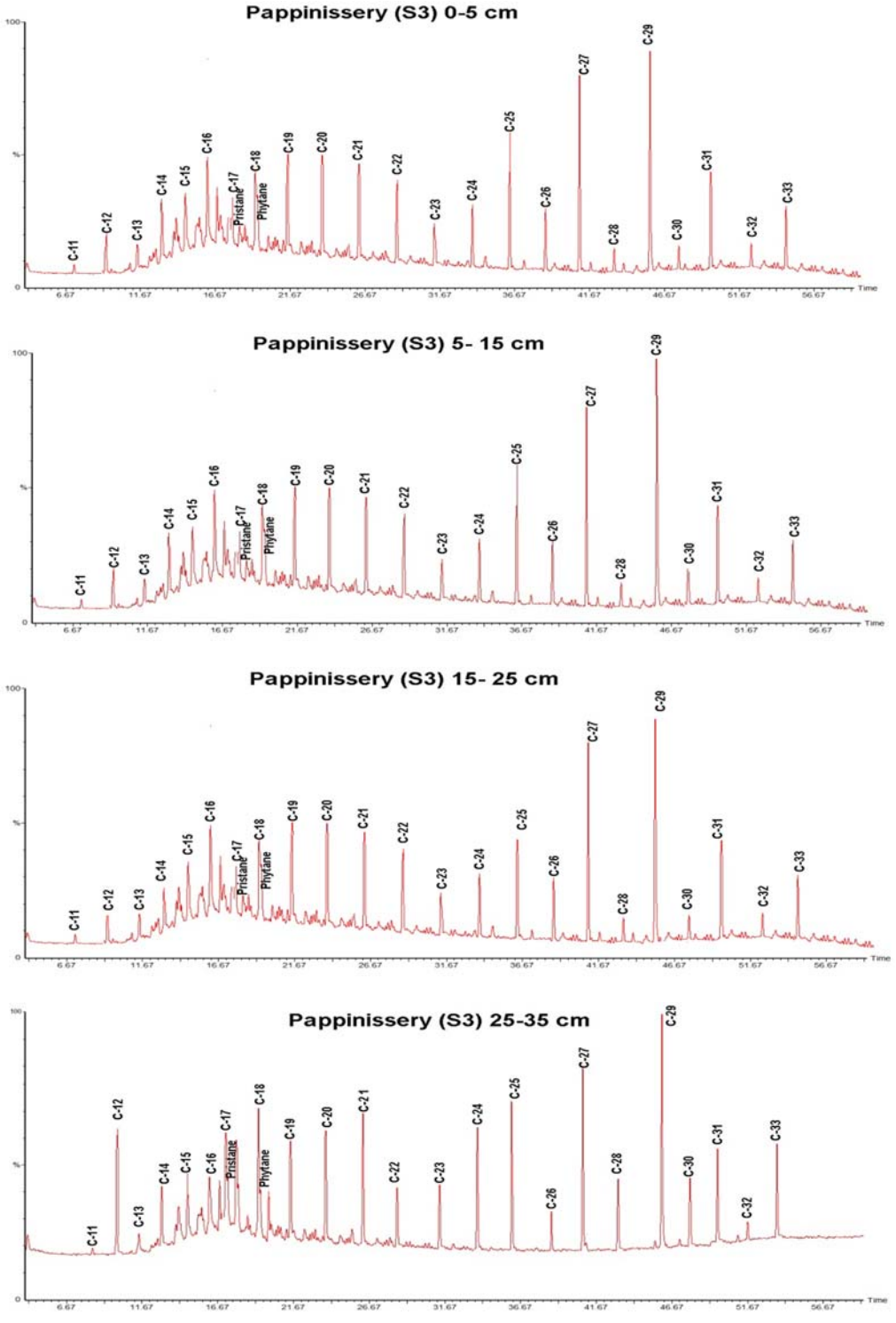

Pazhayangadi (S2) 5-15 cm
C-11
C-12
C-13
C-14
C-15
C-16
C-17
Pristane
C-18
Phytane
C-19
C-20
C-21
C-22
C-23
C-24
C-25
C-26
C-27
C-28
C-29
C-30
C-31
C-32
C-33
Time

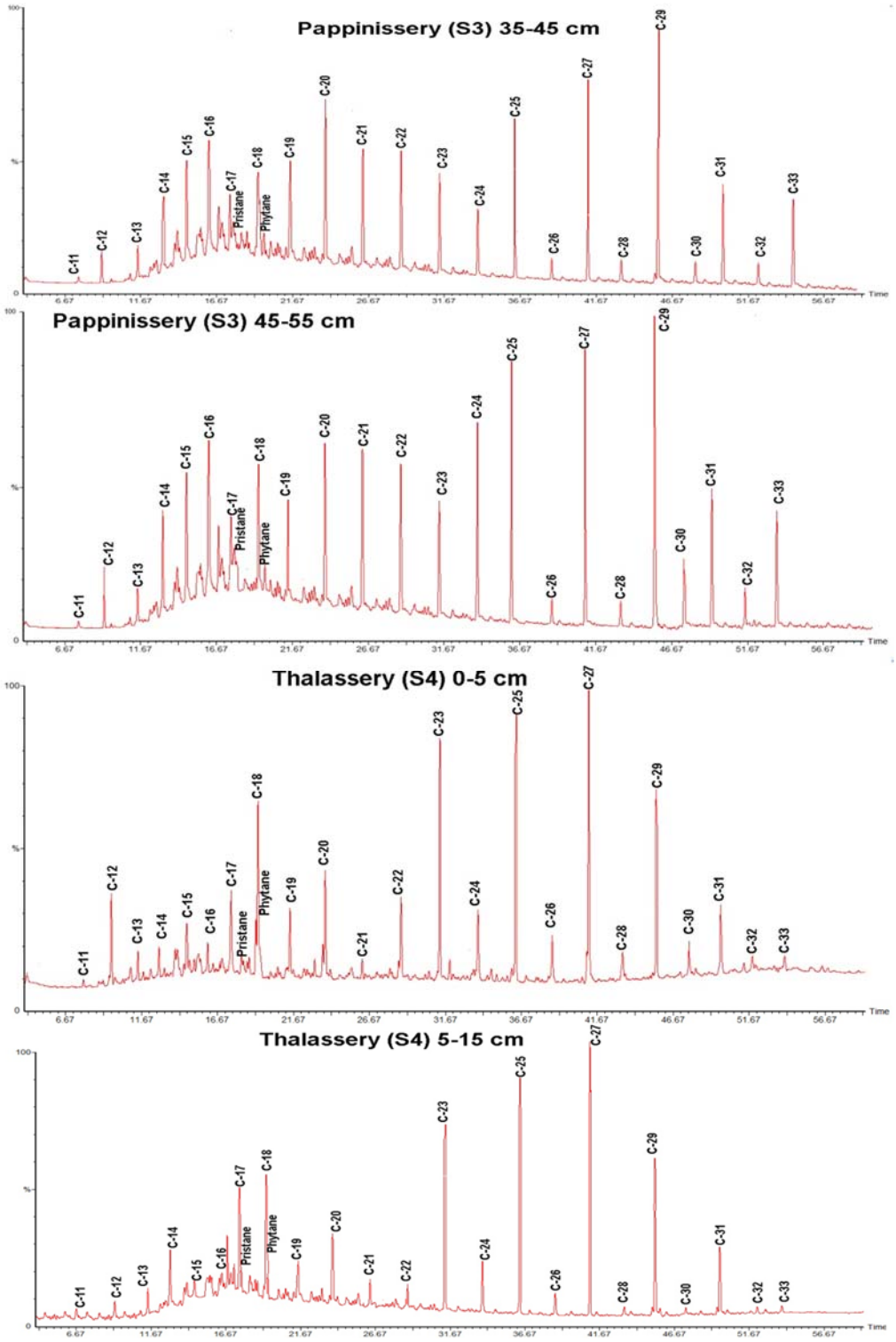

Pazhayangadi (S2) 45-55 cm
C-11
C-12
C-13
C-14
C-15
C-16
C-17
Pristane
C-18
Phytane
C-19
C-20
C-21
C-22
C-23
C-24
C-25
C-26
C-27
C-28
C-29
C-30
C-31
C-32
C-33
Time

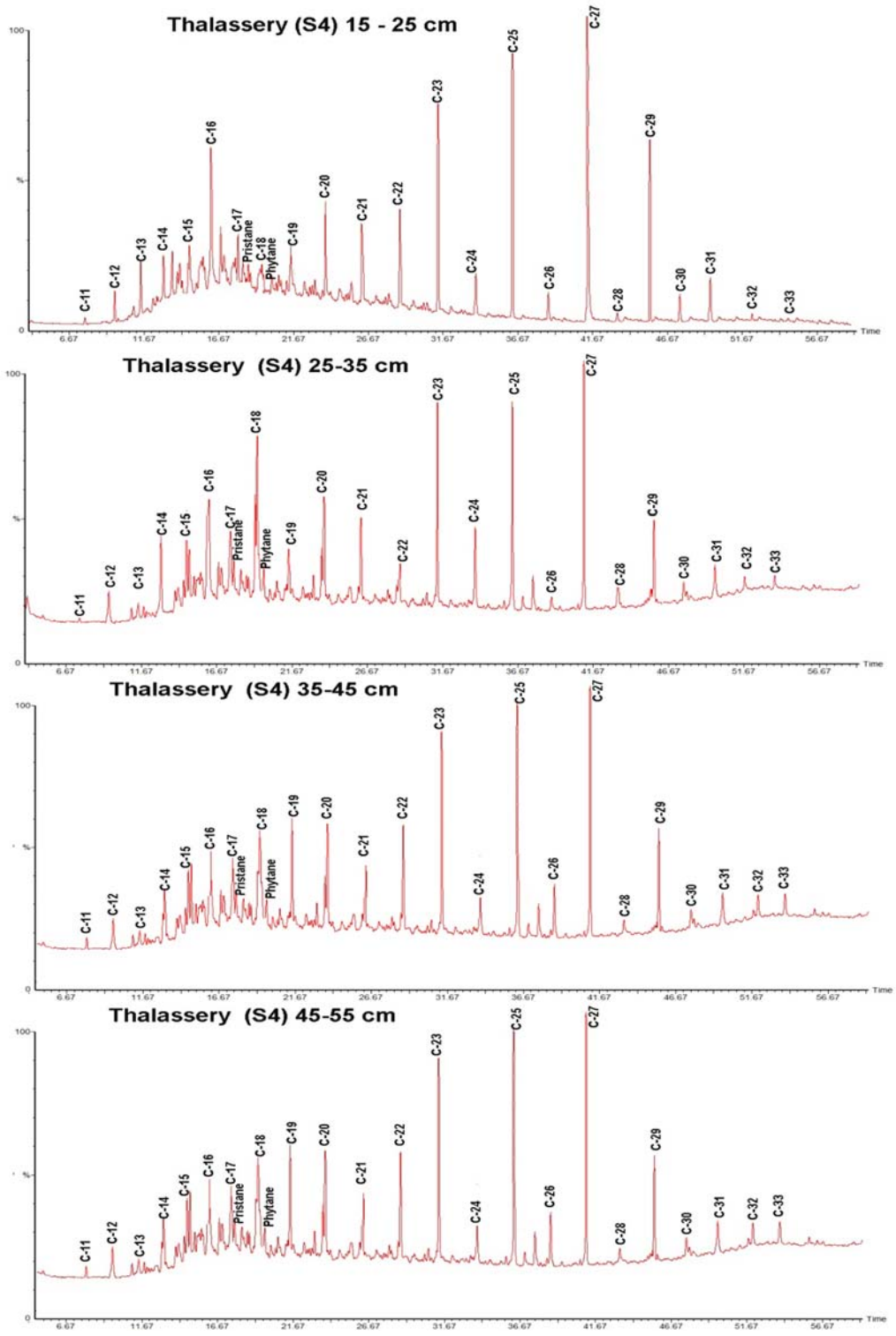

Pazhayangadi (S2) 25-35 cm
C-11
C-12
C-13
C-14
C-15
C-16
C-17
Pristane
C-18
Phytane
C-19
C-20
C-21
C-22
C-23
C-24
C-25
C-26
C-27
C-28
C-29
C-30
C-31
C-32
C-33
Time

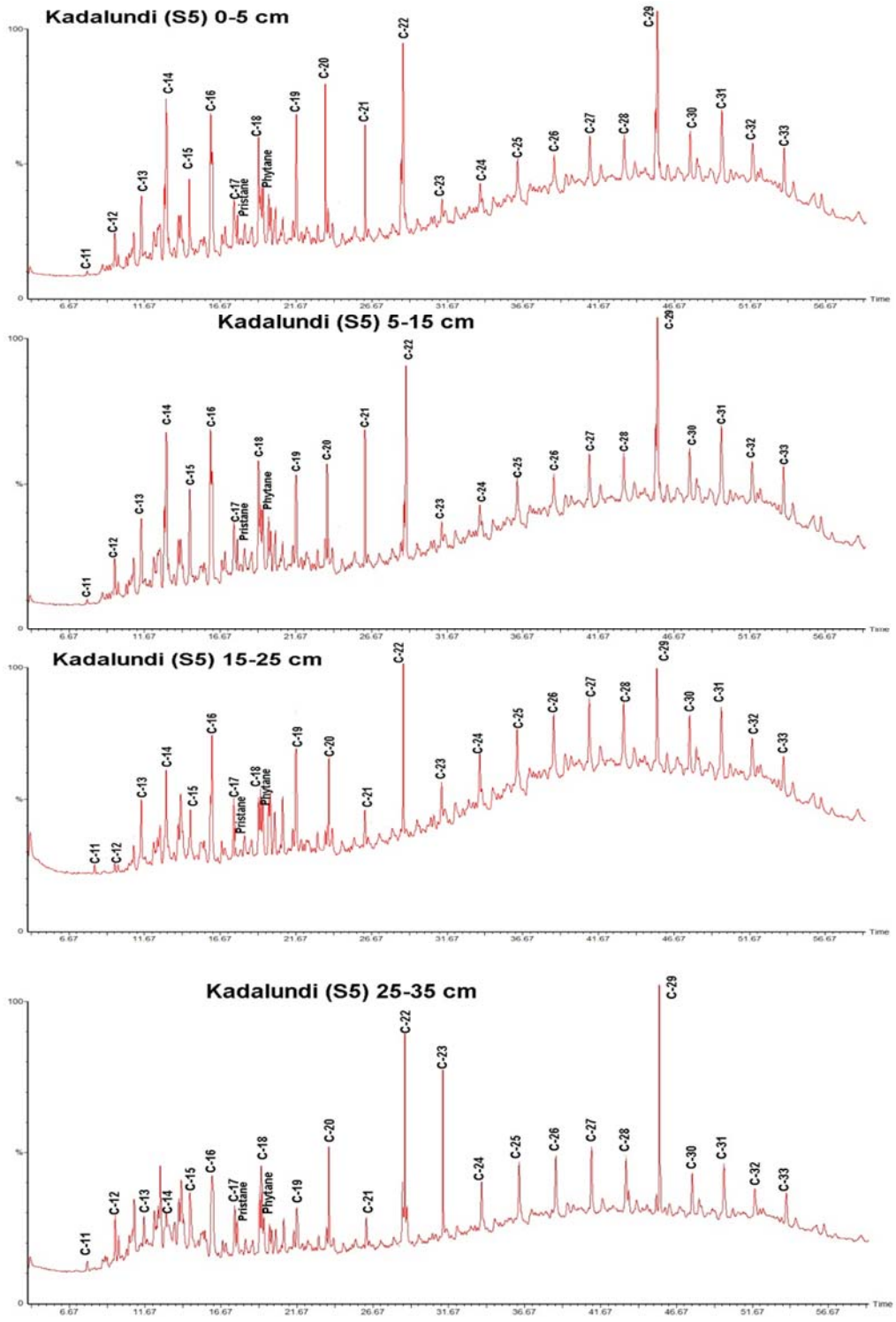

Pazhayangadi (S2) 35-45 cm
C-11
C-12
C-13
C-14
C-15
C-16
C-17
Pristane
C-18
Phytane
C-19
C-20
C-21
C-22
C-23
C-24
C-25
C-26
C-27
C-28
C-29
C-30
C-31
C-32
C-33
Time

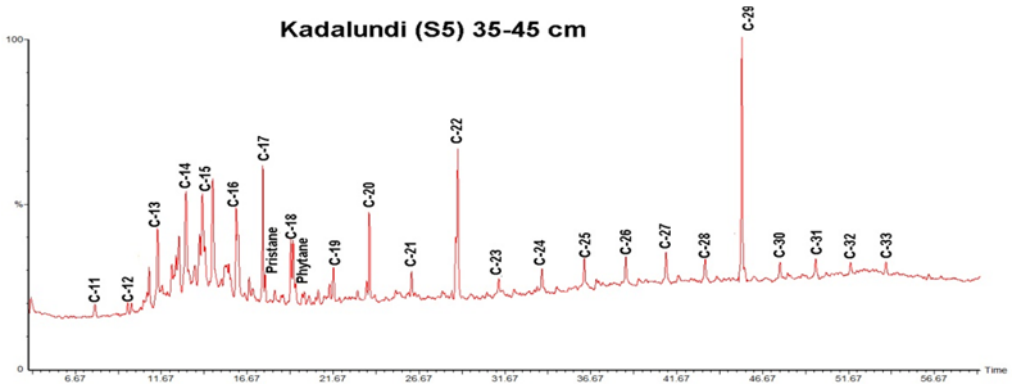

Pazhayangadi (S2) 45-55 cm
C-11
C-12
C-13
C-14
C-15
C-16
C-17
Pristane
C-18
Phytane
C-19
C-20
C-21
C-22
C-23
C-24
C-25
C-26
C-27
C-28
C-29
C-30
C-31
C-32
C-33
Time


Pappinissery (S3) 0-5 cm
Pappinissery (S3) 5- 15 cm
Pappinissery (S3) 15- 25 cm
Pappinissery (S3) 25-35 cm
C-11
C-12
C-13
C-14
C-15
C-16
C-17
Pristane
C-18
Phytane
C-19
C-20
C-21
C-22
C-23
C-24
C-25
C-26
C-27
C-28
C-29
C-30
C-31
C-32
C-33
Time


Pappinissery (S3) 35-45 cm
C-11
C-12
C-13
C-14
C-15
C-16
C-17
Pristane
Phytane
C-18
C-19
C-20
C-21
C-22
C-23
C-24
C-25
C-26
C-27
C-28
C-29
C-30
C-31
C-32
C-33
Time
Pappinissery (S3) 45-55 cm
Thalassery (S4) 0-5 cm
Thalassery (S4) 5-15 cm


Thalassery (S4) 15 - 25 cm
C-11
C-12
C-13
C-14
C-15
C-16
C-17
Pristane
C-18
Phytane
C-19
C-20
C-21
C-22
C-23
C-24
C-25
C-26
C-27
C-28
C-29
C-30
C-31
C-32
C-33
Time
Thalassery (S4) 25-35 cm
Thalassery (S4) 35-45 cm
Thalassery (S4) 45-55 cm


Kadalundi (S5) 0-5 cm
Kadalundi (S5) 5-15 cm
Kadalundi (S5) 15-25 cm
Kadalundi (S5) 25-35 cm
C-11
C-12
C-13
C-14
C-15
C-16
C-17
Pristane
C-18
Phytane
C-19
C-20
C-21
C-22
C-23
C-24
C-25
C-26
C-27
C-28
C-29
C-30
C-31
C-32
C-33
Time


Kadalundi (S5) 35-45 cm
100
%
0
C-11
C-12
C-13
C-14
C-15
C-16
C-17
Pristane
C-18
Phytane
C-19
C-20
C-21
C-22
C-23
C-24
C-25
C-26
C-27
C-28
C-29
C-30
C-31
C-32
C-33
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36.67
41.67
46.67
51.67
56.67
Time

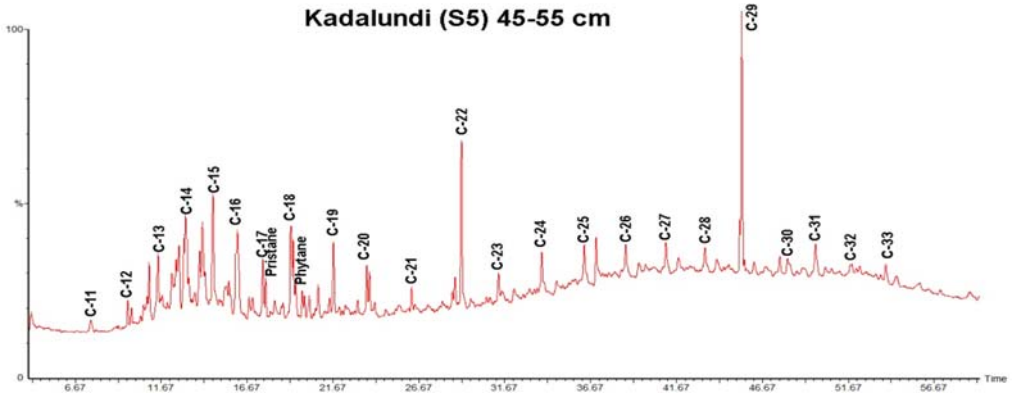

Kadalundi (S5) 45-55 cm
100
%
0
C-11
C-12
C-13
C-14
C-15
C-16
C-17
Pristane
C-18
Phytane
C-19
C-20
C-21
C-22
C-23
C-24
C-25
C-26
C-27
C-28
C-29
C-30
C-31
C-32
C-33
6.67
11.67
16.67
21.67
26.67
31.67
36.67
41.67
46.67
51.67
56.67
Time

Table 6.1 Fatty acids estimated in core sediments from S1

S.I. No	Fatty acids	Concentration, μgg^{-1} (Average± Standard deviation)					
		0-5 cm	5-15 cm	15-25 cm	25-35 cm	35-45 cm	45-55 cm
1	C8	0.02±0.001	0.01±0.002	0.13±0.005	0.04±0.003	0.07±0.002	0.06±0.003
2	C10	0.05±0.002	0.04±0.002	0.08±0.003	0.05±0.002	0.10±0.003	0.09±0.002
3	C11	0.03±0.004	0.03±0.003	ND	ND	ND	ND
4	C12	0.97±0.02	0.80±0.3	0.72±0.02	0.91±0.03	1.13±0.06	1.00±0.08
5	C13	0.03±0.002	0.01±0.003	0.01±0.002	0.003±0.001	0.01±0.004	0.01±0.005
6	C14:1	0.09±0.003	0.04±0.005	0.01±0.003	0.01±0.001	ND	ND
7	C14	0.81±0.06	0.71±0.03	0.16±0.05	0.03±0.007	0.56±0.04	0.49±0.02
8	iC15	0.05±0.006	0.04±0.003	0.04±0.004	0.01±0.002	0.02±0.003	0.02±0.003
9	aC15	0.05±0.004	0.04±0.002	0.04±0.001	0.01±0.002	0.02±0.004	0.02±0.005
10	C15	0.11±0.12	0.10±0.01	0.10±0.01	0.05±0.003	0.07±0.002	0.06±0.003
11	C16:1n7	0.31±0.04	0.20±0.03	0.12±0.05	0.10±0.007	0.07±0.005	0.06±0.005
12	C16	7.87±0.65	6.18±0.53	4.29±0.34	2.57±0.25	2.68±0.17	2.37±0.23
13	iC17	0.12±0.003	0.03±0.002	0.02±0.003	0.01±0.002	0.01±0.003	0.01±0.005
14	aC17	0.14±0.02	0.03±0.004	0.01±0.006	0.04±0.005	0.07±0.006	0.06±0.003
15	C17	0.06±0.004	0.08±0.003	0.09±0.007	0.20±0.01	0.05±0.003	0.05±0.002
16	C18:2n6	0.23±0.001	0.13±0.002	0.06±0.003	0.04±0.002	0.07±0.003	0.06±0.004
17	C18:3n3	0.46±0.05	0.36±0.03	0.27±0.04	0.19±0.05	0.005±0.001	0.005±0.001
18	C18:1n9	0.38±0.02	0.23±0.05	0.15±0.04	0.11±0.02	0.02±0.001	0.02±0.001
19	C18:1n7	0.54±0.06	0.49±0.03	0.03±0.02	0.02±0.01	0.01±0.002	0.01±0.003
20	C18	0.85±0.03	0.77±0.02	0.76±0.11	0.69±0.07	0.92±0.08	0.81±0.04
21	C20:5n3	0.02±0.001	0.01±0.005	0.04±0.002	0.01±0.004	0.02±0.005	0.01±0.006
22	C20:1n9	0.01±0.003	0.01±0.002	0.03±0.001	0.003±0.001	0.01±0.003	0.01±0.004
23	C20	0.09±0.004	0.05±0.002	0.11±0.003	0.04±0.002	0.05±0.003	0.04±0.002
24	C21	0.01±0.002	0.01±0.003	ND	ND	0.02±0.005	0.02±0.004
25	C22:6n3	0.01±0.004	0.01±0.002	0.01±0.005	0.05±0.004	0.03±0.002	0.03±0.001
26	C22:1n9	0.01±0.001	0.01±0.001	0.05±0.003	ND	ND	ND
27	C22	0.11±0.04	0.10±0.05	0.12±0.07	0.16±0.08	0.16±0.05	0.15±0.02
28	C23	0.01±0.001	0.10±0.002	0.12±0.04	0.03±0.007	0.05±0.008	0.04±0.005
29	C24	0.18±0.03	0.17±0.04	0.10±0.02	0.15±0.03	0.15±0.04	0.13±0.02
30	C26	0.52±0.11	0.58±0.09	0.33±0.12	0.24±0.06	0.17±0.08	0.15±0.03
31	C28	0.34±0.04	0.31±0.05	0.15±0.04	0.15±0.06	0.34±0.02	0.30±0.03
32	C30	0.37±0.08	0.56±0.04	0.24±0.05	0.34±0.11	0.29±0.04	0.25±0.05
Total Fatty acid		14.84±1.11	12.24±1.03	8.38±0.67	6.21±0.53	7.13±0.06	6.33±0.009

ND denotes not detected

Table 6.II Fatty acids estimated in core sediments from S2

S.I No	Fatty acids	Concentration, μgg^{-1} (Average± Standard deviation)					
		0-5 cm	5-15cm	15-25 cm	25-35 cm	35-45 cm	45-55 cm
1	C8	0.33±0.04	0.32±0.03	0.20±0.01	0.01±0.001	0.11±0.02	0.07±0.01
2	C10	0.19±0.01	0.19±0.04	0.11±0.03	0.01±0.002	0.10±0.003	0.06±0.002
3	C11	0.02±0.003	0.02±0.004	0.01±0.003	ND	0.01±0.002	ND
4	C12	1.85±0.56	1.81±0.33	0.83±0.13	0.22±0.06	1.22±0.03	1.01±0.03
5	C13	0.07±0.006	0.06±0.003	0.02±0.004	0.003±0.001	0.01±0.003	ND
6	C14:1	0.02±0.006	0.02±0.002	0.01±0.003	ND	ND	0.28±0.004
7	C14	2.38±0.12	2.26±0.23	0.65±0.08	0.25±0.05	0.83±0.07	0.71±0.02
8	iC15	0.03±001	0.03±0.002	0.01±0.002	0.08±0.003	0.01±0.002	0.03±0.003
9	aC15	0.04±0.002	0.04±0.003	0.01±0.001	0.01±0.002	0.01±0.001	0.02±0.002
10	C15	1.25±0.12	1.23±0.13	0.25±0.05	0.17±0.02	0.05±0.007	0.05±0.006
11	C16:1n7	0.22±0.02	0.21±0.01	0.02±0.007	0.01±0.008	0.09±0.005	0.08±0.006
12	C16	11.26±1.07	11.00±0.98	2.73±0.97	11.92±0.07	12.42±0.23	10.04±0.19
13	iC17	0.03±0.004	0.03±0.003	0.07±0.002	0.01±0.004	ND	0.01±0.005
14	aC17	0.01±0.001	0.01±0.002	0.01±0.001	ND	ND	0.002±0.001
15	C17	0.52±0.06	0.51±0.03	0.54±0.02	0.05±0.001	ND	0.05±0.003
16	C18:3n6	0.03±0.002	0.03±0.003	0.01±0.004	0.02±0.002	0.01±0.001	0.005±0.001
17	C18:2n6	0.05±0.01	0.05±0.006	0.04±0.008	0.03±0.007	0.01±0.005	0.01±0.007
18	C18:3n3	0.04±0.002	0.04±0.003	ND	0.01±0.001	0.01±0.001	0.005±0.001
19	C18:1n9	0.21±0.005	0.20±0.007	0.49±0.02	0.93±0.09	0.02±0.007	0.30±0.005
20	C18:1n7	0.19±0.004	0.18±0.003	0.005±0.001	0.05±0.003	0.004±0.001	0.005±0.001
21	C18	3.16±0.98	3.09±0.76	0.82±0.03	0.95±0.05	2.77±0.18	3.71±0.19
22	C20:5n3	0.14±0.15	0.14±0.004	0.07±0.003	0.01±0.002	0.005±0.003	0.01±0.002
23	C20:1n9	0.01±0.003	0.01±0.005	0.05±0.004	0.004±0.001	0.005±0.001	0.005±0.001
24	C20	0.99±0.09	0.97±0.03	0.23±0.04	0.21±0.02	0.02±0.005	0.09±0.004
25	C21	0.89±0.05	0.87±0.06	0.14±0.05	0.11±0.08	0.005±0.001	0.01±0.005
26	C22:6n3	0.38±0.07	0.37±0.03	0.35±0.05	0.31±0.04	0.004±0.001	0.01±0.003
27	C22:1n9	3.36±0.23	3.28±0.18	0.40±0.07	0.41±0.04	0.01±0.001	0.01±0.002
28	C22	3.36±0.97	3.28±0.67	0.49±0.02	0.92±0.07	0.01±0.005	0.18±0.03
29	C23	0.90±0.04	0.88±0.03	0.12±0.02	0.15±0.03	0.11±0.02	0.04±0.005
30	C24:1	1.08±0.07	1.05±0.08	0.07±0.007	0.09±0.008	0.004±0.001	0.004±0.002
31	C24	8.68±0.19	8.48±0.23	1.39±0.31	1.07±0.33	0.01±0.003	0.15±0.005
32	C26	6.97±0.03	6.81±0.73	1.50±0.06	1.00±0.05	0.01±0.005	0.15±0.004
33	C28	13.00±1.12	12.70±1.13	2.29±0.36	2.05±0.32	0.04±0.008	0.20±0.006
34	C30	10.83±0.98	10.58±0.92	2.05±0.23	2.32±0.37	0.02±0.006	0.17±0.02
Total Fatty acids		72.50±3.21	70.77±2.69	15.98±2.33	23.39±1.79	17.93±1.19	17.47±1.24

ND denotes not detected

Table 6.III Fatty acids estimated in core sediments from S3

S.I No	Fatty acids	Concentration, μgg^{-1} (Average± Standard deviation)					
		0-5cm	5-15 cm	15-25 cm	25-35 cm	35-45 cm	45-55 cm
1	C8	0.21±0.03	0.18±0.02	ND	0.49±0.05	0.05±0.01	0.17±0.03
2	C10	0.15±0.04	0.12±0.03	ND	0.85±0.04	0.05±0.006	0.11±0.03
3	C11	0.29±0.05	0.25±0.08	ND	0.03±0.007	ND	0.23±0.02
4	C12	1.00±0.05	0.87±0.03	0.45±0.05	0.19±0.03	0.91±0.09	0.81±0.05
5	C13	0.13±0.02	0.11±0.03	0.09±0.02	ND	0.09±0.03	0.10±0.02
6	C14:1	0.04±0.007	0.03±0.006	0.14±0.005	ND	0.04±0.002	0.03±0.002
7	C14	0.88±0.04	0.77±0.02	0.10±0.03	0.25±0.04	0.89±0.07	0.71±0.06
8	iC15	0.34±0.06	0.30±0.01	0.15±0.07	0.06±0.01	0.15±0.02	0.28±0.04
9	aC15	0.27±0.03	0.23±0.04	0.14±0.03	0.07±0.05	0.14±0.02	0.21±0.02
10	C15	0.26±0.07	0.22±0.08	0.98±0.04	0.05±0.01	0.34±0.02	0.21±0.03
11	C16:1n7	0.04±0.01	0.03±0.01	0.10±0.02	0.07±0.02	0.07±0.03	0.03±0.006
12	C16	2.30±0.94	2.03±0.89	1.54±0.95	1.02±0.75	2.78±0.23	1.87±0.33
13	iC17	0.09±0.01	0.08±0.01	0.11±0.02	0.08±0.01	0.10±0.01	0.07±0.002
14	aC17	0.01±0.001	0.01±0.002	0.06±0.004	0.07±0.003	0.04±0.003	0.03±0.002
15	C17	0.09±0.01	0.08±0.01	0.02±0.01	0.03±0.007	0.09±0.004	0.07±0.005
16	C18:3n6	0.04±0.006	0.03±0.004	0.12±0.01	0.09±0.01	0.07±0.003	0.03±0.004
17	C18:2n6	0.12±0.02	0.10±0.03	0.07±0.01	0.07±0.02	0.03±0.01	0.02±0.01
18	C18:3n3	0.11±0.02	0.09±0.03	0.10±0.03	0.07±0.01	0.04±0.01	0.03±0.01
19	C18:1n9	0.46±0.02	0.40±0.03	0.13±0.02	0.05±0.01	0.44±0.03	0.37±0.10
20	C18:1n7	0.07±0.01	0.06±0.01	0.10±0.02	0.06±0.01	0.52±0.02	0.05±0.01
21	C18	0.63±0.02	0.55±0.03	0.14±0.03	0.28±0.05	0.73±0.03	0.51±0.02
22	C20:5n3	0.61±0.11	0.53±0.10	0.10±0.03	0.05±0.01	0.04±0.01	0.05±0.01
23	C20:1n9	0.35±0.04	0.31±0.02	0.10±0.03	0.03±0.01	0.01±0.005	0.35±0.01
24	C20	0.83±0.11	0.73±0.04	0.19±0.02	0.10±0.03	0.44±0.03	0.67±0.05
25	C21	0.09±001	0.08±0.01	0.12±0.02	0.03±0.001	0.45±0.02	0.07±0.03
26	C22:6n3	0.05±0.01	0.04±0.01	0.12±0.02	0.07±0.01	0.04±0.01	0.03±0.01
27	C22:1n9	0.56±0.13	0.49±0.07	0.12±0.06	0.10±0.04	0.12±0.03	0.45±0.02
28	C22	16.52±1.19	14.58±1.13	0.28±0.07	0.81±0.03	1.83±0.07	13.46±1.15
29	C23	0.97±0.02	0.83±0.03	0.61±0.03	0.46±0.02	1.08±0.03	0.77±0.02
30	C24:1	0.27±0.02	0.23±0.04	0.24±0.05	0.14±0.05	0.08±0.01	0.21±0.08
31	C24	10.73±1.01	9.46±1.12	1.61±0.23	7.26±0.07	10.76±0.06	8.73±0.04
32	C26	10.16±0.05	8.95±0.14	1.70±0.04	6.99±0.05	7.98±0.05	8.26±0.03
33	C28	12.26±0.03	10.81±0.02	3.79±0.04	10.86±0.13	11.14±0.12	9.98±0.04
34	C30	16.05±0.05	14.16±0.06	4.37±0.05	14.93±0.04	14.35±0.05	13.07±0.03
Total Fatty acids		76.97±1.15	67.75±1.27	17.90±1.45	45.73±1.78	55.91±1.49	62.06±1.87

ND denotes not detected

Table 6.IV Fatty acids estimated in core sediments from S4

S.I. No	Fatty Acids	Concentration, μgg^{-1} (Average± Standard deviation)					
		0-5cm	5-15cm	15-25cm	25-35 cm	35-45 cm	45-55 cm
1	C8	0.19±0.02	0.10±0.01	0.05±0.01	0.005±0.001	0.04±0.01	0.32±0.03
2	C10	0.12±0.07	0.05±0.01	0.07±0.01	0.01±0.006	0.06±0.003	0.17±0.01
3	C12	0.81±0.07	0.45±0.04	0.74±0.07	0.13±0.01	0.65±0.02	1.59±0.02
4	C14	1.07±0.03	0.42±0.03	0.06±0.01	0.11±0.02	0.05±0.01	0.77±0.01
5	iC15	1.16±0.11	0.16±0.01	0.10±0.02	0.03±0.005	0.08±0.003	0.06±0.01
6	aC15	0.47±0.02	0.15±0.03	0.10±0.02	0.02±0.004	0.08±0.004	0.06±0.003
7	C15	0.49±0.01	0.01±0.005	0.06±0.01	0.01±0.003	0.06±0.01	0.07±0.01
8	C16:1n7	0.30±0.02	2.19±0.01	0.10±0.01	0.02±0.007	0.09±0.01	ND
9	C16	4.42±0.23	1.64±0.15	1.01±0.03	0.23±0.02	0.88±0.04	1.04±0.02
10	iC17	0.17±0.03	0.04±0.003	0.02±0.004	0.03±0.005	0.01±0.001	0.09±0.002
11	aC17	0.20±0.04	0.05±0.03	0.02±0.01	0.01±0.004	0.02±0.003	0.14±0.004
12	C17	0.23±0.004	0.06±0.005	0.02±0.002	0.004±0.001	0.02±0.006	0.03±0.002
13	C18:2n6	0.55±0.11	0.10±0.02	0.08±0.01	0.05±0.02	0.01±0.002	0.04±0.003
14	C18:3n3	0.44±0.03	0.56±0.04	0.36±0.02	0.21±0.04	0.11±0.01	0.14±0.02
15	C18:1n9	0.99±0.12	0.06±0.01	0.06±0.005	0.05±0.003	0.05±0.002	0.14±0.003
16	C18	1.24±0.07	0.47±0.02	0.14±0.02	0.06±0.01	0.13±0.005	0.21±0.02
17	C20:5n3	0.23±0.01	0.004±0.001	0.003±0.001	0.01±0.002	0.002±0.001	0.07±0.01
18	C20:1n9	0.02±0.006	0.01±0.002	0.02±0.001	0.003±0.001	0.02±0.003	0.05±0.004
19	C20	0.33±0.05	0.13±0.01	0.04±0.004	0.01±0.003	0.03±0.004	0.02±0.003
20	C22:6n3	0.02±0.003	0.14±0.002	0.15±0.01	0.003±0.001	0.13±0.01	0.003±0.001
21	C22:1n9	0.20±0.01	0.05±0.003	0.03±0.002	0.003±0.001	0.03±0.002	0.01±0.001
22	C22	0.80±0.10	0.27±0.05	0.005±0.001	0.02±0.001	0.005±0.001	0.03±0.001
23	C24:1	0.19±0.007	0.05±0.004	0.03±0.003	0.005±0.002	0.03±0.004	0.04±0.006
24	C24	1.88±0.01	0.65±0.02	0.15±0.01	0.08±0.003	0.13±0.01	0.09±0.01
25	C26	0.97±0.007	0.49±0.006	0.16±0.02	0.07±0.02	0.14±0.02	0.11± 0.03
26	C28	1.40±0.02	0.86±0.01	0.37±0.01	0.10±0.01	0.33±0.01	0.14±0.02
27	C30	1.99±0.01	1.13±0.01	0.48±0.02	0.15±0.02	0.42±0.04	0.17±0.05
Total fatty acid		20.86±1.28	10.31±1.34	4.42±1.04	1.42±0.18	3.60±0.97	5.60±0.65

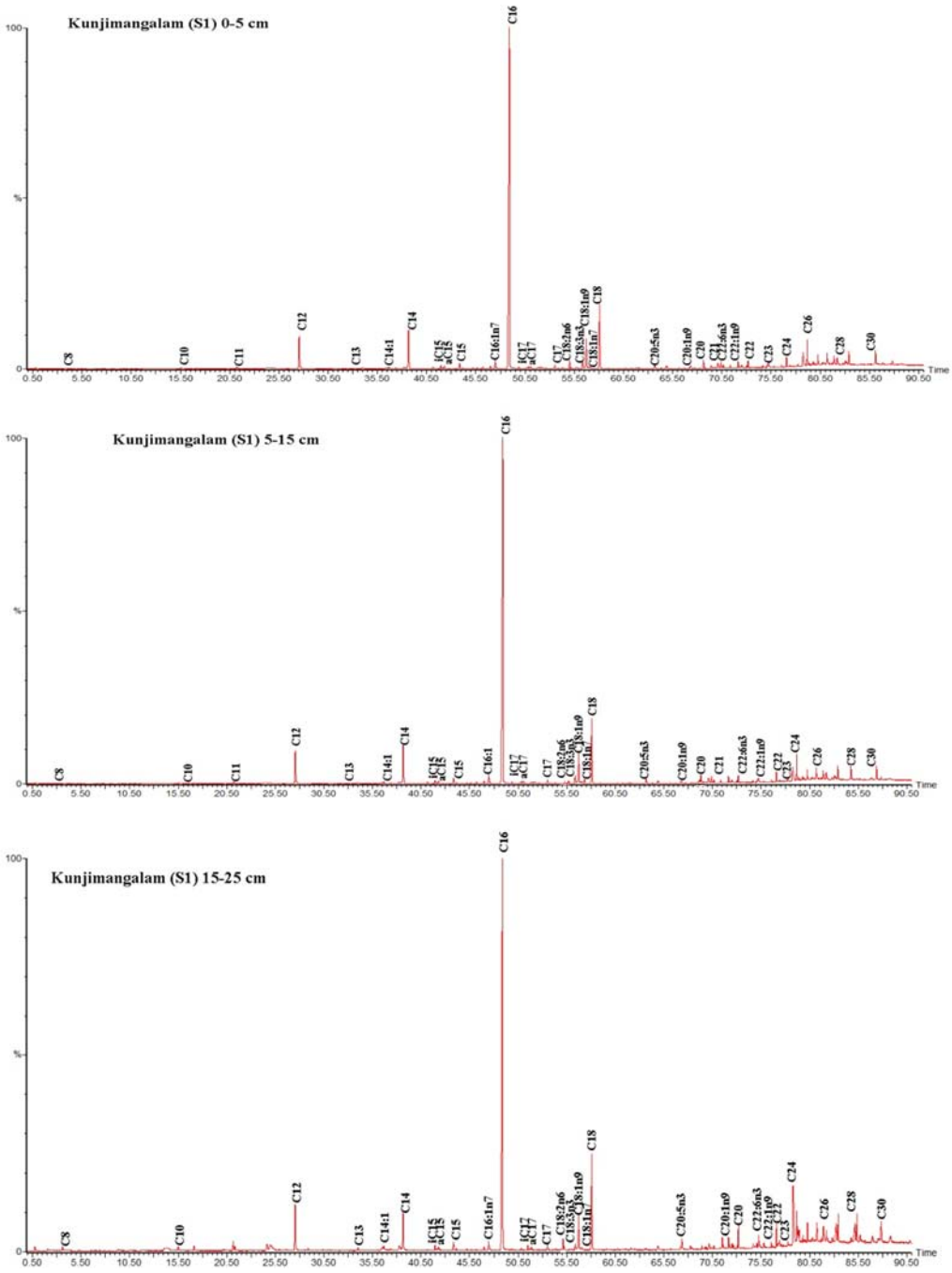
ND denotes not detected

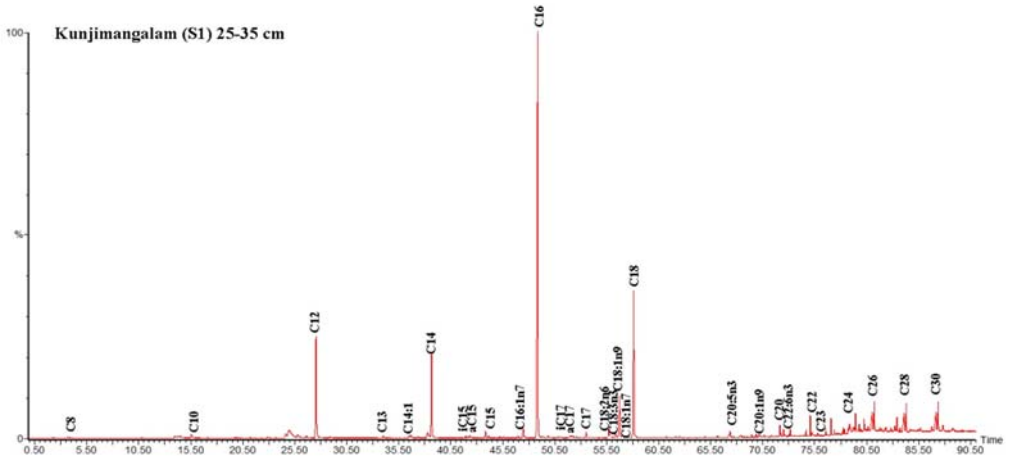
Table 6.V Fatty acids estimated in core sediments from S5

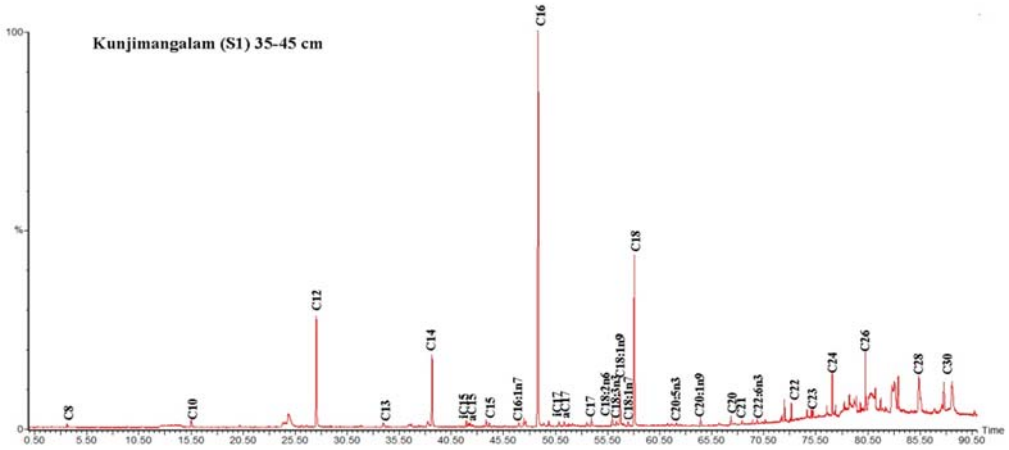
S.I. No	Fatty acids	Concentration, μgg^{-1} (Average± Standard deviation)					
		0-5 cm	5-15 cm	15-25 cm	25-35 cm	35-45 cm	45-55 cm
1	C8	0.10±0.01	0.09±0.008	ND	0.23±0.02	0.30±0.03	ND
2	C10	0.10±0.01	0.09±0.007	0.12±0.01	0.21±0.01	0.27±0.02	ND
3	C11	0.01±0.002	ND	0.01±0.003	0.01±0.001	0.01±0.002	ND
4	C12	1.20±0.04	1.16±0.03	2.40±0.21	2.07±0.08	2.69±0.03	0.40±0.10
5	C13	0.02±0.005	0.01±0.003	0.02±0.004	0.005±0.001	0.02±0.007	0.005±0.001
6	C14:1	0.03±0.006	0.02±0.003	ND	ND	ND	ND
7	C14	0.83±0.02	0.79±0.03	1.53±0.03	1.02±0.02	1.15±0.01	0.24±0.05
8	iC15	0.09±0.02	0.08±0.01	0.21±0.01	0.06±0.008	0.05±0.006	0.01±0.004
9	aC15	0.08±0.006	0.07±0.006	0.12±0.008	0.05±0.03	0.05±0.004	0.01±0.006
10	C15	0.15±0.01	0.14±0.01	0.26±0.01	0.16±0.008	0.10±0.007	0.02±0.005
11	C16:1n7	0.16±0.007	0.15±0.004	0.20±0.01	0.13±0.009	0.07±0.006	0.02±0.007
12	C16	5.06±0.44	4.90±0.32	4.28±0.41	6.66±0.21	2.96±0.14	1.48±0.11
13	iC17	0.04±0.006	0.03±0.004	0.11±0.002	0.02±0.004	0.003±0.001	0.002±0.001
14	aC17	0.03±0.004	0.02±0.003	0.08±0.01	0.02±0.003	0.002±0.001	0.004±0.001
15	C17	0.14±0.01	0.13±0.009	0.08±0.004	0.28±0.003	0.04±0.006	0.02±0.003
16	C18:2n6	0.10±0.001	0.09±0.002	0.03±0.002	0.04±0.001	0.03±0.004	0.01±0.002
17	C18:1n9	0.48±0.01	0.46±0.02	1.04±0.03	0.77±0.01	0.64±0.01	0.09±0.01
18	C18	1.76±0.04	1.70±0.02	5.22±0.11	2.65±0.06	0.46±0.02	0.26±0.03
19	C20:5n3	0.01±0.003	0.01±0.005	0.04±0.004	0.01±0.001	0.05±0.001	0.002±0.001
20	C20:1n9	0.02±0.003	0.01±0.001	0.01±0.001	0.02±0.001	0.003±0.001	0.01±0.001
21	C20	0.13±0.01	0.11±0.02	0.43±0.04	0.31±0.02	0.02±0.008	0.02±0.005
22	C21	0.04±0.005	0.03±0.002	0.13±0.003	0.08±0.004	1.34±0.10	0.01±0.001
23	C22:6n3	0.03±0.002	0.02±0.001	0.03±0.001	0.02±0.002	0.02±0.001	0.01±0.001
24	C22:1n9	0.01±0.001	0.01±0.001	0.02±0.002	0.01±0.001	0.01±0.001	0.01±0.001
25	C22	0.30±0.01	0.28±0.02	0.97±0.03	0.74±0.01	0.10±0.01	0.04±0.003
26	C23	0.14±0.01	0.13±0.01	0.27±0.02	0.20±0.03	0.06±0.01	0.01±0.006
27	C24:1n9	0.05±0.01	0.04±0.01	ND	ND	ND	ND
28	C24	0.46±0.02	0.44±0.01	0.61±0.02	0.49±0.03	0.13±0.02	0.04±0.01
29	C26	0.38±0.01	0.36±0.02	0.18±0.01	0.16±0.02	0.12±0.02	0.03±0.004
30	C28	0.38±0.02	0.36±0.01	0.10±0.02	0.17±0.02	0.17±0.01	0.05±0.002
31	C30	0.53±0.01	0.51±0.02	0.05±0.01	0.10±0.02	0.33±0.01	0.06±0.01
Total Fatty Acids		12.84±0.11	12.22±0.12	18.55±0.17	16.70±0.12	11.19±0.19	2.87±0.08

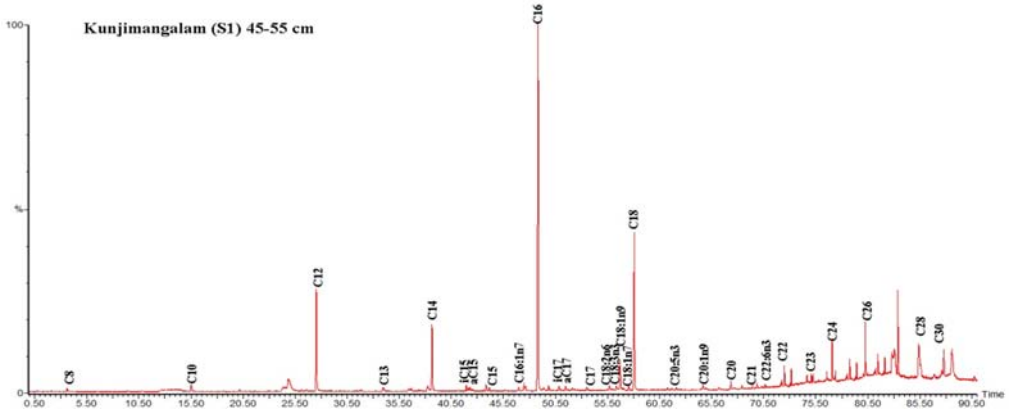
ND denotes not detected

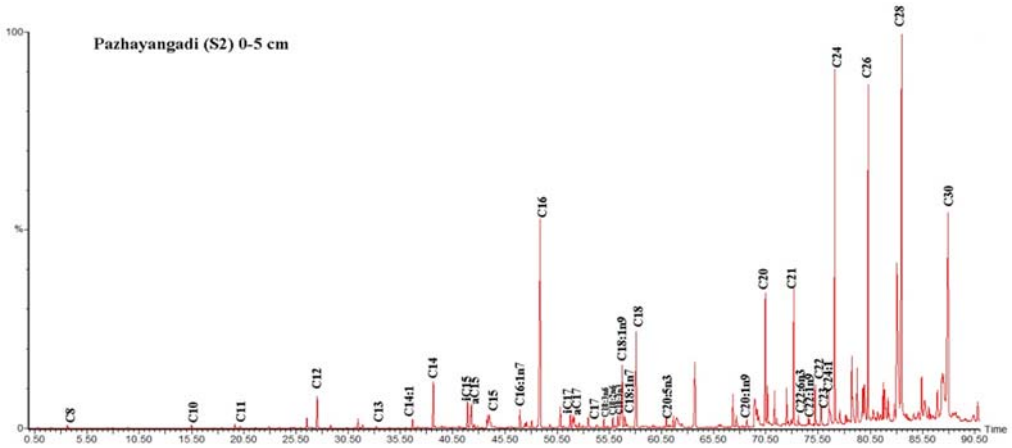
Total ion chromatogram of fatty acids in the study area

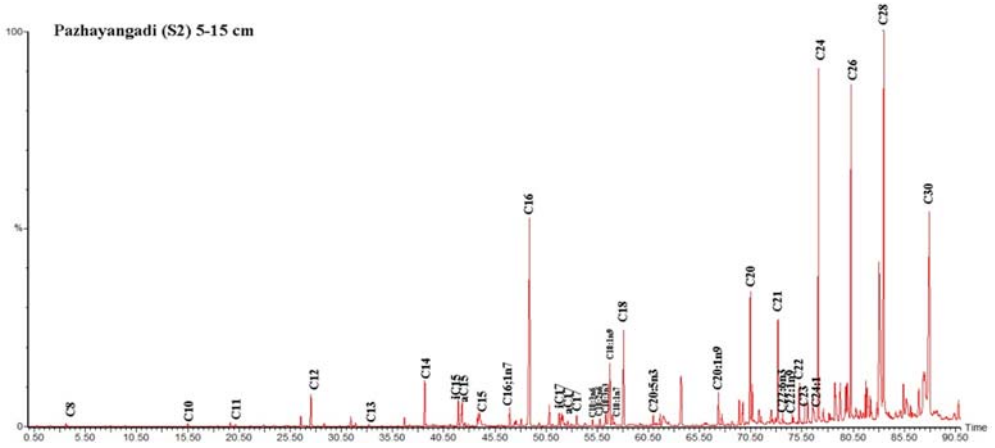


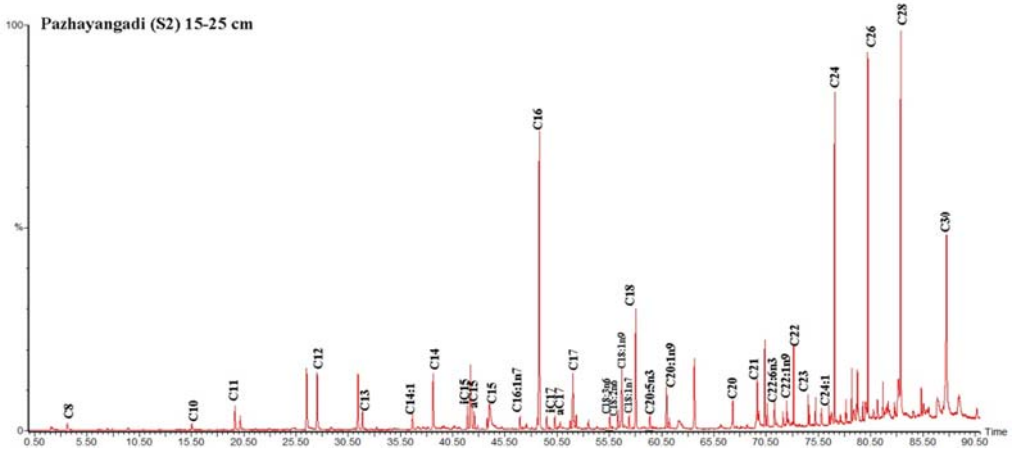

Kunjimangalam (S1) 25-35 cm
100
%
0
C8
C10
C12
C13
C14:1
C14
C15
C16:1n7
C16
C17
C18:2n6
C18:3n3
C18:1n9
C18:1n7
C18
C20:5n3
C20:1n9
C21
C22:6n3
C22
C23
C24
C26
C28
C30
0.50
5.50
10.50
15.50
20.50
25.50
30.50
35.50
40.50
45.50
50.50
55.50
60.50
65.50
70.50
75.50
80.50
85.50
90.50
Time

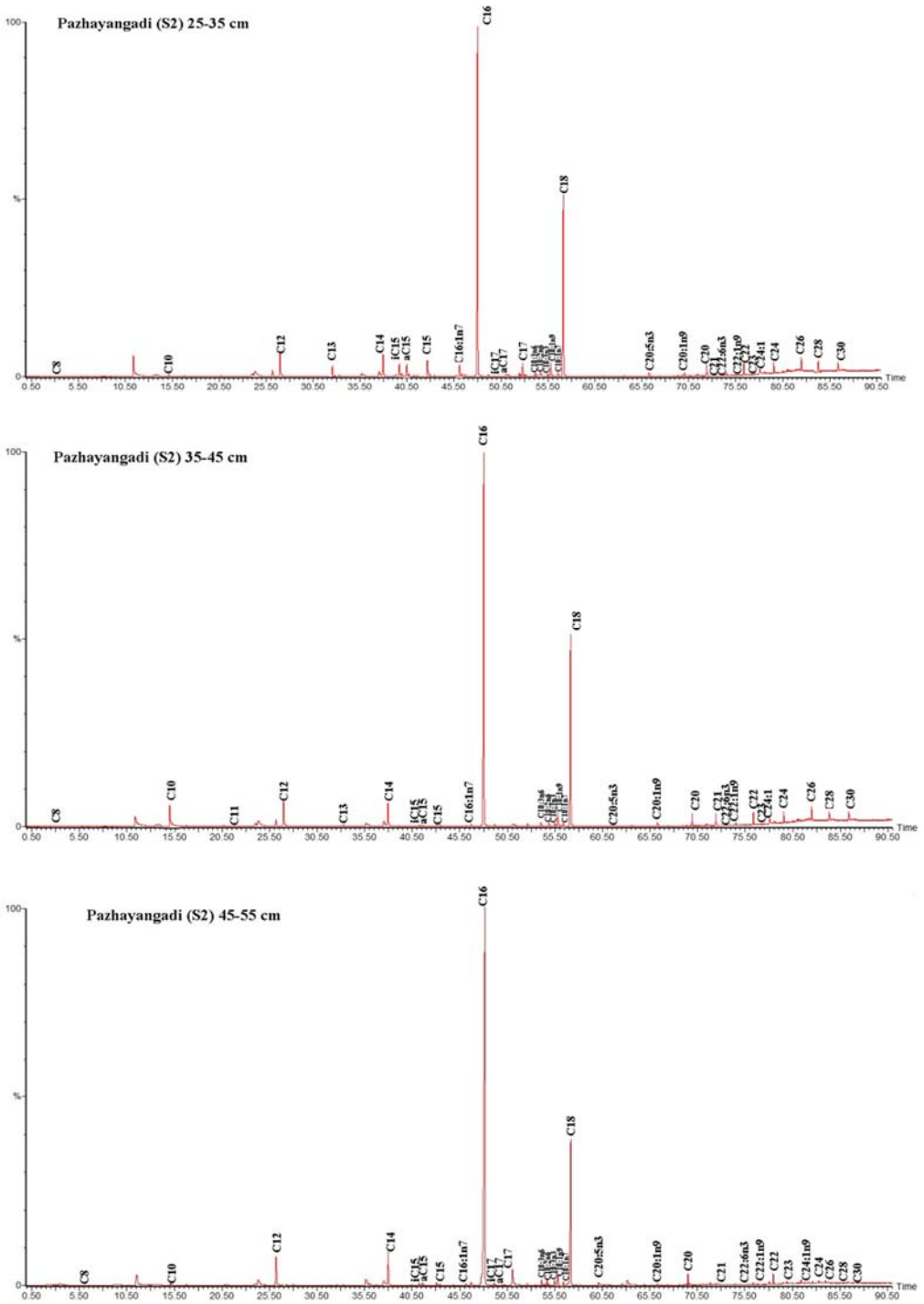

Kunjimangalam (S1) 35-45 cm
100
%
0
C8
C10
C12
C13
C14
C15
C16:1n7
C16
C17
C18:2n6
C18:3n3
C18:1n9
C18:1n7
C18
C20:5n3
C20:1n9
C21
C22:6n3
C22
C23
C24
C26
C28
C30
0.50
5.50
10.50
15.50
20.50
25.50
30.50
35.50
40.50
45.50
50.50
55.50
60.50
65.50
70.50
75.50
80.50
85.50
90.50
Time

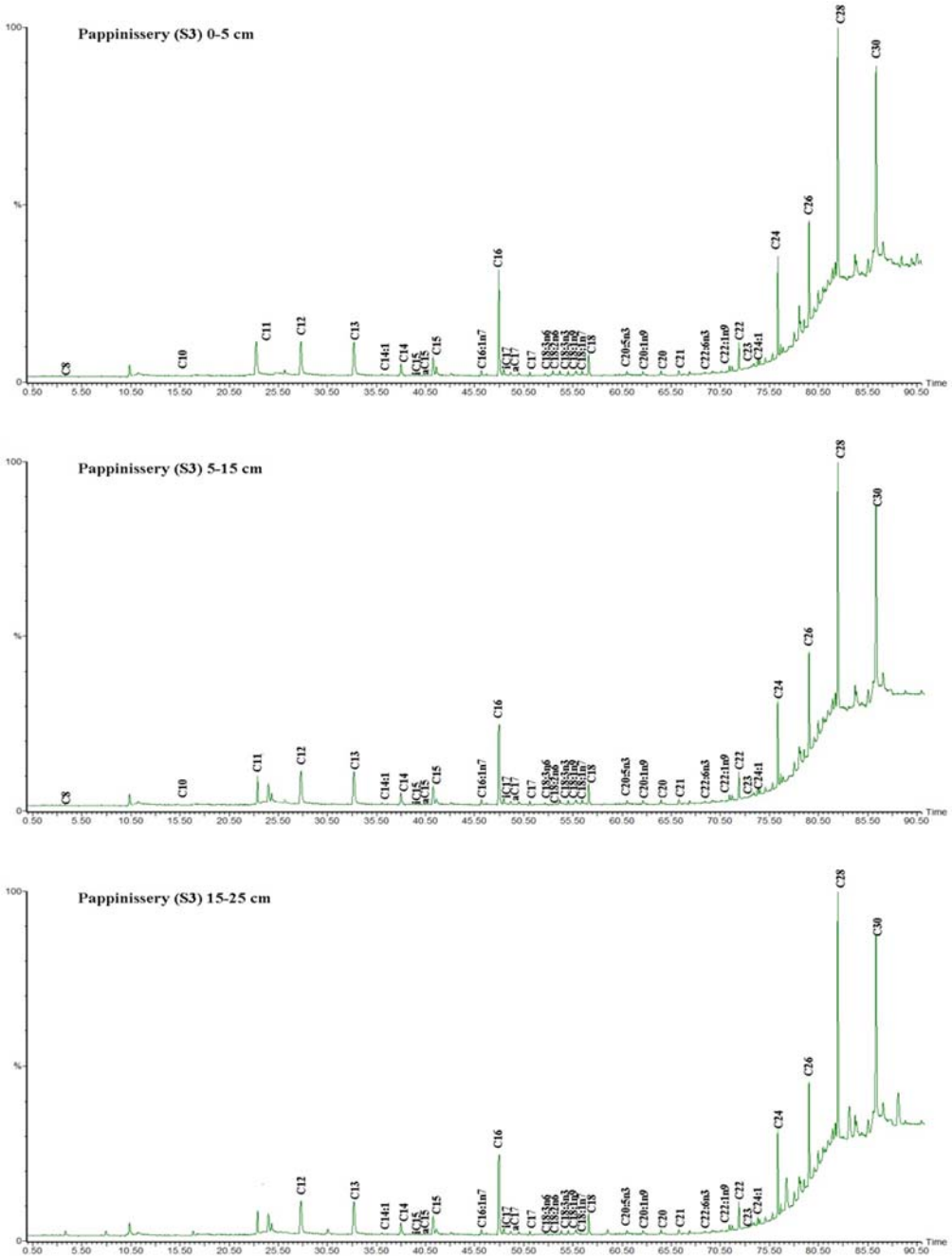

Kunjimangalam (S1) 45-55 cm
100
%
0
C8
C10
C12
C13
C14
C15
C16:1n7
C16
C17
C18:2n6
C18:3n3
C18:1n9
C18:1n7
C18
C20:5n3
C20:1n9
C10
C21
C22:6n3
C22
C23
C24
C26
C28
C30
0.50
5.50
10.50
15.50
20.50
25.50
30.50
35.50
40.50
45.50
50.50
55.50
60.50
65.50
70.50
75.50
80.50
85.50
90.50
Time

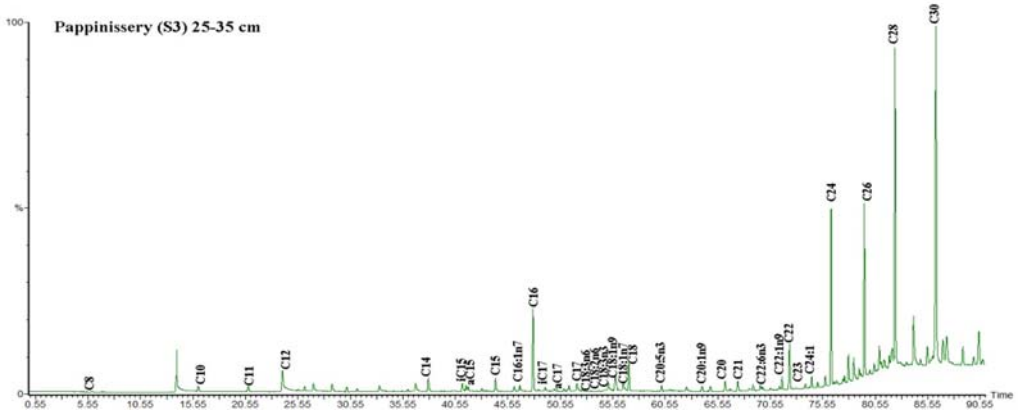

Pazhayangadi (S2) 0-5 cm
100
%
0
C8
C10
C11
C12
C13
C14:1
C14
C15
C16:1n7
C16
C17
C18:1n9
C18
C18:1n7
C20:5n3
C20:1n9
C20
C21
C22:6n3
C22:1n9
C23
C24:1
C24
C26
C28
C30
0.50 5.50 10.50 15.50 20.50 25.50 30.50 35.50 40.50 45.50 50.50 55.50 60.50 65.50 70.50 75.50 80.50 85.50 90.50
Time

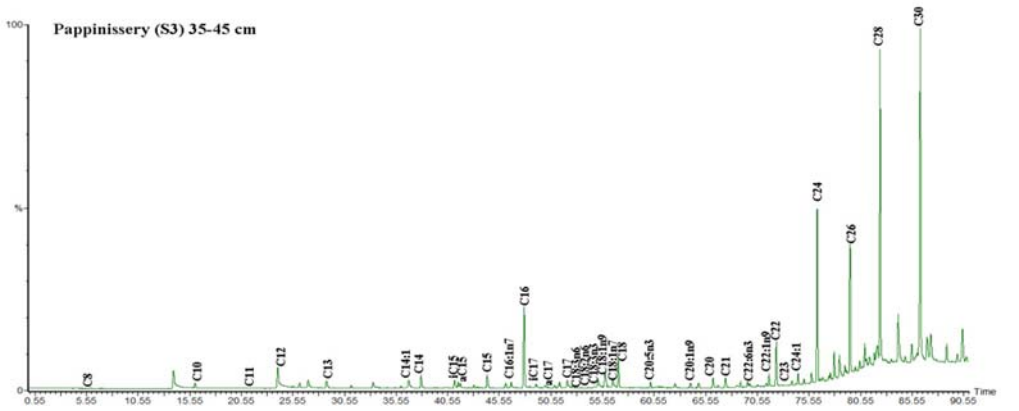

Pazhayangadi (S2) 5-15 cm
100
%
0
C8
C10
C11
C12
C13
C14
C15
C16:1n7
C16
C17
C18:1n9
C18
C20:5n3
C20:1n9
C20
C21
C22
C24:1
C24
C26
C28
C30
0.50 5.50 10.50 15.50 20.50 25.50 30.50 35.50 40.50 45.50 50.50 55.50 60.50 65.50 70.50 75.50 80.50 85.50 90.50
Time

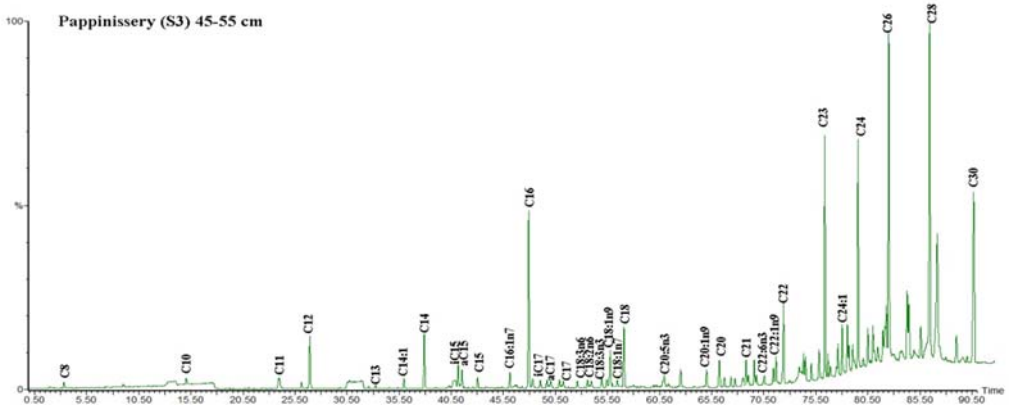

Pazhayangadi (S2) 15-25 cm
100
%
0
C8
C10
C11
C12
C13
C14:1
C14
C15
C16:1n7
C16
C17
C18:1n9
C18
C18:1n7
C20:5n3
C20:1n9
C20
C21
C22:6n3
C22:1n9
C22
C23
C24:1
C24
C26
C28
C30
0.50 5.50 10.50 15.50 20.50 25.50 30.50 35.50 40.50 45.50 50.50 55.50 60.50 65.50 70.50 75.50 80.50 85.50 90.50
Time

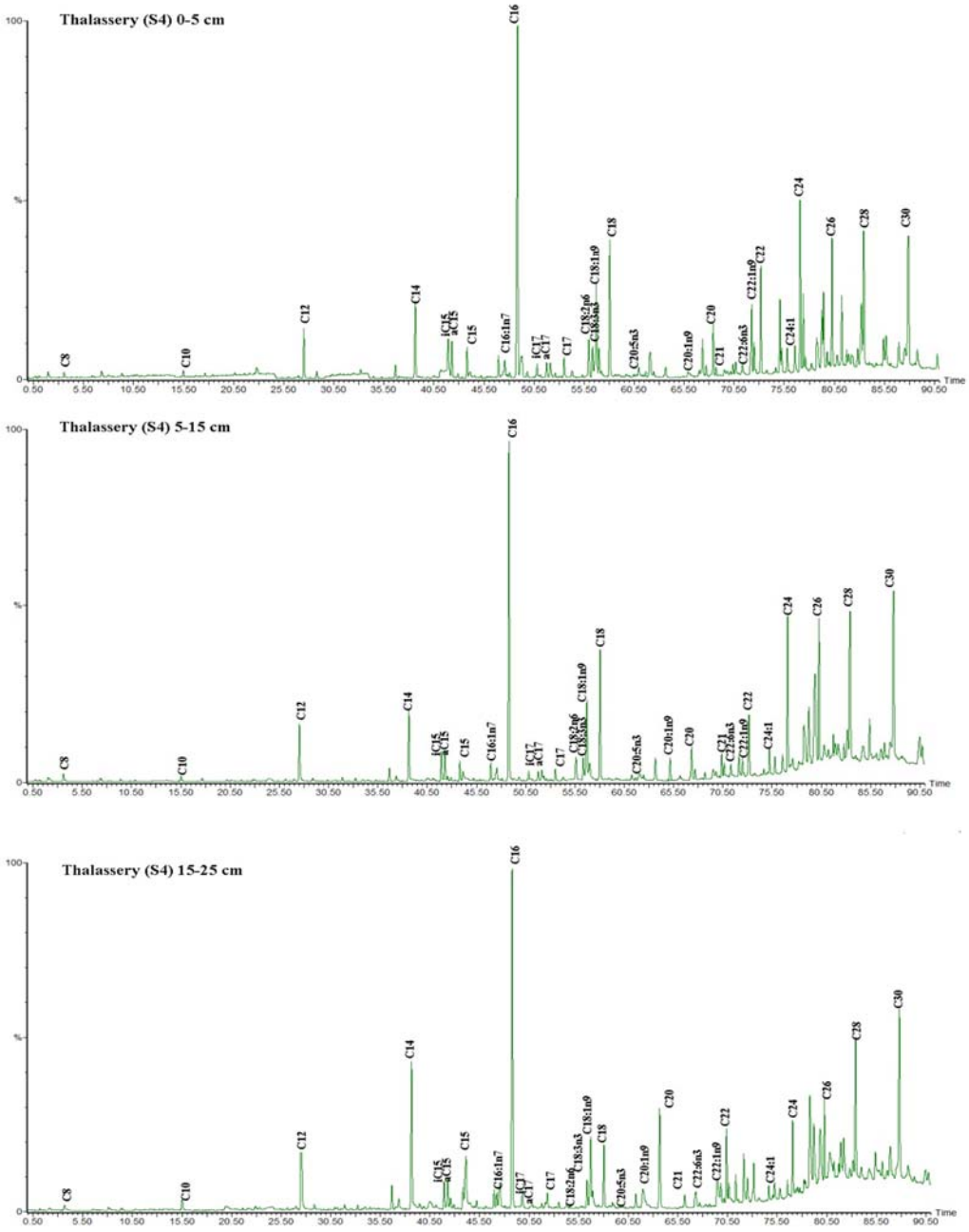

Pazhayangadi (S2) 25-35 cm
Pazhayangadi (S2) 35-45 cm
Pazhayangadi (S2) 45-55 cm
C8
C10
C11
C12
C13
C14
C15
C16
C16:1n7
C17
C18
C20:5n3
C20:1n9
C20
C21
C22:6n3
C22:1n9
C22
C23
C24:1
C24
C26
C28
C30
Time

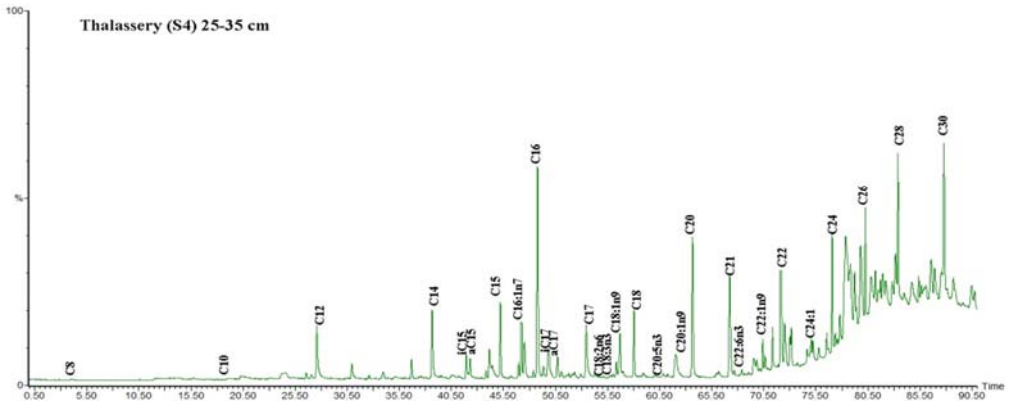

Pappinissery (S3) 0-5 cm
Pappinissery (S3) 5-15 cm
Pappinissery (S3) 15-25 cm
C28
C30
C26
C24
C16
C12
C13
C11
C10
C15
Time

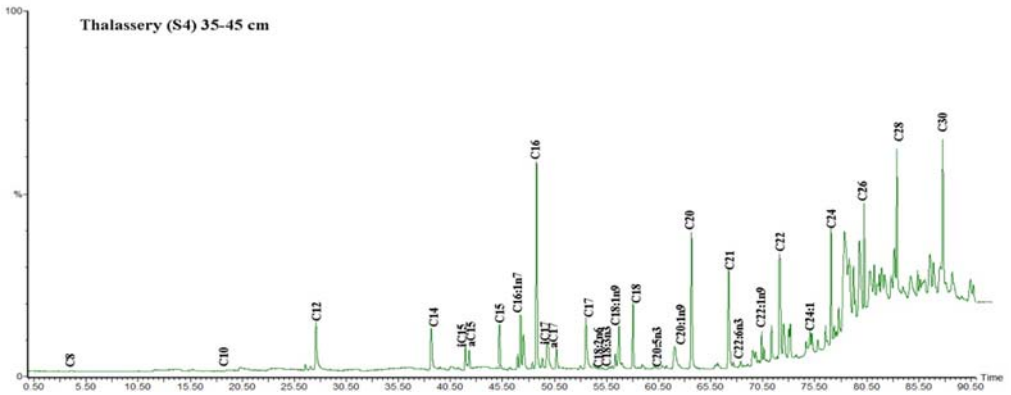

Pappinissery (S3) 25-35 cm
100
%
0
C8
C10
C11
C12
C14
C15
C16
C16:1n7
C17
C20:5n3
C20:1n9
C20
C21
C22:6n3
C22:1n9
C22
C23
C24:1
C24
C26
C28
C30
Time

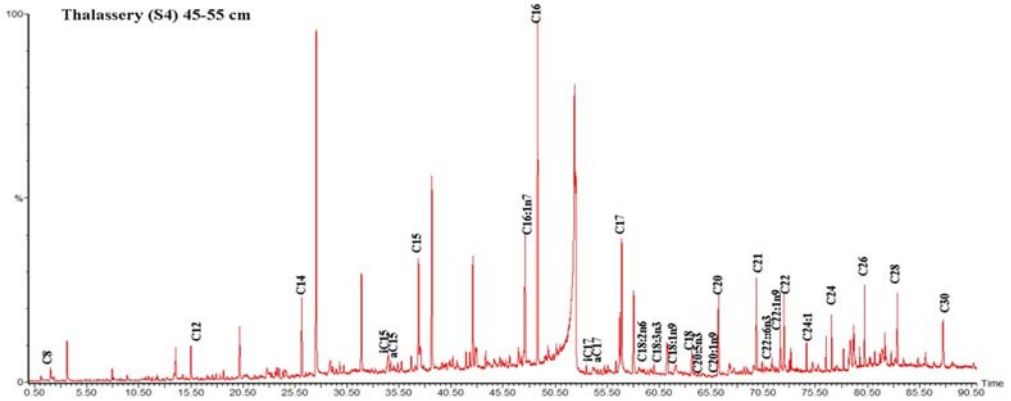

Pappinissery (S3) 35-45 cm
100
%
0
C8
C10
C11
C12
C13
C14:1
C14
C15
C16:1n7
C16
C17
C20:5n3
C20:1n9
C20
C21
C22:6n3
C22:1n9
C22
C23
C24:1
C24
C26
C28
C30
Time

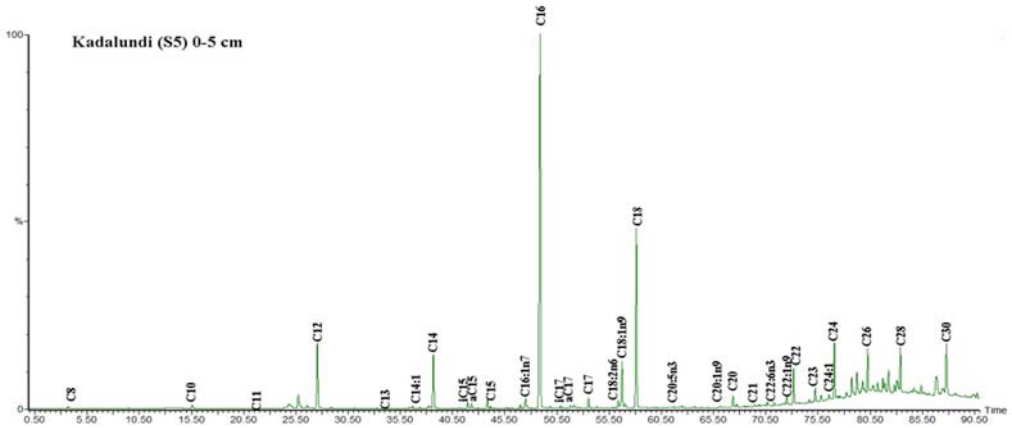

Pappinissery (S3) 45-55 cm
100
%
0
C8
C10
C11
C12
C13
C14:1
C14
C15
C16:1n7
C16
C17
C18:3n6
C18:3n3
C18:1n9
C18:1n7
C18
C20:5n3
C20:1n9
C20
C21
C22:6n3
C22:1n9
C22
C24:1
C23
C24
C26
C28
C30
Time

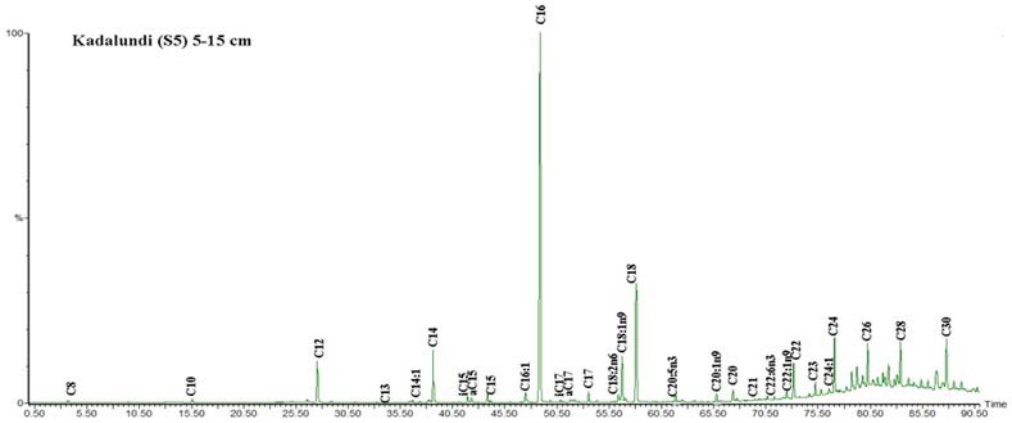

Thalassery (S4) 0-5 cm
Thalassery (S4) 5-15 cm
Thalassery (S4) 15-25 cm
C8
C10
C12
C14
C15
C16
C16:1n7
C17
C18
C18:1n9
C20
C21
C22
C22:1n9
C24
C24:1
C26
C28
C30
Time

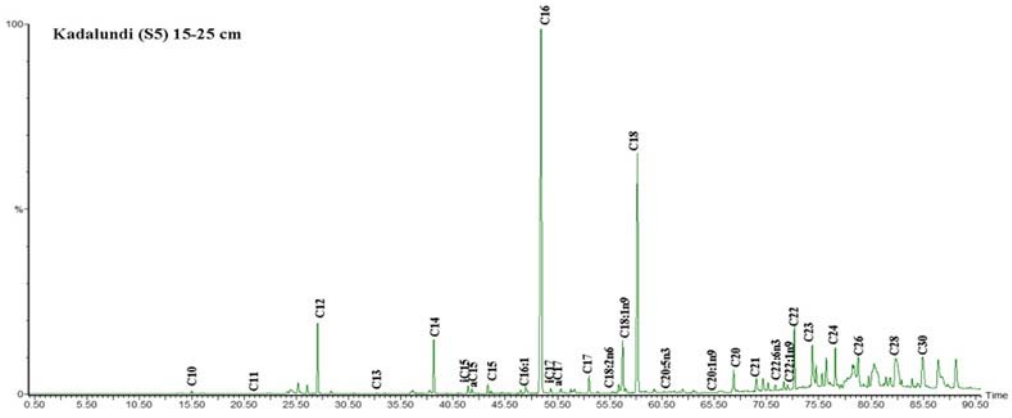

Thalassery (S4) 25-35 cm
100
%
0
C8
C10
C12
C14
iC15
aC15
C15
C16:1n7
C16
iC17
aC17
C17
C18:2n6
C18:3n3
C18:1n9
C18
C20:5n3
C20:1n9
C20
C21
C21:6n3
C21:1n9
C22
C24:1
C24
C26
C28
C30
0.50 5.50 10.50 15.50 20.50 25.50 30.50 35.50 40.50 45.50 50.50 55.50 60.50 65.50 70.50 75.50 80.50 85.50 90.50
Time

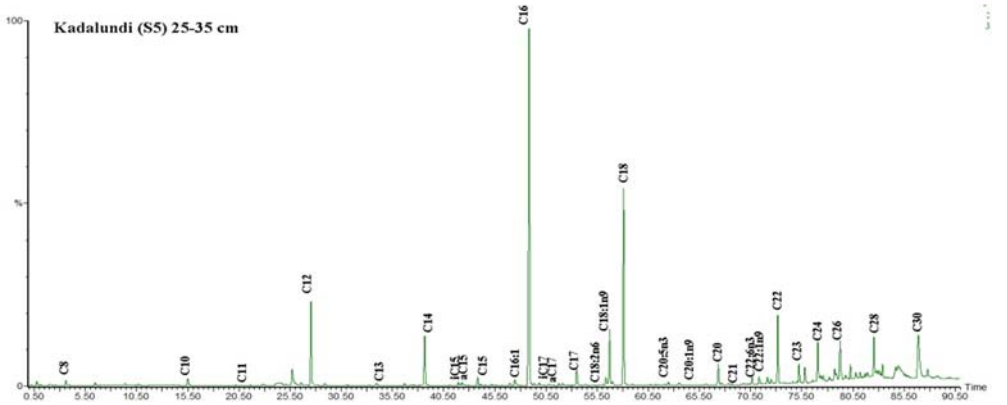

Thalassery (S4) 35-45 cm
100
%
0
C8
C10
C12
C14
iC15
aC15
C15
C16:1n7
C16
iC17
aC17
C17
C18:2n6
C18:3n3
C18:1n9
C18
C20:5n3
C20:1n9
C20
C21
C21:6n3
C21:1n9
C22
C24:1
C24
C26
C28
C30
0.50 5.50 10.50 15.50 20.50 25.50 30.50 35.50 40.50 45.50 50.50 55.50 60.50 65.50 70.50 75.50 80.50 85.50 90.50
Time

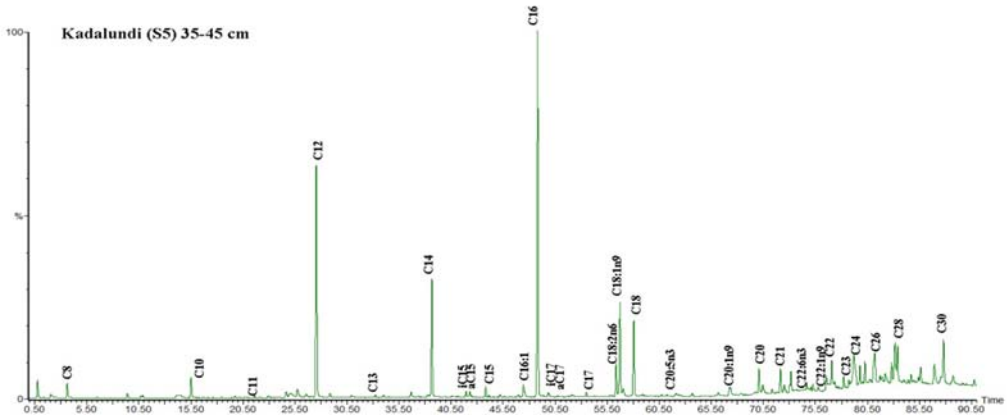

Thalassery (S4) 45-55 cm
100
%
0
C8
C12
C14
iC15
aC15
C15
C16:1n7
C16
iC17
aC17
C17
C18:2n6
C18:3n3
C18:1n9
C18
C26:5n3
C20:1n9
C20
C21
C21:6n3
C21:1n9
C22
C24:1
C24
C26
C28
C30
0.50 5.50 10.50 15.50 20.50 25.50 30.50 35.50 40.50 45.50 50.50 55.50 60.50 65.50 70.50 75.50 80.50 85.50 90.50
Time

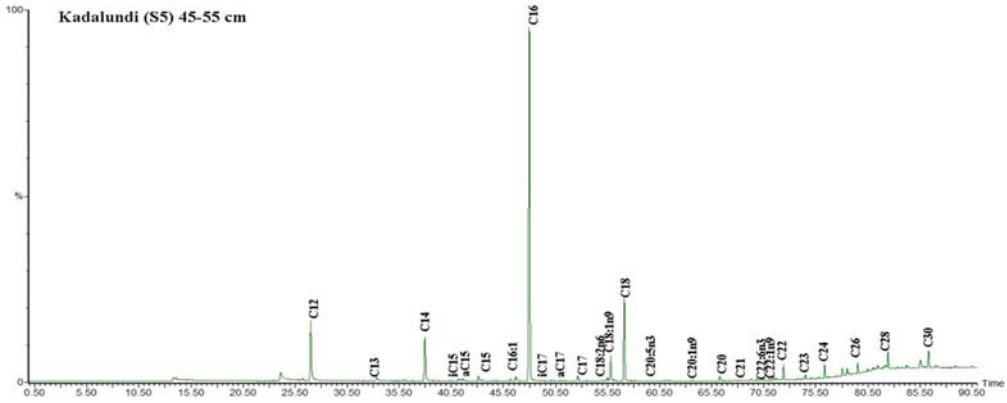

Kadalundi (S5) 0-5 cm
100
%
0
C8
C10
C11
C12
C13
C14:1
C14
iC15
aC15
C15
C16:1n7
C16
iC17
aC17
C17
C18:2n6
C18:1n9
C18
C20:5n3
C20:1n9
C20
C21
C22:6n3
C22:1n9
C22
C23
C24:1
C24
C26
C28
C30
0.50 5.50 10.50 15.50 20.50 25.50 30.50 35.50 40.50 45.50 50.50 55.50 60.50 65.50 70.50 75.50 80.50 85.50 90.50
Time


Kadalundi (S5) 5-15 cm
100
%
0
C8
C10
C12
C13
C14:1
C14
iC15
aC15
C15
C16:1
C16
iC17
aC17
C17
C18:2n6
C18:1n9
C18
C20:5n3
C20:1n9
C20
C21
C22:6n3
C22:1n9
C22
C23
C24:1
C24
C26
C28
C30
0.50 5.50 10.50 15.50 20.50 25.50 30.50 35.50 40.50 45.50 50.50 55.50 60.50 65.50 70.50 75.50 80.50 85.50 90.50
Time


Kadalundi (S5) 15-25 cm
100
%
0
C10
C11
C12
C13
C14
iC15
aC15
C15
C16:1
C16
iC17
aC17
C17
C18:2n6
C18:1n9
C18
C20:5n3
C20:1n9
C20
C21
C22:6n3
C22:1n9
C22
C23
C24
C26
C28
C30
0.50 5.50 10.50 15.50 20.50 25.50 30.50 35.50 40.50 45.50 50.50 55.50 60.50 65.50 70.50 75.50 80.50 85.50 90.50
Time


Kadalundi (S5) 25-35 cm
C8
C10
C11
C12
C13
C14
C15
C16
C16:1
C17
C18
C18:1n9
C18:2n6
C20:5n3
C20:1n9
C20
C21
C22
C23
C24
C26
C28
C30
Time


Kadalundi (S5) 35-45 cm
C8
C10
C11
C12
C13
C14
C15
C16
C16:1
C17
C18
C18:1n9
C18:2n6
C20:5n3
C20:1n9
C20
C21
C22
C23
C24
C26
C28
C30
Time


Kadalundi (S5) 45-55 cm
C12
C13
C14
C15
C16
C16:1
C17
C18
C18:1n9
C18:2n6
C20:5n3
C20:1n9
C20
C21
C22
C23
C24
C26
C28
C30
Time

LIST OF PUBLICATIONS

1. Ratheesh Kumar, C. S., Joseph, M. M., Gireesh Kumar, T. R., Renjith, K.R., **Manju, M. N.,** Chandramohanakumar, N., 2010. Spatial Variability and Contamination of Heavy Metals in the Inter-tidal Systems of a Tropical Environment. *International Journal Environmental Research*, 4(4), 691-700.
2. **Manju, M. N**., Resmi, P., Gireesh Kumar T.R., Ratheesh Kumar, C.S., Rahul, R., Joseph, M. M., and Chandramohanakumar, N., 2012. Assessment of Water Quality Parameters in Mangrove Ecosystems along Kerala Coast: A Statistical Approach. *International Journal of Environmental Research,* 6(4), 893-902.
3. Udayakumar, P., Jean Jose, J., Anoop Krishnan, K., Ratheesh Kumar, C. S., **Manju, M. N.**, Salas, P. M. 2014. Heavy metal accumulation in the surficial sediments along southwest coast of India. *Environmental Earth Sciences*, DOI 10.1007/s12665-014-3097-9.

Seminar presented /accepted in national publications

1. **Manju, M. N**., Resmi, P., Gireesh Kumar T.R., Ratheesh Kumar, C.S., and Chandramohanakumar, N., 2013. Evaluation of nature and quality of organic matter in the core sediments of Mangrove ecosystems along Kerala coast. Paper presented and accepted in Aquasem ’13, Cochin University of Science and Technology.
2. Resmi, P., **Manju, M. N**., Gireesh Kumar T.R., Ratheesh Kumar, C.S., Rahul, R., Joseph, M. M., and Chandramohanakumar, N., 2013. Monitoring Water Quality in Mangrove Ecosystems along Kerala

Coast. Paper accepted in Aquasem ’13, Cochin University of Science and Technology.

3. Resmi, P., **Manju, M. N**., Gireesh Kumar T.R., Ratheesh Kumar, C.S., Joseph, M. M., and Chandramohanakumar, N., 2013. Spatial and seasonal variation of biochemical composition of sedimentary organic matter in Mangrove Ecosystems along Kerala Coast: A baseline study. Paper accepted in Aquasem ’13, Cochin University of Science and Technology.