AN APPRAISAL OF CORE SEDIMENT ARCHIVES ON ORGANOCHLORINE INSECTICIDES IN A TROPICAL ESTUARY, INDIA

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Certificate

*This is to certify that the thesis entitled **"An Appraisal of Core Sediment Archives on Organochlorine Insecticides in a Tropical Estuary, India"** is an authentic record of the research carried out by Mr. Akhil P.S under my supervision and guidance at the Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, Kochi-16, 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. All the relevant corrections and modifications suggested by the audience during the pre-synopsis seminar and recommended by the Doctoral Committee of the candidate have been incorporated in the thesis.*

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Declaration

I hereby declare that the thesis ***"An Appraisal of Core Sediment Archives on Organochlorine Insecticides in a Tropical Estuary, India"*** *is an authentic record of the research carried out by me under the supervision and guidance of Dr. Sujatha C.H, Associate Professor & Head, Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, Kochi-16, in partial fulfilment of the requirements for Ph.D degree of Cochin University of Science and Technology and no part of this has previously formed the basis of the award of a degree, diploma, associateship, fellowship or any other similar title or recognition.*

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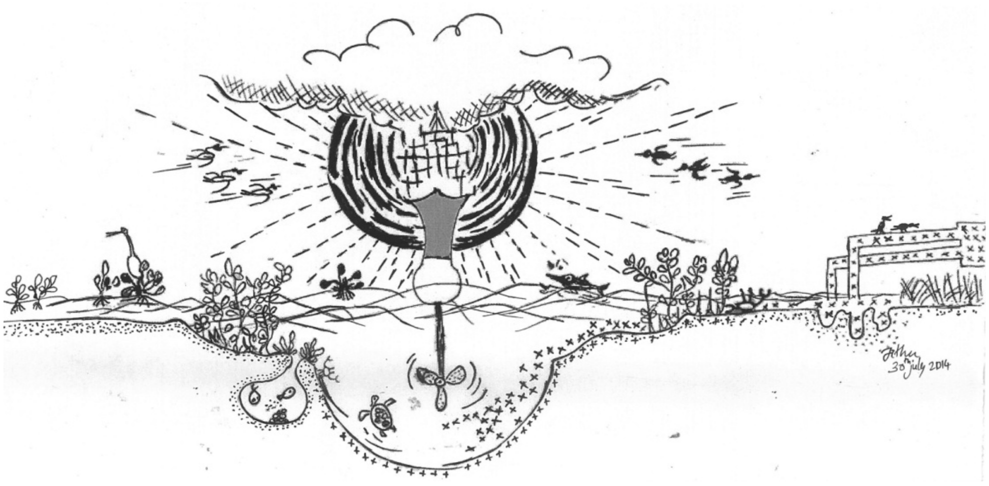
Preface

India has given asylum to huge numbers of people over the years from different parts of the world with deep rooted values of cultures that guide humans to empower the person to grow into a well balanced human being. Unwavering dedication and tireless efforts in coordinating the various team members is indispensable for the successful completion of the derived motto with various scientific disciplines. It is indeed heartening to see their potential manifesting into performance for the protection and achievement of a 'Green India'- which has in the North, the King of Mountains, Himalayas- abode of knowledge and penance- adorning Mother India's head; the (Indian) ocean washing her feet (in the south) and she is surrounded by waters of the ocean in the East and West.

Aquatic ecosystems contribute to a large proportion of the planet's biotic productivity as about 30% of the world's primary productivity comes from plants living in the ocean and are collectively the wet parts of the environment. They can be rivers, streams, swamps, lakes, estuaries, marine systems, and underground aquifers. They have biodiversity value as well as resource value and provide immense services to the environment and humankind. Sustaining biodiversity is essential to the health of our environment and to the quality of human life. Moreover, aquatic and terrestrial biodiversity are the sources of medicine, food, energy, shelter, and the raw materials that we use and need. Each day, the aquatic organisms continually break down/reduced by the reaction of harmful toxins and nutrients that we flush into our sewage systems or discard directly into our sacred rivers and streams.

Chemists have been accredited with several fundamental developments that have advanced to the benefit of society including all aspects of daily life. However, increasing public concerns over the impacts of the chemicals used in large scale on the *environment have blurred this positive image. A classic example among such chemical inventions is the development of insecticides such as Dichlorodiphenyltrichloroethane (DDT). DDT was hailed as a miracle compound because it was very effective for controlling vectors of human diseases such as typhus and malaria. Subsequently, degrading constituents of DDT found to persist in the environment, become biomagnified and cause toxic effects. The controversy continues till this date because DDT, is still manufactured and used in some areas of the world. It has become obvious that the "pollute and cleanup" processes would not be effective for some of the major pollution issues, and an alternative approach has to emerge with a strong focus on pollution prevention. Once dispersed in the environment, persistent pollutants are essentially impossible to remediate. The picture below amply justifies the situation.*



Aquatic toxicology is a relatively new and still evolving discipline, originating from the concern for the safety, conservation, and protection of aquatic environments. Scientists from academic, industrial, consulting/private, and government institutions have made and are making significant contributions to this multidisplinary science and its many applications in managing toxic substances and complex wastes. Almost daily, the media carry alarming reports about the threat of Persistent Organic Pollutants

(POPs) to our health or our environment. Thus the effect of pollutant is not merely one concerning the chemical industry and professional farmers, foresters and applicators, nor one concerning only those wish to protect wildlife or those responsible for control of vector borne diseases of humans and their life stock. Rather, the pesticide problem concerns every person who wants his or her home free of vermin. The problem can be solved only on the basis of sound knowledge on the harmful effects of these xenobiotics to the environment. Thus a cooperative approach on the part of persons professionally responsible for the protection of our environment is called for. Above all, the collective literatures that make up the present thesis work not only illustrate the current state of the science but also conveys the anxiety and commitment of the practitioners to the dynamic field called aquatic toxicology.

The thesis entitled ***"An Appraisal of Core Sediment Archives on Organochlorine Insecticides in a Tropical Estuary, India"*** *presents the first comprehensive investigation on the residual levels of Organochlorine Insecticides in the sediments of Cochin Estuarine System and the study will provide valuable information for assessing the status of POPs in the aquatic environment. In this context, the present thesis is divided into six chapters. Chapter 1 is the* ***Introduction*** *and its deals with literature survey and problem statement. Chapter 2 is* ***Materials and Methods*** *and deals with the nature of sampling location and analytical methods adopted for the research programme. Chapter 3 deals with the* ***Biogeoorganics in the Sedimentary Environment*** *which infers the quality of the biogeochemical constituents in the surface/core sediments of the Cochin Estuary. Chapter 4 comprises the* ***Spatial Budgetary Evaluation of Organochlorine Contaminants in the CES****. Chapter 5 includes* ***Organochlorine Insecticides in Specific Core Sediments of a Tropical Estuary****. Finally Chapter 6* ***Concluding Remarks*** *which covers overall summary of the results and the outcomes are presented with comprehensive explanations.*

Contents

List of Abbreviations

BDL	Below Detectable Limit
BPC	Biopolymeric Carbon
CES	Cochin Estuarine System
CHO	Carbohydrate
Chl a,b & c	Chlorophyll a, b & c
DDT	Dichlorodiphenyltrichloroethane
HCH	Hexachlorocyclohexane
ICTT	International Container Transhipment Terminal
LPD	Lipid
OM	Organic Matter
OCIs	Organochlorine Insectisides
PAHs	Polycyclic Aromatic Hydrocarbons
PCBs	Polychlorinated Biphenyls
PCA	Principal Component Analysis
PEC	Probable Effect Concentration
Pheo	Pheophytin
POPs	Persistent Organic Pollutants
PRT	Protein
SQG	Sediment Quality Guidelines
TOC	Total Organic Carbon
TEC	Threshold Effect Concentration
TIN	Tannin and Lignin
USEPA	United States Environmental Protection Agency

1

INTRODUCTION

1.1 General Introduction

In modern society, thousands of chemicals (both organic and inorganic) are in common use (industrial, medicinal purposes etc) and depending on their life cycle (extraction, manufacturing, transport, use and disposal) finally reach the estuarine and coastal systems through a number of pathways. Many of these compounds enter the aquatic environment via non point sources (eg. agricultural or urban storm water runoff), but a number of them are discharged from point sources such as wastewater treatment plants, which were not designed to deal with the ever increasing diversity of organic compounds that pass through their treatment units (Sujatha et al., 1993; Thomson, 2002; Dsikowitzky et al., 2014). These wastes discharges accompanying complex contaminants either directly enter the estuaries or the coastal areas; but, in many cases, they enter into the freshwater bodies and finally enter the ocean margins. The toxic character of many such compounds has been known for decades; however, in other cases, it has taken considerable effort, both on the analytical side and on the toxicological assays, to determine that even at extremely low concentrations they cause harmful effects. Consequently, the residing bottom sediments are also recognized as an excellent temporary or long-term sinks for many types and classes of anthropogenic contaminants (OCIs, PAHs, PCBs, Trace metals etc).

According to the World Resource Centre, coastal habitats alone account for approximately 1/3 of all marine biological productivity, and estuarine ecosystems (i.e., salt marshes, sea grasses, mangrove forests) are among the most productive regions on the planet (EPA, 1990). Rapidly growing populations and expanding urbanization and land development are exerting escalating pressures on coastal ecosystems worldwide. Therefore, the study on coastal sediments becomes an important step in mapping the possible pollution sources and exposure pathways which would facilitate pollutants' bioavailability to sediment dwelling organisms and their toxicological effect. Thus, a comprehensive insight into the effects of chemicals in the environment requires assessments ancillary to toxicology such as the fate of the chemical in the environment, and toxicant interactions with abiotic components of ecosystems. These assessments necessitate elucidating the adverse effects of chemicals that are present in the environment and predicting any ill/toxic effects of chemicals before they are discharged into the environment. Therefore, the Queen of Arabian Sea (Cochin), Kerala, the aquatic system under consideration is where the present research work focuses on the residual concept pertaining to OCIs, which are widely used/manufactured in the nearby areas of metropolitan city of Cochin and is their ultimate receiver.

1.2 Physiographical Features of the Study Area

The State of Kerala, which is a narrow strip of land lies on the south western part of Peninsular India with a 560 Km long coast and an average width of 80 Km, lying between Arabian Sea on the west and Western Ghats, a continuous mountain chain on the east. Topography of the area covers altitudes ranging from below mean Sea level to above ~2600 m the area of in Western Ghats. It is characterised by 44 short and swift flowing monsoon fed perennial rivers, which originates from the Western Ghats and 41 of them drain into either estuaries or the Arabian Sea. The most conspicuous feature of this coast is that the wide spread distribution of estuaries and lagoons are thought to be the remnants of the receding Sea. The area has a tropical humid climate with a temperature range of 13 to 42° C and an average rainfall of 3000 mm (Krishnan Nair, 1996; Soman, 1997; Menon et al., 2000).

The study area, the Cochin Estuary (Lat. 9° 30’ -10° 10’ N and Lon. 76° 15’ - 76° 25’E) situated in the central part of Kerala extends between the cities of Azhikode in the north and Alleppy in the south, running parallel to the Arabian Sea. It is generally wide (0.8-1.5 Km) and deep (4-13 m) towards south but becomes narrow (0.05-1.5 Km) and shallow (0.5-3 m) in its northern part. Six rivers: Pamba, Achankovil, Manimala, Meenachil, Periyar and Muvattupuzha with their tributaries, along with several canals, bring large volumes of freshwater into the estuary. Tidal intrusion from the Arabian Sea (tidal range avg. 1m) contributes a regular flow of salt water, which diminishes considerably towards the head of the estuary (Madhuprathap, 1987; Balachandran et al., 2008). Among these rivers, Periyar (in the north) and Muvattupuzha (in the south) have an active influence in controlling the salinity of the estuarine system.

1.3 Behaviour and Fate of Trace Organic Contaminants in the Environment

In the natural environment, all chemicals are subject to physical, chemical and biological processes that can act on their chemical structure causing degradation and eventual removal or a considerable reduction in the potential for harmful effects. However, some chemicals do not break down or slowly break down in the environment. In addition, degradation processes might lead to the production of nondegradable by-products. These substances are known as persistent chemicals and are long-lived under prevailing environmental conditions. Moreover, hydrosphere acts as a major reservoir for persistent organic pollutants, they enter into the environment via many pathways, including:-

- Direct application for pest and vector control.
- Urban and industrial waste water discharges.
- Runoff from non-point sources.
- Leaching through soil.
- Aerosol and particulate deposition rainfall.

The issue that arises in these circumstances is whether the presence of the residual concentrations of these contaminants represents a risk to man and to biota.

Persistent organic pollutants (POPs), a group of xenobiotic lipophilic pollutants, are semi volatile, bio accumulative, persistent and toxic in character (Jones and de Voogt, 1999). They can be deposited in marine and freshwater ecosystems through effluent releases, atmospheric deposition, runoff, and other means. Because POPs have low water solubility, they bond strongly to particulate matter in aquatic sediments (Leppanen, 1995). As a result, sediments can serve as reservoirs or 'sinks' for POPs. When sequestered in these sediments, POPs can be taken out of circulation for long periods of time. If disturbed, however, they can be reintroduced into the ecosystem and food chain, potentially becoming a source of local, and even global, contamination. Although the occurrence of POPs at elevated levels is of great environmental concern, the regional and global significance of the problem has received increased attention in the last decades (UNECE, 1998; UNEP, 2001). They have been reported to cause variety of effects including immunologic, tetratogenic, carcinogenic, reproductive and neurological problems in organisms (Kodavanti et al., 1998) and are of considerable concern to human and environmental health (Anupama and Sujatha, 2012). Moreover, POPs work their way in biomagnifications via the food chain by accumulating in the body fat of living organisms and becoming more concentrated as they move from one trophic creature to another. Ecological magnification in organisms through the food chain appears to be the most harmful environmental effect resulting from the general usage of organochlorine insecticides. Sediment-dwelling animals therefore have a greater risk of accumulating toxic substances than pelagic animals, because they are exposed to all possible accumulation routes (Leppänen, 1995). Sharpe and Mackay (2000) estimates that benthic organisms attain about 95% of their accumulated contaminants from the sediment.

In the POPs, 'Pesticides' (lat. *pestis* – pest and *cedeo* – destroy) are the group of anthropogenic compounds that have been used in agriculture and households for several decades to control pests, diseases, and insect-borne diseases (e.g., malaria, dengue, encephalitis, and filariasis). Based on the applications, they can be divided into herbicides, insecticides, fungicides, rodenticides, molluscidies, acaricides, nematocides, aphicides and ovicides (Biziuk et al., 1996). OCIs are mainly synthetic organic insecticides and may also be named as 'chlorinated hydrocarbons' or 'chlorinated insecticides'. Representative compounds in OCIs are DDT, methoxychlor, dieldrin, chlordane, toxaphene, mirex, kepone, lindane, and benzene hexachloride etc. Some persistent pollutants, including several pesticides, traverse to a long distance through air and in water over several hundred miles, and so even wildlife and people living far away from where these substances are used are under significant threat. These persistent organic compounds such as HCH and DDT isomers are the predominant chemical contaminants found along the Indian coast and thus constitute both alluring and vital areas of scientific research (Pandit et al., 2001; Kumar et al., 2006).

Apart from the OCIs, other important toxic pollutant categories are PAHs and PCBs. Among these, polycyclic aromatic hydrocarbons (PAHs) are a class of ubiquitous organic compounds with two to seven condensed aromatic rings. Overall 16 PAHs are considered by the USEPA as priority micropollutants because of their carcinogenic and mutagenic properties. They occur naturally as incomplete combustion products of organic compounds and enter into the aquatic environments via oil spills, waste discharge, runoff etc. Even though they are biodegraded in soils and water within weeks to months, the metabolites are more toxic and may last for long time. In marine ecosystem, PAHs can undergo degradation by photo oxidation in the superficial water layer. Polychlorinated biphenyls (PCBs) are another class of POPs and are among the most important industrial contaminants in marine ecosystems. Theoretically, they are 209 PCB congeners with one to ten chlorine atoms bound to the phenyl rings. They are very resistant to decomposition and have an excellent insulating property as well as a high heat absorbed capacity. Their properties have led to many industrial applications but also make PCBs one of the major environmental pollutant classes. PCBs, the commonly considered key representatives of the industrial pollutants are extensively used in electrical transformers and capacitors as heat transfer fluids and in consumer products (Harrad et al., 1994). They enter the environment through dispersion from their identifiable and specific place of use or from incineration and land fill sites etc.

1.4 A Perusal on Organochlorine Insecticide Pollution Status in the Indian Scenario

Presently, India is considered as the largest pesticides producing country in Asia and 12th largest in the world with 90,000 tons of annual pesticide production (Khan, 2010). Furthermore, India is involved in the manufacturing, use and export of OCIs such as DDTs and HCHs on large scale (Pozo et al., 2011). Both industrial and agricultural sources would contribute significant amount of these contaminants to the environment through seepage, disposal and evaporation (Tolosa et al., 2010). Although substantial fractions of applied pesticides are dissipated at the site of application through chemical and biological degradation processes. Besides, a reasonable fraction of the OCIs' residues reaches the oceans through agricultural run-off, atmospheric transport and effluent discharge (GESAMP, 1989). Since OCIs are known for their persistence, toxicity and bioaccumulation characteristics, there is a concern about their impact on the marine environment. Despite the fact that pesticide consumption is low in India compared to the other developed countries, the indiscriminate use of these pesticides has resulted in sporadic occurrence of the residues in biota and other abiotic compartments. The determination and quantification of those compounds existing in water and sediment may indicate the extent of aquatic contamination and the accumulation characteristics in the aquatic ecosystems (Sujatha et al., 1994; Pandit et al., 2001; Kumar et al., 2006).

There is a scarcity of literature on pesticide residues in air and seawater around India. A study by Babu Rajendran et al., (1999) reported that, higher concentration of HCHs (1.45-35.6 ng/m^3) and DDTs (0.16-5.93 ng/m^3) were detected in the tropical coastal atmosphere from India. Highly populated and agricultural areas along the Indian coastal length were found contaminated with higher levels of OCIs as endorsed by Zhang et al., (2008). Chakraborty et al., (2010) reported that higher concentration of Chlordane, DDTs, HCHs and Endosulfan were detected in the cities of

Mumbai, Bangalore, New Delhi, Kolkata, Chennai and Agra during passive air sampling campaigns. The authors suggested that higher concentrations of γ-HCH were found in Kolkata which indicated widespread use of lindane in India. Devi et al., (2011) reported the seasonal variations and emissions of HCHs and DDTs in various places in India, and the higher concentrations were found in the rural and urban sites during warmer season.

A study by Shailaja and Sen Gupta, (1989) reported that isomers of HCH, aldrin, dieldrin and DDT were detected in water samples collected from different regions of the Indian Ocean, in which total DDT was found to be present in significant level. Moreover, distribution of different chlorinated compounds along the central West Coast of the Arabian Sea reported by Shailaja and Sarkar, (1992) concluded that γ-HCH and the cyclodiene compounds-aldrin and dieldrin were found more consistently in seawater samples than compounds of the DDT family. Contamination by DDT and HCH residues in several rivers of South India was reported by Ramesh et al., (1990a) and Rajendran and Subramanian, (1997). They observed erratic trends in DDT residue concentrations in waters of the river like Vellar, Kaveri and Coleroon and in the Pichavaram mangrove wetland. The authors attributed low residue concentrations in water to high surface water temperatures, which resulted in a high rate of vapourization of pesticides. In southwest coast of India, Sujatha et al., (1994) evaluated the concentration of OCIs in the Cochin backwaters, in which the total DDT concentration was as high as 54.4 µg/l and the predominant metabolite was pp′-DDE. Moreover, the total HCH concentration was as high as 1.1 µg/l in the Cochin Estuary due to premonsoonal accumulation of pesticides (Sujatha et.al., 1993). OCIs show a wide variation in their concentration level in various sampling sites of CES. The riverine nature and acidic pH of the upper estuary combined with the industrial effluents from a pesticide manufacturing plant accounted for the very high concentrations of pesticides. Levels in the mid-estuarine region reflected the prominent influence of agricultural run-off (Sujatha et al., 1993). Furthermore Sujatha et al., (1999) concluded that contamination by Endosulfan isomers varying seasonally, with premonsoon loading always being higher (about two fold greater) than post-monsoon loading, and unnoticeable level throughout the monsoon period. Pandit et al., (2002) reported the elevated concentration of DDT and its metabolite, DDE in the seawater samples from west coast of India. Also, the presence of DDT and HCH isomers can be attributed to the use of these insecticides in agricultural and anti-malaria sanitation activities which have been carried out throughout the country. Recently Dsikowitzky et al., (2014) reported that the highest contamination by HCH isomers, endosulfan, hexachlorobenzene and DDT-metabolites were detected in the water and surface sediment samples collected from the industrial area of CES.

There are only a few studies on the fate and behaviour of OCIs in marine sediments (Sarkar and Sen Gupta, 1985; Sarkar and Sen Gupta, 1986; Shailaja and Sarkar, 1992; Rajendran and Subramanian, 1997; Sarkar et al., 1997; Rajendran and Subramanian, 1999; Senthilkumar et al., 1999; Pandit et al., 2002; Guzzella et al., 2005; Sarkar et al., 2008) from Indian waters. The authors recognise that the stability and fate of the pesticides in sediment samples were influenced by pH, salinity and exchangeable cations. Sarkar and Sen Gupta, (1988a,b) estimated the residues of OCIs in sediments from the Bay of Bengal in the following order: op′-DDE > pp′-DDE> pp′-DDT > op′-DDD > pp′-DDD >op′-DDT. Among the isomers of DDT, both pp′-DDE and op′-DDE, were consistently found high, and explains the degradation of DDT to DDE in the coastal sediments. The unevenness in pesticide residue concentrations was attributed to the presence of numerous rivers along the east coast of India including the Hugli, Mahanadi, Vamsodhara, Godavari, Krishna, Pennar and Palar Rivers. All these rivers transport copious amount of agricultural discharges containing persistent organic pollutants including organochlorine insecticides and dumped into the Bay of Bengal. Sarkar and Sen Gupta, (1991) recorded the residue levels of OCIs in sediment samples off the west coast of India in the Arabian Sea and delineated in the following order: DDT> HCH> aldrin > dieldrin. According to the study by Ramesh et al., (1992) a large amount of technical HCHs were detected in the sediments from western part of Kolkata, along with the high concentrations found in biota. Sarkar et al., (1997) observed the prevalence of ΣDDT and dieldrin in estuarine sediments of the Arabian Sea areas compared to offshore sediments. Their overall assessment revealed that Zuari and Kali estuaries are the most susceptible to DDT as compared to other estuaries. In the east and west coast of India, residues of HCH and DDT metabolites were detected in majority of the surface sediment samples. The predominance of α- and β-HCH reflects the use of technical grade HCH in India Pandit et al., (2001). Moreover, the study infers that significant concentrations of DDE in coastal sediments to the presence of various kinds of marine benthic organisms which accelerate the biodegradation process and the alkaline nature of marine systems which is highly favourable for such types of transformations. In eastern coastal part of India, Guzzella et al., (2005) reported that a wide range of spatial variations of various OCIs in the surface sediments of the Hooghly estuary including Sunderban mangrove wetland, can be supposed to the use of these insecticides in agriculture as well as anti-malaria sanitary activities in these regions. Sarkar et al., (2008) reported that occurrence of organochlorine pesticide residues in core sediments of Sunderban wetland ecosystem. Prevalent nature of DDT and its metabolites were detected in all sediment samples, but the concentration of individual metabolites showed differences, which revealed an irregular pattern, either top to bottom or vice versa, reflecting non-homogenous input of these compounds.

Wide variations of OCI residues have been reported in the zooplankton samples from Indian coastal waters. Kureishy et al., (1978) reported the presence of DDT, HCH along with unidentified compounds in the eastern Arabian Sea. DDD was the major metabolite detected in most of the samples off the Saurashtra Coast, Gujarat in the northern Arabian Sea (Kannan and Sen Gupta, 1987). Toxicity studies on zooplankton (Venugopalan and Rajendran, 1984; Rajendran and Venugopalan, 1988) indicated that DDT was more toxic than either lindane or endosulfan. Moreover, study by Shailaja and Sen Gupta, (1990) confirmed the metabolic activity of DDT in zooplankton.

Bivalves have been widely accepted and used as sentinel organisms to monitor the concentration of pollutants in coastal marine environments. Venugopalan and Rajendran, (1984) detected pesticide residues in three species of molluscs (the oyster *Crassostrea madrasensis* and the clams

Meretrix casta and *Katalysia opima*) collected from Vellar Estuary of South India adjoining the Bay of Bengal. The mean pesticide residues in these three species were 3.4 ng/g ww for DDT, 0.8 ng/g ww for lindane and 0.42 ng/g ww for endosulfan. The authors also studied the toxicity of DDT, lindane and endosulfan using the same three species of molluscs and the order of toxicity was found to be DDD>endosulfan>lindane and the sensitivity of the bivalves was in the order: *C. madrasensis* >*K. opima* >*M. casta*. Ramesh et al., (1990b) measured the concentrations of OCIs residues in green-lipped mussels *Perna viridis L.* (Mollusca: Bivalvia) collected from nine locations along the South Indian Coast, which includes the east and west coasts covering the Bay of Bengal and the Arabian Sea, respectively. Mussels collected from the west coast had higher levels of DDT, suggesting the use of DDT for vector control in urban locales and it eventually dispersed into the aquatic niche. However, in Porto Novo and Pondicherry harbours on the east coast and Suratkal on the west coast, HCH levels were slightly higher than DDT, which is indicative of the use of HCH for agricultural purposes in the nearby areas Ramesh et al., (1990b). However, an overall uniform concentration of pesticide residues was observed in the bivalves from Indian coastal waters.

Fish have been selected for environmental pollution monitoring studies because they concentrate pollutants in their tissues directly from water and through diet enabling the assessment and transfer of pollutants through the pelagic food web (Bruggeman, 1982). A study by Venugopalan and Rajendran, (1984) revealed that there was no significant variation in the concentration of OCIs among fish species collected from Vellar Estuary.

Shailaja and Sen Gupta, (1989) measured HCHs and DDTs in various fish species collected from different regions of the seas around peninsular India. However, the concentration of the isomers of HCHs was too low to be quantified. Shailaja and Nair, (1997) established that the liver generally accounted for the highest level of total DDT, followed by the gills among the different fish tissues. Pandit et al., (2001) studied accumulation of OCIs in the muscle tissues of different fin fishes and shell fish (prawn) from Alibagh and Mumbai, west coast of India. They observed predominance of α- and γ-HCH which reflected the use of technical grade HCH in India. A high concentration of HCH in biota was also reported near the industrialized cities such as Mumbai (Monirith et al., 2003). The data on the distribution of OCIs in fishes is important not only for ecological reasons, but also because of their impact on human health.

Despite being banned, OCI concentrations remain higher in the environment due to illegal use, re-emission from soils and glaciers, terrestrial runoff and atmospheric deposition. A regular monitoring, assessment and reporting machineries should be implemented in accordance with appropriate environmental policies, laws and regulations. The Government and other related agencies should educate farmers and agriculture managers on Good Agricultural Practices (GAP). Furthermore, national and international monitoring programs helped to understand the relationship between the over use of chemicals in the environment.

1.5 Aim and Scope of the Study

Cochin Estuary, one of the largest tropical estuaries of India is facing gross pollution problems following the release of untreated effluents from industries and domestic sectors. The developmental activities in and around the estuarine system have added to the complexities and environmental dilemmas in this coastal niche. For a long period, there were no pollution control regulations and the untreated effluents including those from heavily polluting industries were being discharged into the aquatic niche. As a result of careless disposal practices, they have become major pollutant in many areas of CES. Thus understanding the transport, distribution and characterization of Persistent Organic Pollutants (POPs) in the sediments of the estuaries is a challenging area of research for environmental chemists, because of their resistance to degradation has resulted the presence globally as contaminants in the environment. The increasing importance assigned to pesticide compounds like organochlorins and the tendency to deal with them as a generic group in regulatory actions, is imperative that the nature and profile of their distribution be assessed quantitatively and rigorously. A greater tendency shown by OCIs for bioaccumulation and biomagnifications in the food chains is due to their resistance to chemical and biological decay. In the absence of any authentic reports on the status of contamination by these toxicants in the sediments of this estuary, there exists a lot of uncertainty about even the orders of magnitude in which these substances present in the aquatic niche. This investigation will provide the baseline data on these xenobiotics being freely used in this part of the Indian sub-continent. Most of the earlier research contributions were based on one-time or seasonal sampling during a year, from the areas known for environmental pollution. An approach based on the analysis of OCI residues in sediments collected over a considerable time period can provide a clue for a change in environment and such studies are limited. The findings of this research work constitute the first judicious base line data set for the OCI residues in the sediments of CES.

The objectives of the present study are:

- To investigate the spatial and temporal variability of
  a) Biogeoorganic constituents &
  b) Organochlorine Insecticides (OCIs) in the surface sediments of CES.
- To assess the Biogeochemical parameters in the core sediments of CES
- To evaluate the distribution pattern of OCIs in specific core sediments of the aquatic system.

In order to fulfil these objectives, the research was carried out by adopting suitable scientific approaches and methodologies are well presented in the 2nd Chapter.

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2

MATERIALS AND METHODS

2.1 Description of the Study Area

Cochin Estuary, one of the largest tropical estuary in India is facing gross pollution problems followed by the release of untreated effluents from industries and domestic sectors. The major polluting industries in the region include fertilizer plant, oil refinery, rare earth processing plant, minerals and rutiles plant, zinc smelter plant, insecticide manufacturing unit and organic chemical plant. These industries take large amounts of freshwater from the river Periyar and in turn discharge 260 million liters of effluents daily into the aquatic niche (CPCB, 1996; KPCB, 2000) as depicted in Table 2.1. The estuary receives untreated effluents (104 billion liters per day) from domestic sectors (CPCB, 1996). In addition, wastes from aquaculture fields (62 Km^2), agricultural fields (80 Km^2), coconut husk retting yards, fish processing plants, and animal bone processing units have increased the organic pollution in the estuary (Thomson, 2002). The magnitude of siltation in the Cochin estuary is reflected in the removal of silt by dredging every year in order to maintain the shipping channel at Cochin harbour. The average amount of dredged materials removed from the Mattanchery and Ernakulam channels comes up to 3.61x10^6 m^3 (Rasheed 1997). Sediment accumulation rate in the estuarine and mangrove areas of the Cochin Backwater is 3-6 times higher than that in the adjacent inner-shelf area (Manjunatha et al., 1998). As estuaries are geochemical barriers regulating the export of materials, emerging metropolises like Cochin necessitates information on the fate of contaminants in the coastal environment. The booming city of Cochin has population of nearly 1.5 million (Anonymous, 1998) and 60 % of the chemical industries of Kerala are situated in this area. The anthropogenic influence in the estuary began in the second part of 19th century (Gopalan et al., 1983).

Further, the construction of hydraulic barriers on the northern and southern limbs of the estuary to prevent saline intrusion into the upstream agricultural fields has imposed severe flow restrictions and increased sedimentation in the estuary (Menon et al., 2000). The development activities in and around Cochin Backwater System have added to the complexities and environmental dilemmas in this coastal niche.

According to the topographical, hydrological and ecological features of the estuary study area is divided into three zones viz South, Middle, and North (Figure 2.1& 2. 2) and Table 2.2.

South Zone: The zone situated in the fresh water region, originates from southern branch of Moovattupuzha. Major source of pollution is from agriculture runoff. Six surface sediment samples (Station No:1-6) and two sediment cores (S_1 and S_2) were taken from this zone which is far from Industrial effluents.

Middle Zone: This zone has a perennial connection with the Arabian Sea and experiences an irregular encroachment of saline water intrusion there by making cradle grounds for diverse types of flora and fauna. With the advent of International Container Transshipment Terminal (ICTT) project, this area has become a backbone for the economy of State of Kerala. Due to enhanced containerization, resulting in improved trade and economic growth, widespread activities like dredging, piling, along with anthropogenic inputs are increasing frequently. Moreover, this zone is well regulated by a bund (namely Thannirmukham), which was constructed in order to prevent the salt water intrusion into the paddy fields. The bund remains open during monsoon season. Five surface sediment samples (Station No:7 -11) and two sediment cores (M_1 and M_2) were taken from this zone.

North Zone: This zone originates from the industrial locale of Periyar - the life line of Kerala. Large scale industries on the river bank discharge effluents directly into these waterways resulting in the accumulation of varying amounts of nutrients in the Periyar River. Six surface sediment samples (Station No: 12 -17) and two sediment cores (N_1 and N_2) were taken from this zone.

Table 2.1 Major Industries and their effluent discharge to Cochin Estuary

No.	Industry	Products	Production (Tones/Month)	Effluent Discharge (m3/day)	Major Pollutants
1	Hindustan Insecticides Ltd	DDT	336	1000	Insecticides
		HCH	500		
		Endosulfan	—		
		Mancozeb	—		
		Hydrochloric Acid	140		
		Sulphuric Acid	100		
2	FACT	Ammonium Chloride	2250	25400	Free Ammonia Phosphate Suspended Solids
		Ammonium Sulphate	18000		
		Ammonium Phosphate	16500		
		Ammonia	10200		
		Phosphoric Acid	3750		
3	FACT Pertochemical	Caprolactum	—	5040	—
		Nitric Acid			
		Soda Ash			
4	Travancore Cochin Chemicals	Caustic Soda	2775	6680	Free Chloride Suspended solids
		Liquid Chlorine	2487		
		Hydrochloric Acid			
		Sodium Sulphate	54		
5	Binai Zinc Ltd	Zinc Slabs	1400	550	Zinc and Lead
		Cadmium	3		
6	Periyar Chemicals Ltd	Formic Acid	85	330	—
		Sodium Formate	165		
7	Travancore Chemicals Manufacturing Co.Ltd	Copper Sulphate	250	720	—
		Copper oxy chloride	75		
		Sodium Aluminate	85		
		Sulphate of Alumina	100		

Figure 2.1 Map of the study area and surface sediment sampling sites

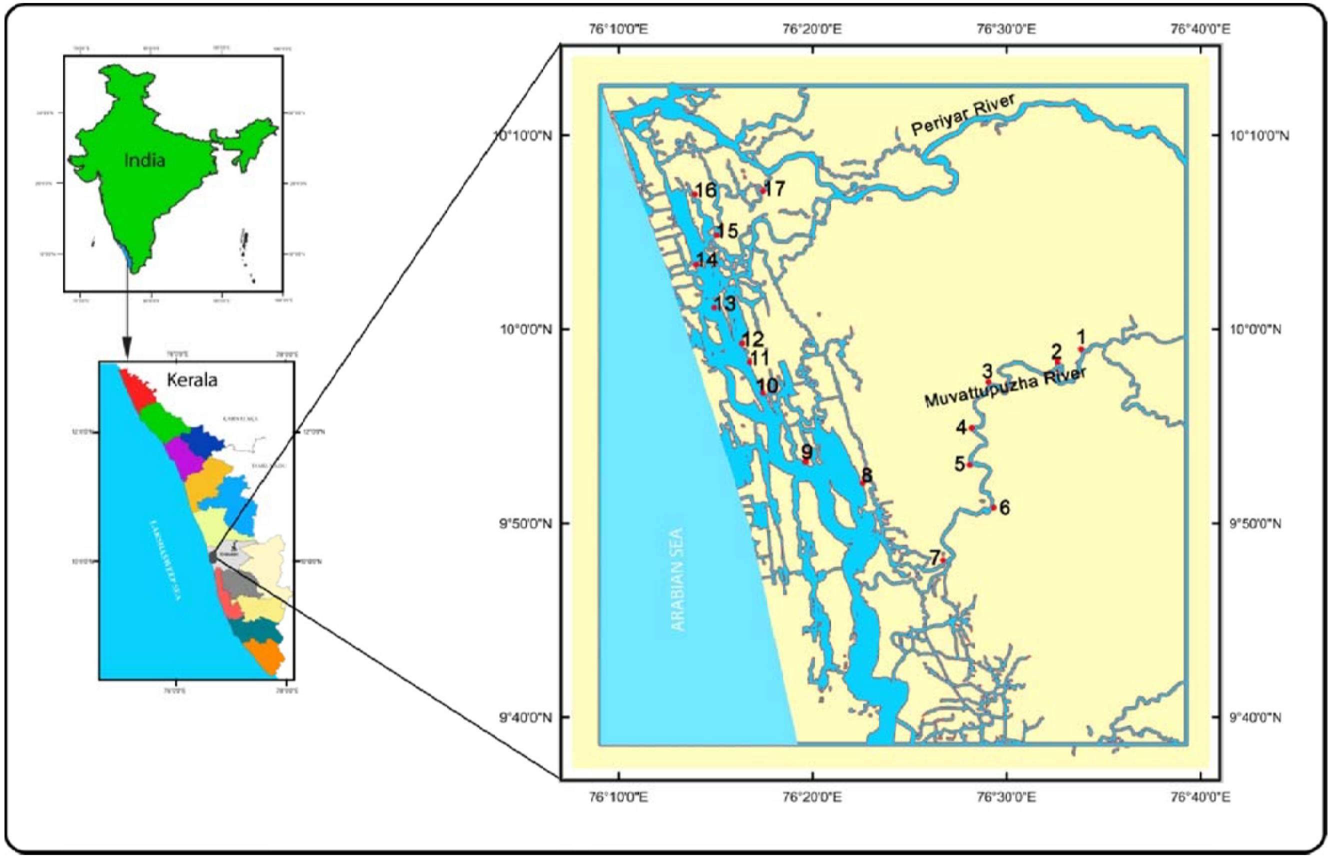

Figure 2.2 Map of the study area and core sediment sampling sites

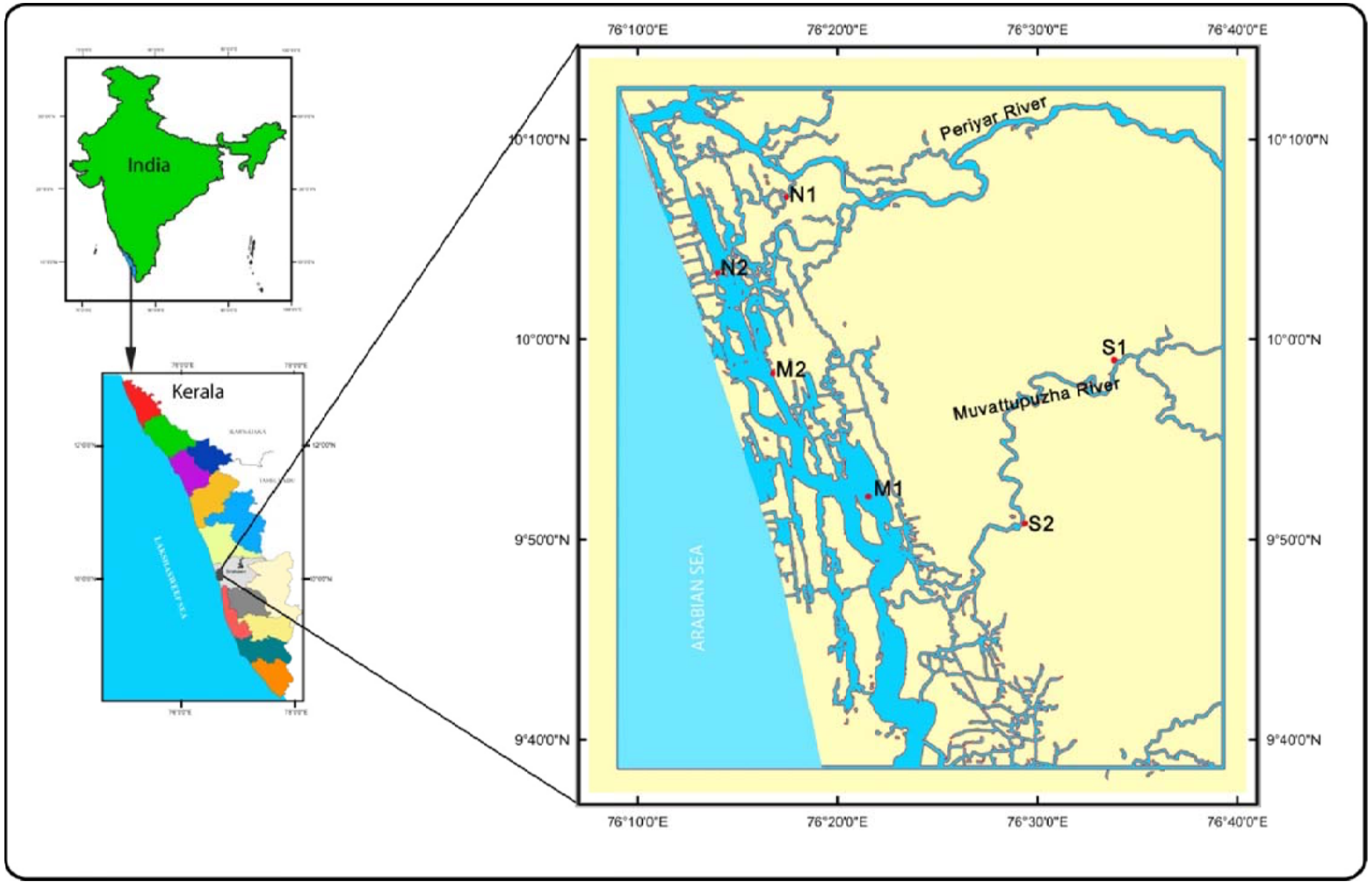

Table 2.2 Core Sediment Sampling Strategy

	Stations	Year of sampling	No. of sediment cores collected	Length of the core (cm)	Total no. of sediment cores
South Zone	S1	2009	One	45	2
		2011	One	45	
	S2	2009	One	30	2
		2011	One	51	
Middle Zone	M1	2009	One	55	2
		2011	One	57	
	M2	2009	One	63	2
		2011	One	51	
North Zone	N1	2009	One	29	2
		2011	One	42	
	N2	2009	One	63	2
		2011	One	54	

2.2 Sampling

Surface sediments (top 0-5 cm) were collected from seventeen locations of CES during November 2009 and November 2011 (post monsoon season). This was performed using a stainless steel grab sampler used repeatedly (three to five times) at each station, followed by thorough mixing of collected sediment on an aluminium tray in order to obtain a more representative sediment sample. Besides, two sediment cores each from three zones of CES were collected by pushing a hand held PVC core (150 cm long with a diameter of 6.3 cm) by the help of a skin diver, in varying depths (1-3.50 m) of the water body. All samples were kept in ice chest boxes on board and during transportation. All visible marine organisms, coarse shell fragments, and sea grass leaves and roots, when present, were removed manually with the help of stainless-steel forceps. In the laboratory, the cores were sectioned at 1 cm intervals, immediately measured for pH (Thermo Orion 420A+ model) and Eh (Portable ORP meter) then they were frozen at 4°C for further analysis. According to the study, sub samples were pooled into 3-5 cm intervals. Freeze dried samples were disaggregated and divided into two aliquots. One aliquot was used for measuring the sedimentary parameters (TOC, OM, Pigments) and the other part was sieved through a 250 µm sieve and stored at -20 °C for OCI analysis.

2.3 Analytical Methodology

2.3.1 General Sedimentary Parameters

Textural characteristics (sand, silt, and clay) and quantification of OM (Protein, Lipid and Carbohydrate) were carried out by standard procedure. Texture was determined using pipette analysis (Lewis, 1984). Total Organic Carbon (TOC) was processed by treating the samples with 1M HCl to remove the carbonates and repeated two/three times in order to ensure the complete exclusion of carbonates. Samples were washed with Milli-Q water to remove salts and finally freeze dried. Organic carbon was determined using Total Organic Carbon (TOC) analyzer (Elementar Vario Select, Germany). Samples were run with blank cups in order to correct the carbon associated with the tin cups. Standard sediment supplied by Elementar Vario Select, Germany, were used for calibration in the TOC analyzer. The detection limit for OC is 0.06%. Total Proteins were determined using the method of Lowry et al., (1951). Carbohydrate estimation was done by Phenol- Sulphuric acid method (Dubois et al., 1956). Tannin and lignin were batch-extracted from the sediments with

0.05M NaOH solution for 90 minutes and filtered. To 5 ml aliquots of filtrates, 1ml of citrate solution was added followed by 1ml folin reagent and 10 ml carbonate tartarate reagent and kept it for 30 minutes. The optical density was measured at 765 nm (APHA, 1995; Jose et al., 2008). Total lipid was estimated by the Sulphophosphovanillin method (Barnes and Black stock, 1973). All the analysis was carried out in triplicate and the average was reported. Protein, carbohydrate and lipid concentrations were converted to carbon equivalents by using the following conversion factors: 0.49, 0.40 and 0.75 g of C/g respectively (Fabiano and Danovaro, 1994). The sum total of protein, carbohydrate and lipid carbon were referred to as biopolymeric carbon (BPC) (Fichez, 1991; Fabiano et al., 1995) and the study accounted accordingly. Sediment samples for the pigment analysis were immediately collected in 15 cm plastic vials for preservation by direct freeze drying. For the analysis of the sedimentary chlorophyll and their degradation products, 0.5-1 g of freeze dried sample was added to the glass centrifuge tube with 90% acetone and the mixture was sonicated at 5 atm for 30 sec to disrupt the cells and kept in dark at 4°C for nearly 5 hrs in order to ensure the complete extraction of the pigment. The mixture was then centrifuged at 3000 rpm to separate the pigment solvent complex from the remaining sediment. This process was repeated until the colour of the extract was clear. The supernatant liquid was then transferred to UV spectrometer (GENESYS 10 UV Thermo spectra) for further analysis. The concentrations of chlorophyll, pheophytin and carotenoid pigments were measured by the spectrophotometric method (Parsons et al., 1984; APHA, 1995; Aneesh Kumar, 2009). Elemental compositions, CHNS of the samples were determined using Vario EL 111 CHNS Analyzer.

2.3.2 Trace Organic Contaminants

About 5 to 10 g of the sediment samples were accurately weighed and then extracted twice with 50 mL portions of 1:1 hexane-acetone mixture (HPLC grade, Glaxo, Mumbai, India). Activated copper granules were added to each collection flask in order to remove potential elemental sulphur (Sarkar et al., 1997; Lino et al., 2007). The extract was subjected to a cleanup procedure involving elution through a Florisil column (60 cm × 22 mm i.d) with 50 mL 1:1 hexane-acetone mixture and the aliquots were fractionated by elution through silica column (250 mm × 10 mm i.d) to separate PCBs from the polar OCIs (EPA Method 3630C and 8081A). The extract was concentrated to about 5–6 mL by means of a rotary evaporator at 50–60°C for further analysis. Separation and analysis of the OCIs were performed on a gas chromatograph (GC) (model 7890A, Agilent, Waldbronn, Germany) with a Ni-63 ECD and equipped with capillary column (HP-35, 30m × 0.320mm ×0.5 mm) using nitrogen as carrier gas (1.5 mLmin^{-1}). The GC was calibrated with a standard solution of a pesticide mixture (Supelco, USA) prepared in HPLC grade n-hexane. Solvent blanks were used to confirm the absence of any pesticide residues. Analytical reproducibility was checked by replicate measurements. Also, the quality of the analytical data of OCIs was assured using the certified reference material (CRM) 804-050 soils (Sigma-Aldrich). Identification and quantification of OCIs were accomplished by using reference solutions supplied by EPA (USA) and Supelco (USA). 1 µL of aliquot samples were injected onto the column. The following GC conditions are maintained: injection port temperature 250 $^{\circ}$C, detector temperature 350°C, oven temperature program: 110° C (5 min) at 5°C min^{-1} to 190 $^{\circ}$C (2 min) at 15 $^{\circ}$C min $^{-1}$ to 280 $^{\circ}$C (10 min).

2.3.3 Analytical Quality Controls

All data were subjected to strict quality control procedures, including the analysis of procedural blanks and spiked samples with each set of samples analyzed. None of the target compounds were detected in the procedural blanks for sediment samples. Spiked samples (10 ng of pesticide mix standard) were determined with good precision and high recoveries. Limit of detection (LOD) and relative standard deviation (RSD) of the analytical method for OCIs is as follows. The instrumental detection limit values were calculated from the lowest standards, extrapolating to the corresponding amount of analytes that generate a signal-to-noise ratio of 3:1. The detection limit was lowest for aldrin (0.04 ng/g) and highest for endrin and 4,4’-DDT (0.19 ng/g), while the detection limit of other analytes lies within the range. The average recoveries (n=3) for OCIs in the sediments were revealed an efficiency of 87–103%. Moreover, the recoveries of the analysed concentrations of OCIs in CRM samples were from 75-107%, showing that the analytical protocols used in this study can effectively determine OCI residues in sediments. Table 2.3 illustrates the recoveries and detection limits (DLs) of OCIs in sediments. The relative standard deviations (RSD) were below 5.0% and fall within the requirement criteria of US-EPA (Recovery: 70–130%, RSD is <30%). The residue levels of OCIs were quantitatively determined by the external standard method using peak height and the calibration curves of the standards. For every set of 10 samples, a procedural blank and spike samples consisting of all reagents was run for to check the interference and cross contamination. Moreover, peak identification was conducted by the accurate retention time of each standard (± 1%) and selected samples were analyzed by GC-MS (Agilent 6890N-5975) for confirmation. The mass spectrometer was operated in positive ion electron impact energy of 70 ev and an emission current 60 µA. Full scan data were obtained with a mass range of m/z 40-450. Scanning interval and selected ion monitoring (SIM) sampling rate were kept at 0.5 and 0.2 sec, respectively. The following organochlorine insecticides were quantified: α-hexachlorocyclohexane (α-HCH), β-HCH, γ-HCH, heptachlor, heptachlor epoxide (B), aldrin, dieldrin, endrin, 4,4’-DDE, 2,4’-DDD, 4,4’-DDD, 2,4’-DDT, 4,4’-DDT, α-endosulfan, and β-endosulfan.

Table 2.3 The recoveries, detection limits (DLs), and the analyzed results of CRM standards (804-050) of OCls in sediments.

Insecticides	Recovery (%)	DL (ng/g)	CRM standard (mg/Kg)	
			Certified value	Analyzed value
α-HCH	90 ± 3	0.10	-*	-
β-HCH	87 ± 4	0.13	-	-
γ-HCH	88 ± 3	0.09	491.6	526.1
Heptachlor	89 ± 5	0.18	-	-
Heptachlor epoxide (B)	90 ± 3	0.18	-	-
4,4’-DDE	88 ± 2	0.06	1519.6	1246
Dieldrin	88 ± 4	0.06	1862.5	1508.7
Aldrin	90 ± 5	0.04	18.04	19.1
Endrin	103 ± 4	0.19	62.2	68.3
2,4’DDD	92 ± 3	0.18	-	-
4,4’DDD	91 ± 5	0.16	1530.6	1193.9
2,4’-DDT	90 ± 2	0.15	-	-
4,4’DDT	87 ± 4	0.19	1060.1	795.1
α-Endosulfan	89 ± 5	0.18	1464.3	1142.2
β-Endosulfan	90 ± 5	0.13	1128.2	1028.8

* Not available

2.3.4 Statistical Techniques

All data were subjected to statistical analysis wherever necessary. Pearson correlation was employed to find out the inter relationship between different parameters. The principal Component Analysis (PCA) method, which enables a reduction in data and description of a given multidimensional system by means of small number of new variables, has been applied to the data. The data processing was carried out using the software Statistica 6.0.

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3

BIOGEOORGANICS IN THE SEDIMENTARY ENVIRONMENT

3.1 Introduction

Estuaries are commonly described as semi-enclosed bodies of water, situated at the interface between land and ocean, where seawater is measurably diluted by the inflow of freshwater (Hobbie, 2000). These dynamic ecosystems have the highest biotic diversity and production in the world. Previous estimates indicate that about 61% of the world population lives along the coastal margin (Alongi, 1998). Improper land use, urbanization, industrial and harbour activities among others, generally intensify the eutrophication process through the introduction of several classes of organic and inorganic compounds. Impacts of demographic changes in human populations have clearly had detrimental effects on the overall biogeochemical cycling in the estuaries. Nutrient enrichment is perhaps the most widespread problem in estuaries around the world (Howarth et al., 2000, 2002).

The biogeochemical and physical processes play an important role in regulating the chemistry and biology of estuaries which are fundamental to evaluate the complex management issues (Hedges and Keil, 1995; Middelburg et al., 1996; Bianchi et al., 1999; Hobbie, 2000). Biogeochemical cycles involve the interaction of biological, chemical as well as geological processes that determine sources, sinks, and fluxes of elements through different reservoirs within the ecosystems. Consequently marine sediments represent the largest reservoir of organic carbon on earth and act as an important contributing factor in climate change. The major part of organic carbon is generated by the photosynthetic fixation of inorganic carbon from atmospheric CO_2 by terrestrial plants and marine phytoplankton (Sarmiento and Gruber, 2002). Accumulation of organic matter in recent and ancient sediments is the most important link between the biosphere and geology. Most of the organic matter sequestered in marine sediments is ultimately derived from organic matter synthesized by marine organisms inhabiting the surface waters of the oceans and transported to the seafloor. However, only a small fraction of the sinking organic matter survives transport to the seafloor to be preserved in the sediments (Sarmiento and Gruber, 2002). In general, the preservation of organic materials depends on the interaction between the oxygen content of a system and the type of organic matter deposited within it. In the presence of oxygen, organic matter can be remineralized or converted to CO_2. However, if this material is protected in some manner or is deposited in a suboxic or anoxic environment, it is likely to be preserved. Preservation is also enhanced in sediments underlying highly productive surface waters. In these environments, production of organic matter is much greater than its oxic degradation, so that much more organic matter reaches the sediments and is preserved. Despite differences in OC concentration and key variables that influence organic matter preservation, a common mechanism appears to control organic matter preservation in these environments. More than 90% of the sedimentary OC from marine environments cannot be physically removed from its mineral matrix (Hedges and Keil, 1995). Consequently, organic matter must be sorbed to mineral surfaces. The concentration of sorbed organic matter varies with mineral surface area, such that more OC is associated with sediments that have highly irregular surfaces with small pores (Mayer, 1994). Sorption of organic matter forms protective coatings that typically approach a single molecule-thick covering (often expressed as a monolayer equivalent, 0.5–1.0 mg OC m^{-2}; Hedges and Keil, 1995). These coatings contain both *refractory* (not easily degraded) and *labile* (easily degraded) organic matter that is preserved in the underlying anoxic sediments, because it is protected from mineralization during transport through the water column and oxygenated surface sediments. Formation of monolayer equivalents of organic matter on marine sediments implies that, at one time, the organic matter was in the dissolved phase, because it is unlikely that particulate organic matter would spread uniformly over mineral surfaces.

Thus the study on sediment biogeochemistry is being considered as record of impact, relying on the time integrative capacity of the sediment in the aquatic system (as long as erosion and resuspension processes can be ruled out). The sediments themselves are also the storage of the contaminants that can directly impact on the benthic ecosystem. Some contaminants, such as radionuclides and certain trace organic compounds (OCIs, PCBs, and PAHs etc) have both a geochemical and environmental half-life from which can predict their persistence in the estuarine environment. Further, using a range of trace contaminants provides an important and verifiable approach to ecosystem health assessment. In short, there are too many avenues of decay to be able to sort out the meanings effectively. Therefore their origin and fate in ecosystems cannot be understood without a fair knowledge on biogeochemical cycles. There are many more questions that organic geochemists try to answer, not only in the petroleum and paleoclimatic fields but also from the modern environmental/ contamination point of view. Therefore, the present chapter intend to explain a brief explanation with how the biogeochemical studies of surface and sediment core profiles helps to describe the encapsulated various types and biogenic compounds; and also provide useful information on the changes in the quality of the sediments from the past period.

3.2 Results and Discussion

3.2.1 Spatial Physicochemical and Sedimentary Characteristics

General hydrographical characteristics of overlying water and sedimentary parameters were studied by means of standard procedures. During the first sampling campaign (2009) the pH values ranges from 6.70

to 8.40 and the highest value was noted at middle zone. Concentration of dissolved oxygen varied from 2.24 mg/L (Station No.5) and maximum at Station No.16 (7.02 mg/L) and the highest concentration was noted at north zone followed by south zone. Salinity showed wide variation from 0.24 PSU (Station No.2) and 33.75 PSU (Station No.11) and the highest value was noted at middle zone. In general, all the hydrographical parameters were found to exhibit with minor fluctuations during second sampling period (2011).

General sedimentary parameters showed that pH values varied from 5.4 to 8.7 and the highest value was noted at middle zone during 2009 and it was found to exhibit minor fluctuation during 2011 sampling period. Eh value ranged between -109 mV to +274 mV, indicating the periodic anoxic/oxic nature of the sediments and it was prevailed during 2011. Texture analysis showed a progressive increase with fine fractions at southern (96%) and northern part (80%) of the estuary during 2009, and it was found a mixed nature of clayey- sand during 2011. Percentage of TOC ranged from 0.34 to 6.25 during both sampling periods and it was significantly higher at southern and northern part of the estuary (Figure 3.1). This could be attributed to the enhanced adsorption of organic carbon onto the clay minerals in the low salinity regimes (Borsheim et al., 1999; Burdige et al., 2000). Brief descriptions of sedimentary parameters are given in Table 3.1.

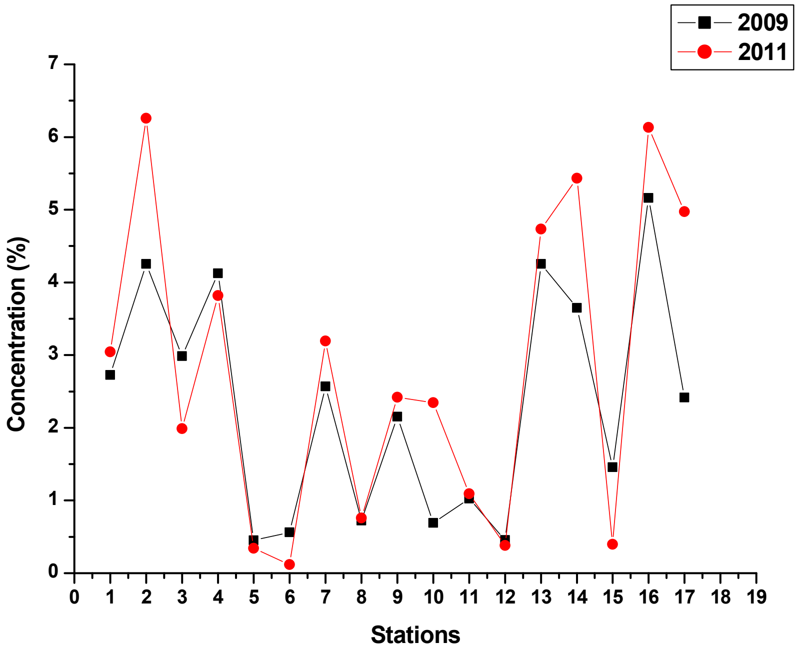

Figure 3.1 Spatial variation of TOC (%) in the surface sediments of CES during both sampling period.

Table 3.1 Descriptions of Spatial Sedimentary Parameters.

Station No.	Eh (mV)		pH		Sand(%)		Clay(%)		Silt(%)	
	2009	2011	2009	2011	2009	2011	2009	2011	2009	2011
1	+28	+117	6.2	5.9	9.28	20.55	79.32	72.33	11.4	7.12
2	+16	+12	7.9	7.4	4.75	79.5	82.64	19.08	12.61	1.42
3	+218	+76	6.9	6.2	7.47	2.8	68.32	90.4	24.21	6.79
4	+118	+162	7.2	7.4	5.81	32.87	73.85	53.69	20.34	13.43
5	-12	+98	8.1	8.2	2.53	80.01	90.11	19.85	7.36	0.14
6	+218	-12	7.8	7.8	1.08	87.61	95.91	11.51	3.01	0.89
7	+21	+84	5.9	5.1	90.11	37.47	3.98	62.06	5.91	0.48
8	-109	-96	6.1	8.4	89.81	15.88	1.83	25.18	8.36	58.94
9	-102	-107	8.7	7.9	87.73	94.56	1	5.2	11.27	0.24
10	-106	-12	6.9	7.4	86.71	7.08	4.81	79.33	8.48	13.59
11	-98	-74	7.1	6.4	91.82	13	5.72	61.17	2.46	25.83
12	-86	-89	8.1	7.6	17.61	93.2	58.81	6.76	23.58	0.04
13	+216	+114	6.2	6	10.21	85.55	65.32	11.07	24.47	3.39
14	+126	+208	7.1	6.4	15.32	11.58	63.48	49.07	21.2	39.34
15	+110	+124	6.2	5.7	16.81	44.77	62.83	35.41	20.36	19.82
16	+274	+286	5.4	6.1	6.86	5.47	75.31	39.01	17.83	55.52
17	+184	+207	5.8	5.4	5.72	30.29	79.81	48.47	14.47	21.24

3.2.2 Spatial Biogeochemical Characteristics

Amongst the labile fraction of organic matter (LOM), protein ranged from 0.13 to 5.7 mg/g (2009) and 0.15 to 8.39 mg/g (2011) and exhibited slightly highest concentration at southern and northern zone of the estuary during both the sampling periods, the reason could be owing to the accumulation of plant material into the clay minerals of sediments where they were particularly resistant to chemical and biological breakdown. Further, a number of fish peeling and processing units are housed on the banks of the estuary and the wastes from these units undergo decomposition and liberate proteins, which are adsorbed /settled into the sediments. Apart from this, the wastes from the 'Modern food industries' also drains into the estuary, results slightly highest concentration of protein in this region. A decrease in the concentration of protein at middle zone may be due to the preferential utilisation of protein by the benthic organisms and biological activity or may be the nitrogen compounds incorporated into humic matter through various humification pathways (Bhosle and Dhople, 1988).

Lipid in the surfacial sediments is probably part of a common pool of OM in which in most cases, is cycled by microorganisms at a speedy level relative to the rate of burial. They are widely distributed in the sediments and its abundance depends on the environmental conditions such as production, anthropogenic inputs etc. Concentrations of lipid ranged from 0.35 to 4.30 mg/g (2009) and 0.62 to 7.34 mg/g (2011) and were significantly higher in northern part of the estuary during 2011 sampling period, might be due to the influence exerted on the composition of organic matter by the bottom fauna which was capable of resynthesising of lipid from organic matter during the course of their vital activity. However, biochemical and chemical alteration of lipid appears immediately. Proliferation of minerals might also influence the degradation of lipids into other compounds and the decreased concentration of lipid observed at middle zone of the study area indicated their availability for biological utilization as high energy rich compounds.

Carbohydrates are the most abundant class of compounds produced in the biosphere. Generally they are linked together into polymers, and there are several important polymeric sugars that decompose and enter into the aquatic system. Concentration of total carbohydrate varied from 1.11 to 6.67 mg/g (2009) and 1.88 to 10.88 mg/g (2011) and like other labile fractions, its level was enriched in southern and northern part of the estuary. Occurrence of carbohydrate concentrations in these regions could be attributed to the anthropogenic input and the death and decay of aquatic organisms including the floating plants.

Tannin and Lignin (collectively referred to as hydroxylated aromatic compounds) are high molecular weight polycyclic aromatic compounds, widely distributed throughout the plant kingdom and its concentration varied from 0.05 to 1.73 mg/g and slightly higher at southern and northern part of the estuary during 2009, but its level was diminished during 2011. The increased hydroxylated aromatic compounds concentrations observed at these zones could therefore be attributed to the influence of the effluents and to the gravitational settling of the organics found in this region. The lower level of tannin and lignin noticed in the middle zone of the estuary was the consequence of the increased particle size which decreased the adsorption / incorporation of organics. The spatial sedimentary OM was in the order CHO>PRT>LPD>TIN and it was shown in the Figure 3.2 and the Table 3.2 depict the comparison of bulk sedimentary parameters in the surface sediments from different study regions.

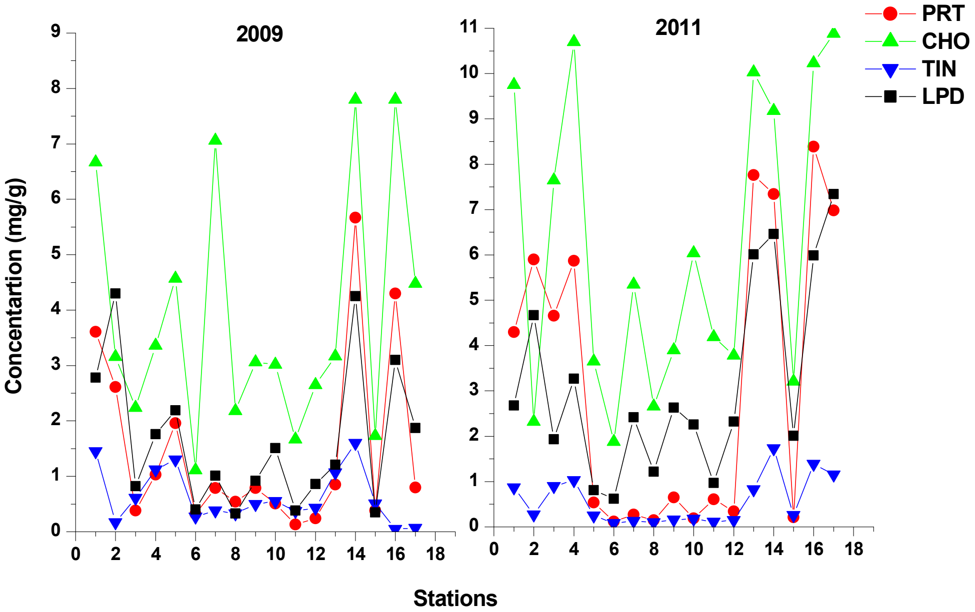

Figure 3.2 . Distribution profile of organic matters (mg/g) in the surface sediments of CES

Table 3.2. Comparison of bulk sedimentary parameters from different study regions

Study Region	LPD	PRT	CHO	Pigments	Reference
Cochin Estuary	0.0310.14 mg/g	0.034-6.09 mg/g	0.33-22.86 mg/g	chl a: BDL*-119.54 µg/g; pheo: 8.9811.19µg/g	Vasudevan Nayar, 1992
Tyrrhenian Sea	2.92-12.6 µg/g	0.25-1.67 µg/g	0.35-1.89 µg/g	chl a: 0.09-1.50 µg/g; pheo: 0.03-1.90 µg/g	Fabiano and Danovaro ,1994
Lower St. Lawrence estuary	820-1470 mg/Kg	110-400 mg/Kg	7580-10700 mg/Kg	NA*	Colombo et al., 1996
Yangtze estuary, China	NA	NA	NA	chl a : 0.05 to 8.01 mg/g	Liu et al., 2006
Mundaka estuary	300-5000 mg/Kg	BDL- 16700 mg/Kg	200- 5700 mg/Kg	NA	Cotano and Villate, 2006
Cochin Estuary	312-2815 mg/Kg	205-1924 mg/Kg	250- 1229 mg/Kg	NA	Joseph et al., 2008
Rio de la Plata estuary	0.50- 8.35 mg/g	1.08-16.37 mg/g	0.29-8.86 mg/g	chl a: 0.1-11.6 mg/g; pheo: 1.7-35 mg/g	Natalia Venturini et al., 2012
Cochin Estuary	41.50- 3160 mg/Kg	24.48- 2600 mg/Kg	166-6339 mg/Kg	chl a: 0.22-37.80 mg/Kg; chl b: BDL- 16.71 mg/Kg; chl c: BDL- 8.97 mg/Kg; pheo: 0.36-64.52 mg/Kg	Renjith et al., 2013
East coast of India	NA	NA	2.8-4.71 mg/g	NA	Kumar et al., 2013
South eastern Arabian sea	0.9-5.1 mg/g	0.1- 7.3 mg/g	0.4-3.5 mg/g	NA	Remya et al., 2013
Cochin Estuary (2009 & 2011)	0.35-4.30 mg/g & 0.62-7.34 mg/g	0.13-5.7 mg/g & 0.15-8.39 mg/g	1.11-6.67 mg/g & 1.88-10.88 mg/g	chl a: 0.4-20.6 mg/Kg; chl b: 0.1-13.4 mg/Kg; chl c: 1.2-11.8 mg/Kg; pheo: 3.7-60.6 mg/Kg; Carot: 1.38-36.25 mg/Kg & chl a: 2-40.1 mg/Kg; chl b: 0.1- 13.4 mg/Kg chl c: 1.2-11.8 mg/Kg; pheo: 3.7-60.6 mg/Kg carot: 1.38-36.25 mg/Kg	Present Study

*BDL: Below Detection Limit; NA: Not Available

The abundance and ratios of biologically important elements in the biogeochemical cycles provide fundamental information on OM sources and cycling in estuaries. In the present study, biochemical composition of sedimentary organic matter revealed that the dominance of carbohydrate and low PRT/CHO (Figure 3.3) establish the detritus heterotrophic nature of the aquatic niche except at Station No. 2 . Lipid to carbohydrate ratio (LPD: CHO) ranges from 0.15 to 1.36 (2009) and 0.22 to 2.01 (2011). The lower LPD/CHO ratio in the study zones (Figure 3.3) in turn reflects the presence of lower nutritive quality of the organic contents during both sampling periods.

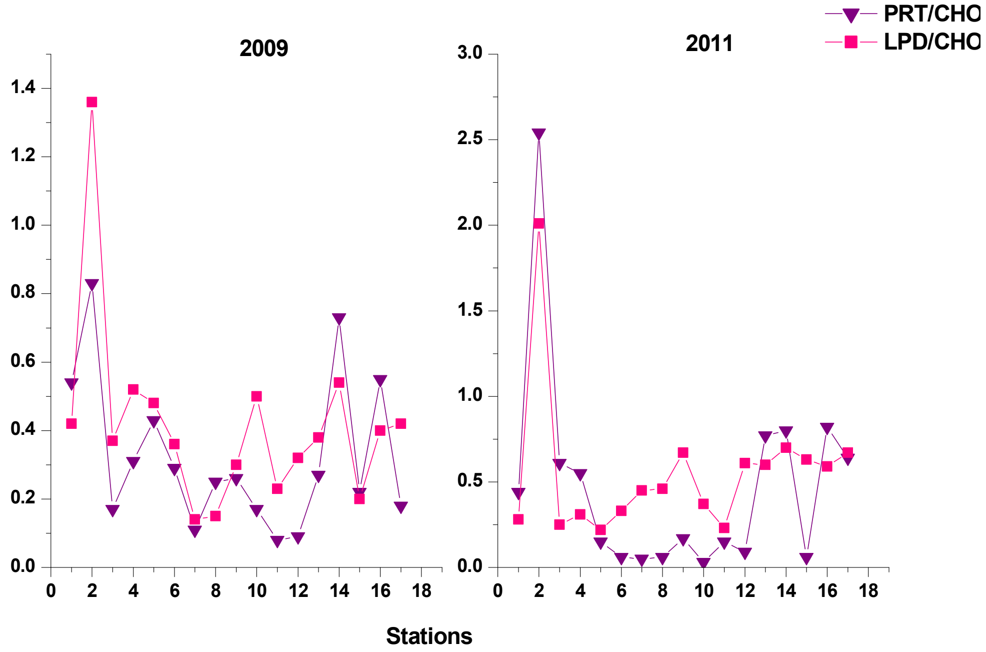

Figure 3.3 Ratios of PRT:CHO and LPD:CHO in the surface sediments of CES.

The amount of metabolizable organic matter available to support sulphate reducing bacteria increases with the total amount of organic matter arriving at the sediment water interface. As a consequence, the sedimentary pyrite sulphide content is positively correlated with the non metabolized (resistant or unused) organic matter content (TOC). Therefore, the ratio of total organic carbon to total sulphur (TOC:TS) in sediments will provide the nature of sediment in the aquatic environment. Under anoxic conditions, dissolved sulfate is reduced to hydrogen sulfide gas, which reacts with iron minerals to form iron sulfides and resulted a qualitative redox status of the environment under deposition. TOC/TS ratio >5 are considered as oxic sediment with oxygenated bottom water, TOC/TS=1.5-5 indicates sediments deposited under periodic anoxia and TOC/TS<1.5 represents anoxic sediment with anoxic water (Hedges and Keil, 1995; Niffy Benny, 2009). Thus, TOC/TS in the sediments of study region can be included predominantly in the oxic/periodic anoxic category during both sampling periods (Figure 3.4) and the values of Eh also well support these results.

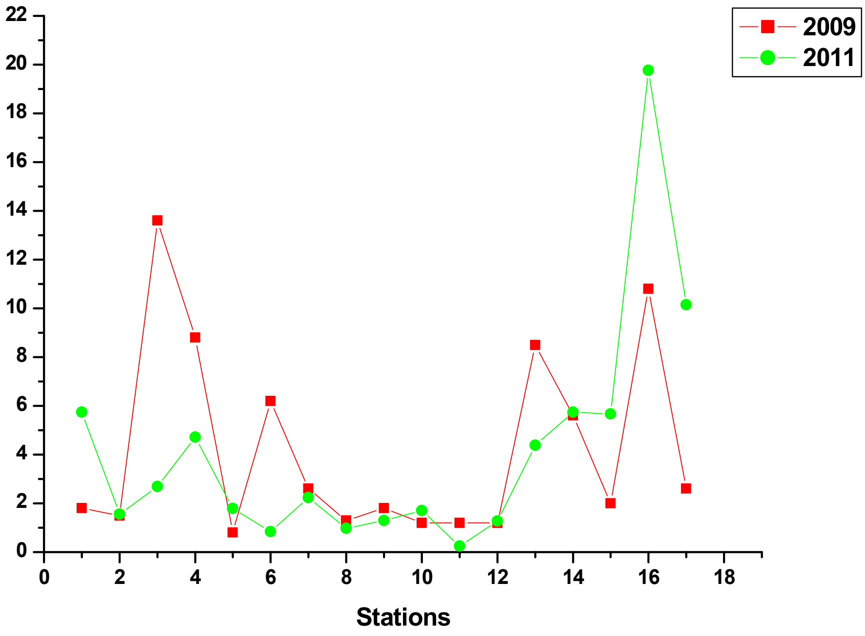

Figure 3.4 TOC: TS ratio in the surface sediments of CES.

Amongst the phytopigments, chlorophyll-a ranged from 0.4 to 20.6 mg/Kg (2009) and 2 to 40.1 mg/Kg (2011) and was significantly higher at stations situated in the middle to northern part of the estuary with minor fluctuations in both the sampling periods. Favourable conditions of salinity, dissolved oxygen, temperature and light intensity prevailing in these stations during both the sampling periods may greatly influence the level of chlorophyll-a as higher. Concentration of chlorophyll-b and chlorophyll-c varied from BDL to 6.6 mg/Kg (2009) and from BDL to 5.5 mg/kg (2009); 0.1 to 13.4 mg/Kg (2011) and from 1.2 to 11.8 mg/Kg (2011) respectively (Figure 3.5).

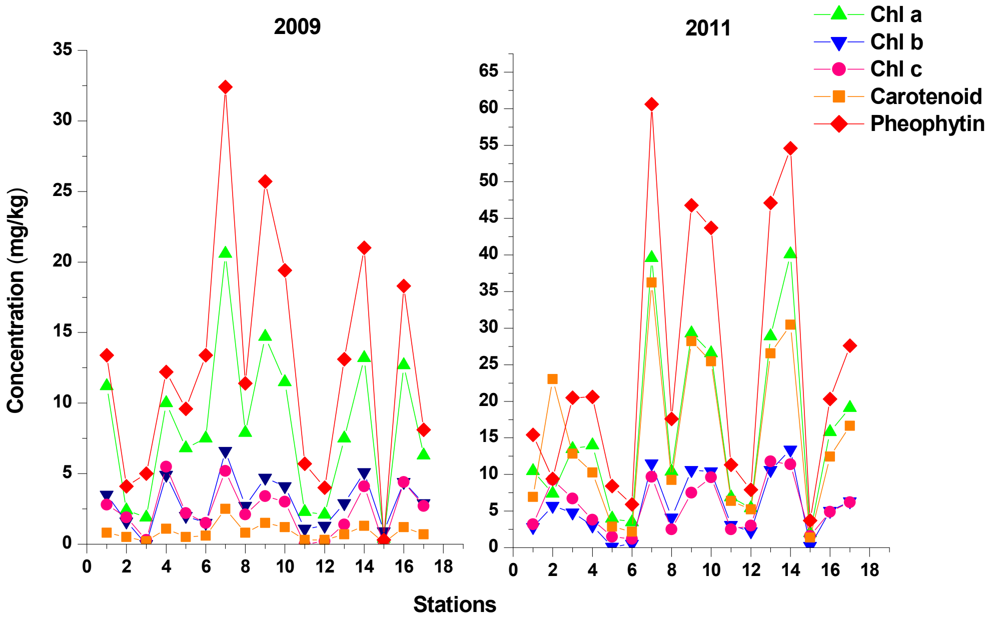

Figure 3.5 . Distribution profile of pigments (mg/kg) in the surface sediments of CES

The dominance of chlorophyll-b and chlorophyll-c at middle zone might be due to the endurance of diatom and dinoflagellates species diversity and the earlier studies conducted by Aneesh Kumar, (2009) also supports these results. Carotenoid and pheophytin concentration ranged from 0.1 to 36.25 mg/Kg and 0.3 to 60.6 mg/Kg and showed significantly higher at middle parts of the estuary during 2011 sampling period (Figure 3.5). The data indicated that pheopigments constituted the major fraction of the pigments in estuarine sediments. This might suggest that the dead plant material was retained in the sediment and might come under the influence of biological activity which brought about the conversion of chlorophyll to pheopigments. Lower pigment concentration in Station No:15 might be due to the enhance of industrial effluents in the region. In both the sampling periods, chlorophyll-a to pheophytin ratio shows <1 in all the stations which indicates the prevalence of detritus in the sedimentary environment.

C/N values are typically lower for aquatic organic matter than for terrestrial organic matter (Meyers and lallier-Verges, 1999) and it ranges from 6 to 9 for planktonic organisms and 20 to 100 for terrestrial plant tissue and soil (Tyson, 1995). C/N values varied widely in the study region 10.5 to 39 (2009) and 10.6 to 42.1(2011) and it could clearly ascertain the input of terrestrial organic matter as the dominant contributor in the study region (Figure 3.6). Recently, Renjith et al., 2013 reported that the $\delta^{13}C$ values obtained from the CES ranges from (-28.25 to -24.75‰) which also confirms a mixed origin of organic matter in the estuary with significant allochthonous contribution.

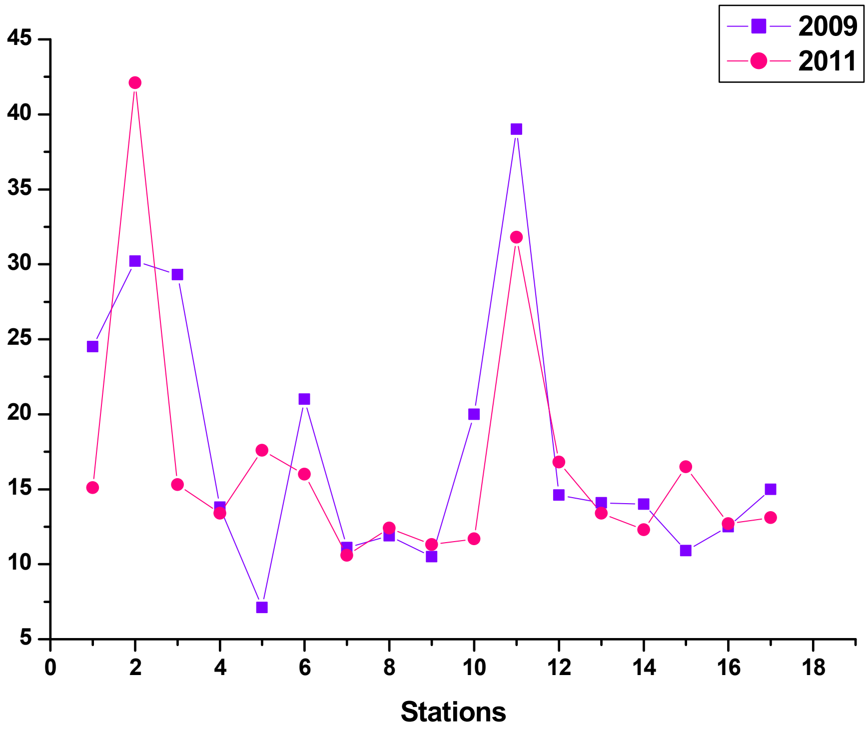

Figure 3.6 Spatial trends of C: N ratios in the surface sediments of CES.

To confirm the different variable associations of parameters controlling the OM distribution, factor analysis was carried out and was depicted in the Table 3.3 a &b. Varimax orthogonal was employed to transform the analysis matrix and to limit the number of variables loaded in each factor (Buckley et al., 1995). Four factors accounts for 89.7% to 94.5% of total variance during 2009 and 2011 respectively. In both sampling periods, first factor exhibit significant positive loadings for all sedimentary parameters with TOC and BPC, hence this can be called the “OM controlled factor”. During 2009, factor-2 shows significant positive loadings for clay and good loading on PRT and LPD. This factor can be called the “Clay controlled factor". In the case of factor -2, a substantial change in the environment was observed during 2011, a significant positive loading to all pigments were exhibited, hence it can be called the "Pigment controlled factor". An innovative approach regarding a combination of chemical and biological analysis will provide a comprehensive evaluation of these changes exerted in the aquatic system in future**.** Factor 3 and 4 shows no such high positive loadings. Thus from factor analysis it is inferred that "OM controlled factor" has a maximum amount of total variance during both sampling periods, indicating good relationship of OM in most of the variables studied. This was also justified by correlation analysis and was depicted in the Table 3.4 a & b. The sum of lipid, protein and carbohydrate carbon taken as the sedimentary biopolymeric carbon fraction and assumed as a reliable estimate of the labile fraction of total organic matter; ie, the fraction which was readily available to deposit feeders. Sedimentary biopolymeric organic carbon (BPC) in general, accounted for (0.09 to 0.76%), (0.13 to 1.33 %) during 2009 and 2011 respectively. The percentage was highest at southern and northern part of the ecosystem. A significant correlation was observed between all OM and BPC, and it establishes them as the major contributors. However, combining the sedimentary record with other biological and geochemical indicators in multiproxi studies still consists the most robust method for interpreting long term changes in ecosystem structure.

3.2.3 Core Sediment Biogeochemistry

3.2.3.1 Part A

This section details the salient portrayal on biogeochemical characteristics of six sediment cores collected from specific zones of CES during November 2009 and the samples are grouped into South, Middle and North zones as discussed previously in the Chapter-2. These core sediments are named as S_1, S_2, M_1, M_2, N_1 and N_2.

3.2.3.1 a General Sedimentary characteristics

General sedimentary characteristics like colour, pH, Eh and texture for each sediment core are discussed in this section and are appended in the Table 3.5 and 3.6.

Core (S_1): Varying colour combination in the physical appearance of core sediment was observed. Up to 10 cm it showed blackish brown, brownish black till 40 cm and then blackish brown towards bottom. pH values ranged from 5.4 at 3 cm depth to 7.2 at 42 cm depth and it was found to exhibit an increasing trend with minor fluctuations from surface to bottom. Values of Eh ranged from -263 mV to -107 mV, and it was found highest negative value at bottom portion of the core. Clay content dominated in this core and showed a variation ranging from 32% to 97.8%. Along the core, increased clay fraction was observed at top and bottom portion and in the middle section sand content was dominated (48% to 70%).

Core (S_2): Uniform black colour up to 12 cm and mixed black and grey colour up to 30 cm section of the sediment core was noted. Values of pH ranged from 7.53 to 8.75 and it was found to exhibit an increasing trend towards bottom parts of the sediment core. Eh value ranged from +102 mV to +264 mV, and noted highest at top portion of the sediment core. Sand content dominated in this core, and it was seen almost equal (81.7 % to 95.5%) to the entire core.

Core (M_1): The whole sediment core appeared blackish brown in colour. Values of pH ranged from 7 to 8. Eh value ranged from -324 mV to -263mV, and it was found highest negative value at bottom portion of the core. Sand content dominated (54.6% to 93.7%) in this core. Relative textural distribution was in the order; sand > clay > silt.

Core (M_2): Mixed black and grey colour up to 36 cm and uniform black colour up to 63cm were noted in this sediment core. Values of pH ranged from 7.9 at 63 cm depth to 8.7 at 9 cm depth and it was found and exhibited a decreasing trend with minor fluctuations from surface to bottom. Eh value ranged from -412 mV to -310 mV, and it was found highest negative value at bottom portion of the core. Sand content was intensified (38% to 77%) in this core. The textural variation was in the order; sand> clay> silt.

Core (N_1): The entire sediment core was blackish brown in colour. Values of pH ranged from 6.1 to 6.6 and exhibited a decreasing trend towards bottom of the sediment core. Values of Eh ranged from -376 mV to -252 mV, and it was observed as the highest negative value at middle to bottom portion of the core. Clay content varied between 1.9 % and 85.4 %. Increased sand content was observed at bottom portion of the core.

Core (N_2): Varying colour combination in core sediment was observed. Up to 18 cm, it showed uniform black colour, brownish black till 45 cm and then followed by mixed black and grey colour towards bottom. Values of pH ranged from 5.6 to 7.54 and highest at bottom portions of the sediment core. Values of Eh ranged from +172 mV to +284 mV, and it was found highest at top portion of the sediment core. Increased clay content was observed in the top to middle section of the core (11.3% to 88.9 %). Towards bottom portion of the core sand content was dominated (64% to 96%).

3.2.3.1 b Organic matter (OM)

Core (S_1): Percentage of TOC ranged from 2.7 to 3.8, showing almost equal trend at entire portion of the sediment core (Figure 3.7a). Total carbohydrate concentration ranged from 4.7 mg/g to 11.7mg/g. Maximum and minimum concentrations were observed at 3-6 cm, 15-18 cm depths respectively. Towards the lower end of the sediment core, concentration of carbohydrate was found increased. Concentration of total protein ranged from 0.9 mg/g (36-39 cm) to 7.1 mg/g (3-6 cm) and its level was slightly high at top portions. Concentration of lipid exhibited almost equal trend in the entire core and at 36- 39 cm section, the concentration reached maximum (34.1 mg/g). Concentration of tannin and lignin ranged from 1.0 mg/g to 1.6 mg/g and slightly highest value was noted at 36-39 cm depth and the lowest at 15-18 cm depth respectively. Relative OM distribution was in the order: LPD >CHO >PRT >TIN (Figure 3.7b).

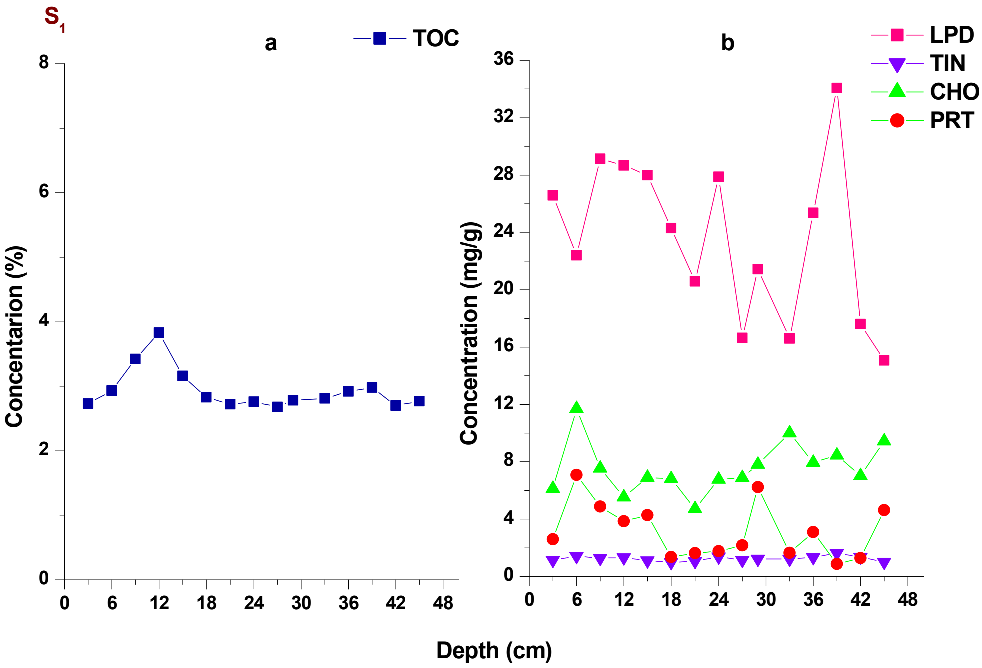

Figure 3.7 Distribution pattern of a) TOC and b) Organic matter in the sediment core S_1 (2009).

Core (S_2): Percentage of TOC ranged from 0.44 to 0.56 showing almost equal in the entire portions of the sediment core (Figure 3.8a). Total carbohydrate concentration ranged from 1.15 mg/g to 11.35 mg/g. The lowest concentration was observed at 27-30 cm depth and the highest at 6-9 cm depth respectively. Prevalence of carbohydrate concentration in the sediment core could be attributed to the anthropogenic input, death and decay of aquatic organisms and floating plants. Total protein concentration ranges from 0.19 mg/g to 0.9 mg/g and its level was slightly high at top and middle portions of the core sediment. Concentration of tannin and lignin ranged from BDL to 0.45 mg/g. Total lipid concentration (1.63 mg/g) was highest at (3-6 cm) portions of the sediment core. The relative OM distribution was in the order CHO>LPD >PRT>TIN (Figure3.8b).

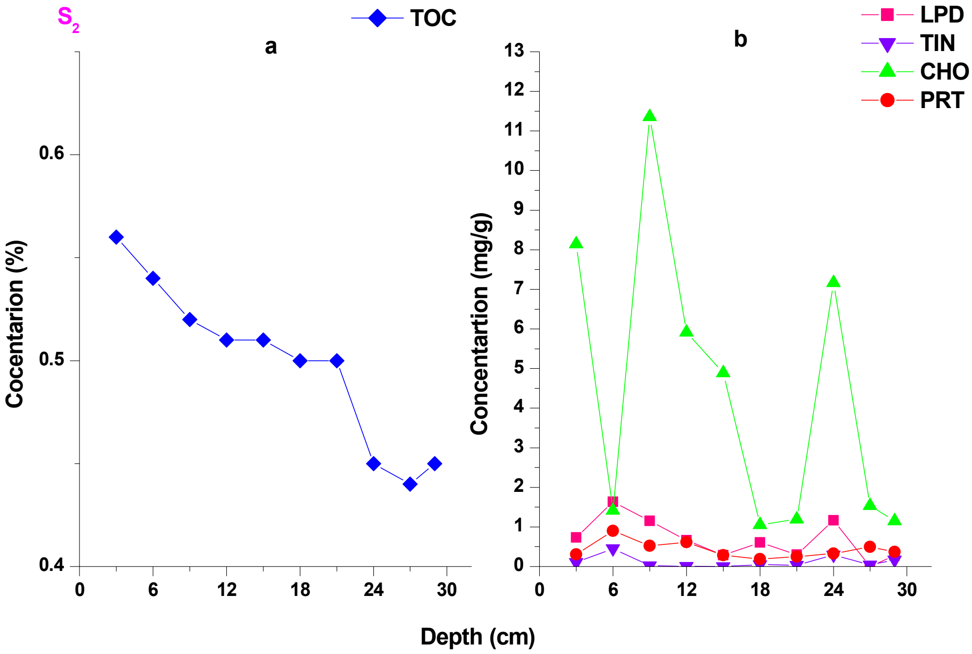

Figure 3.8 Distribution pattern of a) TOC and b) Organic matter in the sediment core S_2 (2009).

Core (M_1): TOC decreased from top (0.72%) to bottom (0.55%) of the sediment core (Figure 3.9a). Total carbohydrate concentration ranged from 0.7 mg/g (21-24 cm section) to 9.1 mg/g (36-39 cm section) and its level was slightly enriched at the bottom portion of the sediment core. Concentration of total protein ranged from 0.2 mg/g and 1.6 mg/g at 0-3 cm and 21-24 cm depth respectively. Concentration of protein was the highest at the middle and almost constant towards the bottom of the sediment core. Total lipid concentration ranged from 1.3 mg/g to 9.1 mg/g and lowest at 42-45 cm depth and the highest at 36-39 cm depth respectively. Concentration of lipid was slightly enriched at the surface to the middle portions of the sediment core. The concentration of tannin and lignin ranged from 0.09 mg/g (0-3 cm) to 0.46 mg/g (54-57 cm) and its level was slightly highest towards the bottom of the sediment core. Relative OM distribution was in the order; LPD >CHO >PRT >TIN (Figure 3.9b).

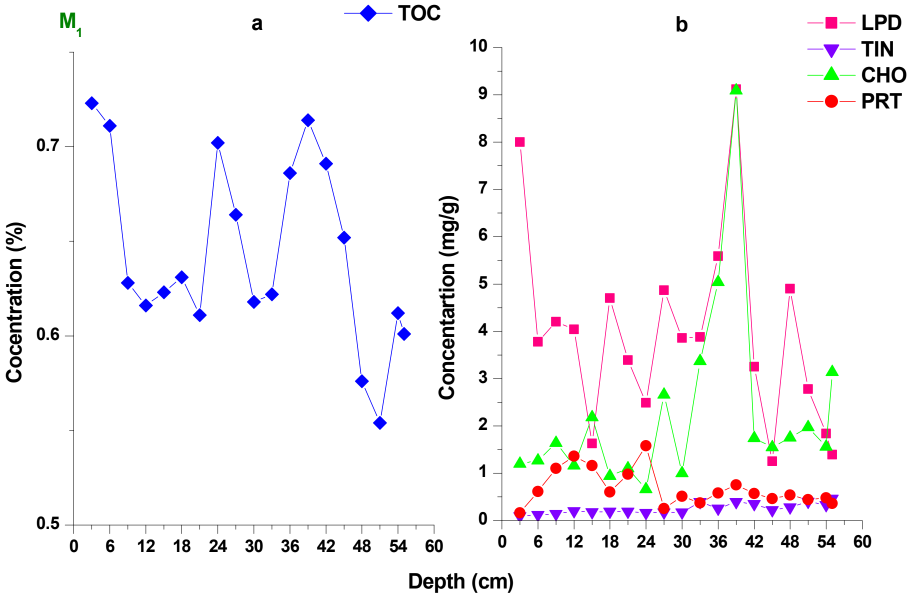

Figure 3.9 Distribution pattern of a) TOC and b) Organic matter in the sediment core M_1 (2009).

Core (M_2): Percentage of TOC ranged from 0.68 to 1.22. The maximum was noted at 24-27 cm depth and minimum at 6-9 cm of the sediment core. TOC values were highest at middle to bottom section of the sediment core (Figure 3.10a). Concentration of total carbohydrate ranged from 0.9 mg/g (51-54 cm) to 2.83 mg/g (27-29 cm) section respectively. Concentration of carbohydrate was enriched in the surface and middle portions of the sediment core. Total protein concentration ranged from 0.2 mg/g to 0.8 mg/g. The lowest concentration was observed at 3-6 cm depth and the highest at 27-29 cm depth of the sediment core. Protein concentration increased from the middle to the bottom portions of the sediment core. Total lipid concentration ranged from 1.6 mg/g to 18.3 mg/g. The lower concentration was observed at the depth of 9-12 cm and the higher at 21-24 cm depth. Concentration of tannin and lignin ranged from 0.1 mg/g to 0.8 mg/g. The lowest concentration was observed at 6-9 cm depth and the highest concentration was at 36-39 cm depth of the sediment core. Concentrations of tannin and lignin were found increasing towards the bottom portions of the sediment core. Relative OM distribution was in the order: LPD >CHO >PRT >TIN (Figure 3.10b).

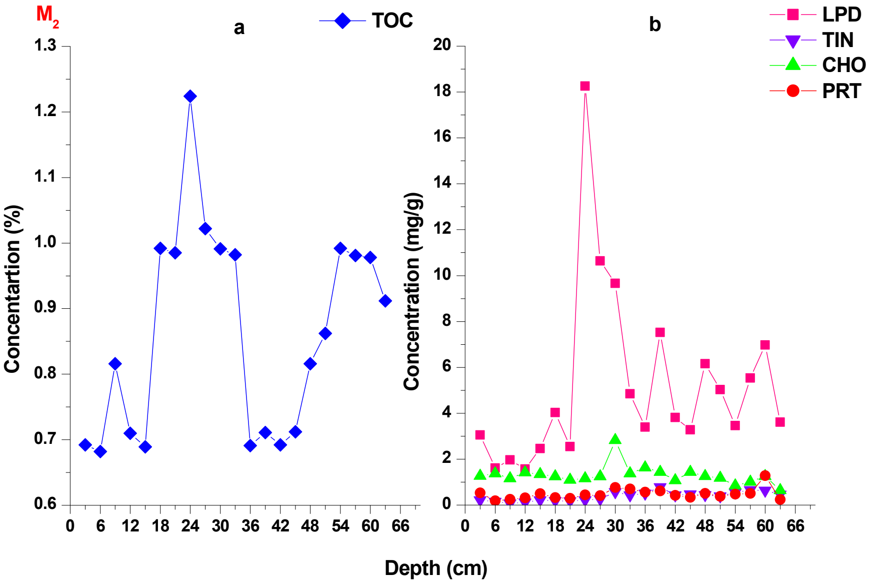

Figure 3.10 Distribution pattern of a) TOC and b) Organic matter in the sediment core M_2 (2009).

Core (N_1): Percentage of TOC ranged from 0.62 to 2.9. The maximum was noted at of 12-15 cm depth and the minimum at 27-29 cm of the sediment core (Figure 3.11a). In this core the amount of all the OM was exhibited in the same manner and its concentration was highest in the middle portions and lowest in the bottom portions of the sediment core. Concentration of the total carbohydrate ranged from 3.9 mg/g to 37.1 mg/g. Concentration of total protein ranged from 0.34 mg/g to 4.6 mg/g. Total lipids concentration ranged from 4.0 mg/g to 19.5 mg/g and finally the tannin and lignin content ranged from 0.3 mg/g to 2.4 mg/g. The relative OM distribution was in the order: CHO>LPD>PRT>TIN (Figure 3.11b).

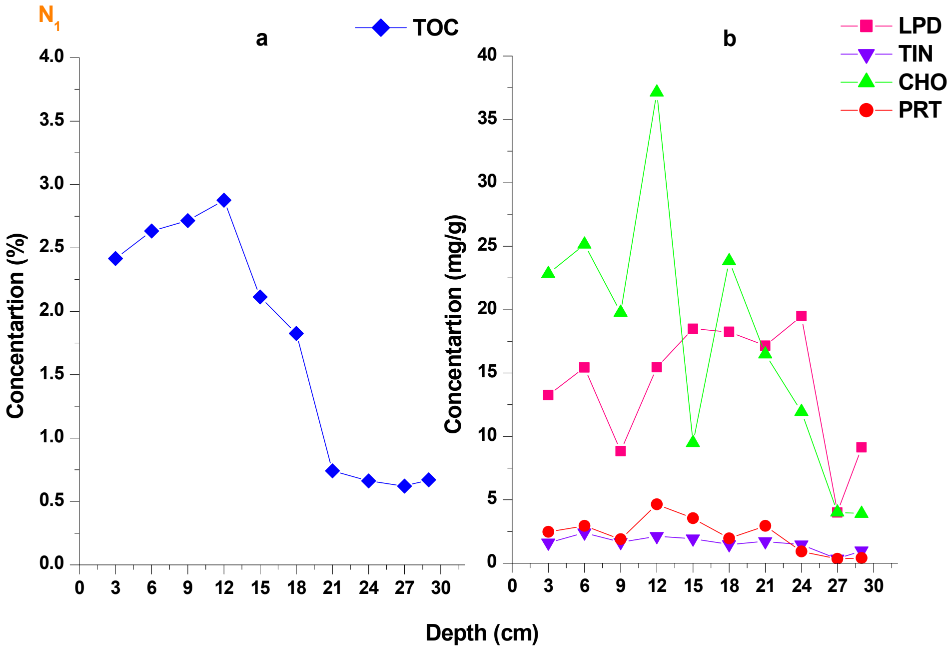

Figure 3.11 Distribution pattern of a) TOC and b) Organic matter in the sediment core N_1 (2009).

Core (N_2): Percentage of TOC ranged from 0.74 to 4.01, showing the lowest at bottom and highest at top portions of the sediment core (Figure 3.12a). Total carbohydrate concentration ranged from 2.32 mg/g to 15 mg/g. Maximum and minimum concentrations were observed at 36-39 cm, 57-60 cm depths respectively. Towards the lower end of the sediment core, concentration of carbohydrate was found to be decreased. Concentration of total protein ranged from 0.82 mg/g to 12.37 mg/g, and its level was highest at top portions of the sediment core. Slightly highest levels of lipid concentration were found at the core sediment and its concentration was prime (10.69 mg/g) at the top and middle portions. Concentration of tannin and lignin in the core ranged from 0.28 mg/g to 1.80 mg/g. The relative organic matter (OM) distribution was in the order: CHO> PRT>LPD>TIN (Figure 3.12b).

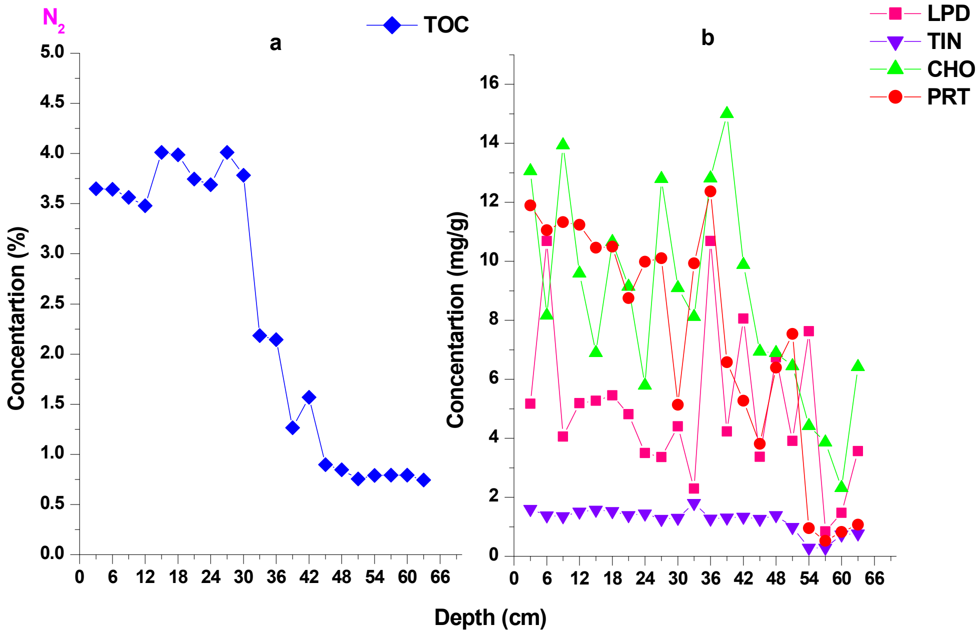

Figure 3.12 Distribution pattern of a) TOC and b) Organic matter in the sediment core N_2 (2009).

3.2.3.1 c Pigment Characteristics

Core (S_1): Amongst the phytopigments, concentration of chlorophyll-a ranged from 3.27 to 16.68 mg/Kg and it was significantly higher at bottom portions of the sediment core. The same trend was observed in the case of chlorophyll-b and chlorophyll-c. Concentration of pheopigment ranged from 4.14 to 23.48 mg/Kg. Levels of carotenoid were subjugated in this sediment core and it ranges from 7.06 to 40.73 mg/Kg and was significantly higher at middle to bottom portions of the sediment core(Figure 3.13).

Core (S_2): Among the phytopigments, chlorophyll-a ranged from 2.09 to 12.30 mg/Kg and was significantly higher at top to middle portions of the sediment core. The same trend was observed in the case of remaining pigments and the highest concentration of carotenoid (32.47 mg/Kg) was observed at 18-21 cm portion (Figure 3.13).

Core (M_1): Among the sedimentary pigments, chlorophyll-a ranged from (5.32 to 19.57 mg/Kg) and its level was slightly higher at middle to bottom portion of the sediment core. The same trend was observed in the case of carotenoid pigment (5.4 to 19.4 mg/Kg). In the case of chlorophyll-b, and c, its level was exhibited in the zig-zag motion. Concentration of pheophytin pigment was prime and the highest concentration (35.97 mg/Kg) was observed at mid portions of the core (Figure 3.13).

Core (M_2): Amongst the phytopigments, chlorophyll-a ranged from 1.3 to 6.4 mg/Kg and it was slightly higher towards bottom portions of the sediment core. The same trend was observed in the case of chlorophyll-b, c and carotenoid (Figure 3.13). Levels of pheophytin were subjugated in this sediment core and it was highest (11.44 mg/Kg) at bottom section.

Core (N_1): Concentration of chlorophyll-a ranged from 0.46 to 10.14 mg/Kg and it was highest at top to middle portions of the sediment core. The same trend was observed in the case of carotenoid, pheohytin and chlorophyll-b, c. Levels of pheophytin were dominated in this sediment core and it was highest (96.33 mg/Kg) at 3-6 cm portion (Figure 3.13).

Core (N_2): The concentration of all pigments (chlorophyll a, b, c ; pheophytin and carotenoid) were highest in this sediment core, in which pheophytin pigment was subjugated, and it was prime (87.45 mg/Kg) at top and followed by middle portions of the core (Figure 3.13).

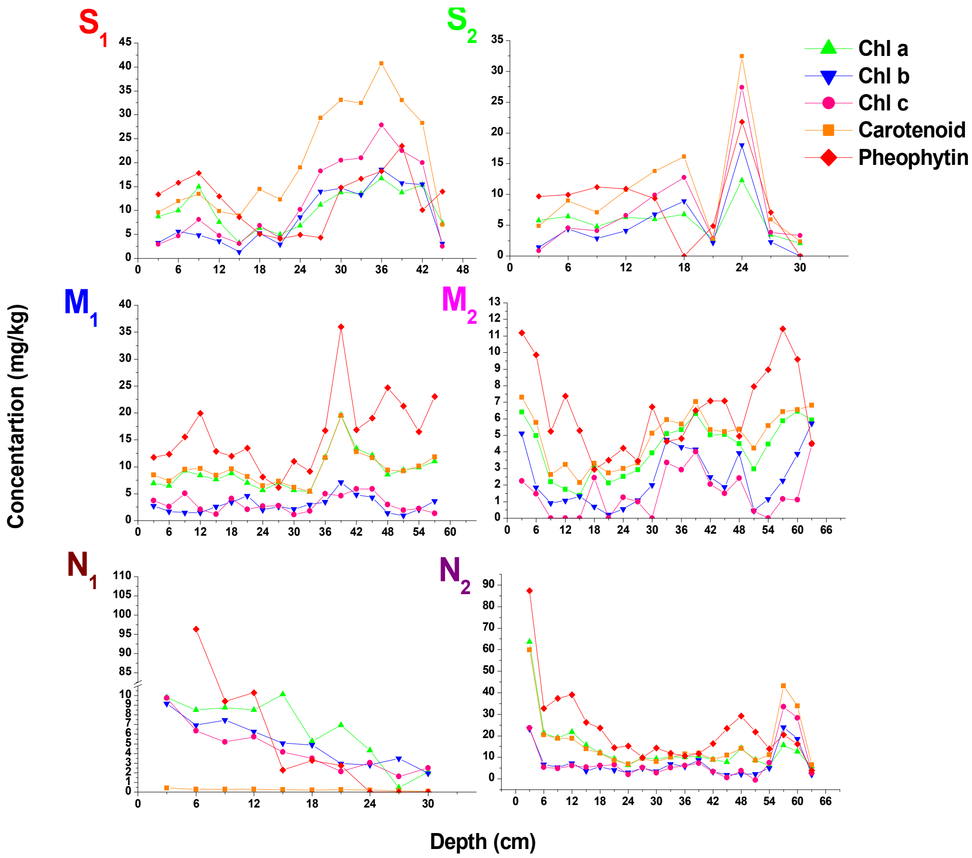

Figure 3.13 Down core variation of pigments in the sediment cores from CES (2009).

3.2.3.1 d Discussion

Estuaries are highly dynamic and influenced by strong tidal action, entangled with fresh water and coastal discharges. A number of investigations in recent years have shed light on the varied nature of biogeochemical characteristics of the estuarine and mangrove sediments in and around Cochin estuary (Joseph et al., 2008; Geetha et al., 2008; Niffy Benny, 2009; Deepulal et al., 2011; Aneeshkumar and Sujatha, 2012; Renjith et al., 2013). All these research works mainly concentrated in the spatial biogeochemical aspects in the CES. A general consensus on the biogeochemical pattern and its counter parts in the sediment cores of this unique system is seriously lacking. Therefore, the present study focussed on the detailed biogeochemical assessment of sediment cores in the CES and it constitute first detailed research work on core sediment biogeochemistry in the specific zones of CES.

In sediments, a wide variety of organic carbon forms are present and they range from freshly deposited litter to highly decomposed forms such as humus. The quality of organic matter in sediments is critical to the partitioning and bioavailability of sediment associated contaminants. Influence of total organic matter (TOM) in sediments is important to assess the fate, transport, deposition and retention of various inorganic and organic constituents in the aquatic environment.

Among the OM, **Lipid** is one of the major biochemical compound produced by living organisms and constitute an important fraction of dissolved and particulate OM (Skoog and Benner, 1997, Borsheim et al., 1999; Burdige et al., 2000). Besides, they are consumed by microheterotops in both fresh water and marine ecosystems and contribute essentially to the bacterial production (Rich et al., 1996). Its concentrations have been associated with the most labile fraction of sedimentary organics and is considered as the best descriptor of meiofauna abundance and biomass, over enzymatically hydrolysable aminoacids or protein contents (Gremare et al., 1997; Fabiano and Pusceddu, 1998; Gremare et al., 2002). In the present study, concentration of lipid was slightly higher in three core sediment (S_1, M_1 &M_2) collected from riverine and estuarine region, which indicates the intense biological activity associated with the productive nature of the environment.

Carbohydrate concentration in the sediment cores (N_1 ,N_2 and S_2) could be attributed to the anthropogenic input and the death and decay of aquatic organisms and floating plants. In addition to this, the carbon normalized value was suggestive of its terrestrial origin and similar observation was reported earlier by Joseph et al., 2008; Geetha et al., 2008; Niffy Benny, 2009 and Renjith et al., 2013. Moreover, the effluents from the industrial units and the discharge of wastes from the fish market have influenced the carbohydrate concentration to increase in great extent in these stations.

Proteins, the most important nitrogen bearing compound in most of the organisms. Present study revealed that concentration of protein accounted was slightly high at core N_2 and maximum at 33-36 cm depth (12.37 mg/g). The abundance of protein was seen to be influenced by the substratum as well as the season and the anthropogenic inputs. Previously, Niffy Benny, (2009), reported that the higher concentration of protein in the surface sediments from northern part of the estuary also corroborated with the present study. A decrease in the concentration of protein at other zones may be due to the preferential utilisation of protein by the benthic organisms and various biological activity or the other means of incorporation into humic matter by the nitrogen compounds through various humification pathways and previous research work of Bhosle and Dhople, (1988) also supports this inference. Both carbohydrates and protein serve as structural and storage components and comprise up to 40% of the OM in the marine niche and 75% of the OM in terrestrial organisms (Biersmith and Benner, 1998).

The high molecular weight polycyclic aromatic compounds **Tannins and lignins** are widely distributed throughout the plant kingdom. They are highly resistant to biological degradation and have a great potential to damage the aquatic environment. The identification and quantification of these compounds in these marine environments infers the importance of land derived organic detritus (Schnitzer et al., 1972; Finar, 1976; Field and Lettinga, 1987). Concentration of tannins and lignins was found slightly enriched at cores collected from the northern and the southern region, establishes the character of allochthonous origin and it could clearly ascertain the input of terrestrial OM as the dominant contributor in the study region. The increased hydroxylated aromatic compound concentrations observed at these stations could therefore be attributed to the influence of the effluents and to the gravitational settling of the organics occurring in this region. The 2D hydrodynamic model data in CES reported previously by Balachandran et al., 2008, reasonably conceptualised that the northern and southern zones are sensitive to environmental stress. Decreasing trends of organic carbon detected in the middle zone may be due to strong rectilinear current, which maintains an effective flushing.

For the past several years scientists have been considered the sedimentary plant pigments as a valuable indicator of paleoecology and paleolimnology (Vallentyne, 1954; Brown, 1969; Sanger and Crowl, 1979; Sagar, 1988; Steenbergen et al., 1994; Vaalgamaa, 2004; Weckstrom et al., 2004). It is well known that the majority of pigments are degraded in the water column and in the upper most sediment before being incorporated into the fossil record (Leavitt, 1993; Bianchi et al., 2002), in which the pheo-derivatives are common throughout in the aquatic sedimentary columns rather than the unaltered chlorophyll molecules. Factors that promote pigment preservation are contrasted to those that alter and cause destruction of organic molecules. Thus the value of fossil pigments is considered in ascertaining the sources of OM to sediments and for providing clues to the changing diversity of aquatic flora, both rooted and planktonic and the present result also try to answer these aspects. According to the study by Sun et al., (1993) attributed that pheophytins were the dominating degradation products of chlorophyll-a and are known to be some of the major degradation products and are very stable under anoxic conditions. Moreover, good pigment preservation has previously been found at other anoxic estuarine sites (Villanueva and Hastings, 2000; Bianchi et al., 2002). In the present study, concentration of pheophytin pigment subjugated in four cores (M_1, M_2, N_1 and N_2) collected from middle and northern zone of the CES. Among these, core N_1 exhibit the highest concentration (96.3 mg/Kg) pheophytin at a depth of 3-6 cm and towards the bottom, concentration was below detectable level due to the low adsorbing nature of the sandy sediment. Dell's Anno et al., (2002) reveals that the predominance of pheopigments might be attributed to high turbidity, chemical contamination or other governing factors which affects the photosynthetic potential of the primary producers. The ratio of chlorophyll-a to pheophytin was used to describe the pigment preservation at each site. Estimated chlorophyll-a to pheophytin value were <1 in all the sediment cores under this investigation, which indicates the prevalence of detritus in the sediments. Moreover, it can suggest a clue for relative rate and time frame of phytoplankton deposition (Josefson and Conley, 1997; Hagy et al., 2005). The higher concentration of carotenoid (40.7 mg/Kg and 32.5mg/Kg) detected in the fresh water augmented cores, S_1 (at 33-36 cm depth) and S_2 (at 18-21 cm depth) respectively and significantly higher concentration of pheophytin was detected at top portions. The result shows that the taxonomical specificity and high stability of carotenoids relative to other pigments which may hold the largest potential for identifying the phototropic community contributing to the sedimentary record. Individual carotenoids can be used as indicators of specific algae classes (Jeffrey et al., 1997). Indicator carotenoids include fucoxanthin (diatoms), diatoxanthin and diadinoxanthin (diatoms, dinoflagellates), alloxanthin (chryptophytes), lutein (green algae anf higher plants), and zeaxanthin (cyanobacteria), while β-carotene and chlorophyll-a are more general indicators of total algal abundance. However, selective pigment loss with different stabilities during deposition can affect the relative abundance of specific carotenoid pigments (Leavitt, 1993; Bianchi et al., 2000). Besides, slightly higher concentration of chlorophyll-b and chlorophyll-c were found in the deeper portion of the sediment cores collected from riverine stations except in the cores S_2 and N_1. This may be due to the clear succession of diatoms and dianoflagellates species in the past period. Moreover, high productivity and high grazing pressure established an equilibrium maximum, resulting in an effective production of organic material. In this circumstances, effective uptake of phytoplankton by organisms would produce large amounts of phytoplankton in the fecal pellets, which would easily sink to the bottom segment because of their larger size (Aneesh Kumar, 2009). Thus the changes in grazing pressure can affect both the digestive degradation and preservation through escape from oxidation in the water column by faster downward transport in faecal pellets (Leavitt, 1993), while the presence of anoxia at the sediment- water interface and lack of benthic macrofauna has been shown to substantially increase the preservation of pigments in sediments (Sun et al., 1993; Bianchi et al., 2000). Higher concentration of these phytopigments in the study region also justifies the above results. Also the factors influencing the sediment pigment record include photo and chemical oxidation as well as herbivore digestive processes in the water column during deposition and post depositional degradation in the sediment.

A number of important bulk sediment parameters are available for the evaluation of OM sources and its fate within the marine sediments. However, C/N ratios of sediments in the aquatic systems are often used to differentiate marine from terrestrial OM. Selective degradation of the different minerals in sediments can also affect the C/N ratios of OM and the similar observation was reported previously by Redfield et al., (1963); Atkinson and Smith, (1983); Muller, (1997); Perdue and Koprivnjak, (2007). C/N values are typically lower for aquatic OM than for terrestrial OM (Meyers and Lallier-verges, 1999) and it ranges to 6-9 for planktonic organisms and 20-100 for terrestrial plant tissue and soil (Tyson, 1995). In this research findings, C/N ratio varied from 18.5 to 25.23, averaging 22.75 for core (S_1); from 15.3 to 25 averaging 20.4 for core (S_2); from 11.9 to 14.2, averaging 12.9 for core (M_1); from 20 to 22, averaging 21 for core (M_2) and from 14.4 to 32.8, averaging 20.7 for core (N_1); from 13.51 to 17.42 averaging 14.9 for core N_2. Among the six cores, C/N ratio was > 20 in four cores (S_1, S_2, M_2, & N_1) ascertaining the input of terrestrial material into the area, justifying that the source of organic matter is allochthonous. Recently, Renjith et al., 2013 reported that the $\delta^{13}C$ values obtained from the surface sediments of CES ranges from (-28.25 to -24.75‰) which also confirms a mixed origin of organic matter in the estuary with significant allochthonous contribution. Moreover, the elevated C/N ratio which presumably represents greater input of eroded material from the surrounding land as can be concluded from the high sand percentage observed in the middle to lower portions of these cores which might have resulted from increased precipitation during that period. However, the succession of post depositional changes may also modify the environment niche drastically. Percentage of elemental distributions (CHNS) in all the six sediment cores were in the order: C> S>H>N.

Previously, Cividanes et al., (2002) studied the temporal variability in the biochemical composition of sedimentary organic matter in an intertidal flat of the Galician coast (NW Spain) and used protein to carbohydrate ratio (PRT:CHO) as an index to evaluate the origin of material present in sediments and to determine the age of sedimentary organic matter. This ratio was generally higher in estuarine sediments which point to the presence of low dead organic matter accumulation, probably due to the vibrant condition of estuaries. In the present study, this ratio showed an average value of 0.42, 0.19, 0.50, 0.4, 0.1 & 0.83 in S_1, S_2, M_1, M_2, N_1 and N_2 cores respectively. Even though the middle zone is subjected to strong hydrodynamic conditions, sediments from this region also showed less PRT: CHO value. This may be due to the influence of anthropogenic inputs and rapid development activities in and around the study area. Low protein to carbohydrate ratios suggest the presence of aged OM and the role of protein as a potentially limiting factor for benthic consumers. Less dynamic nature of waters in northern and southern part of the study area also caused low protein to carbohydrate ratio. Earlier report by Danovaro, (1996) detailed the detritus–bacteria–meofauna interactions in a seagrass bed (Posidonia Oceanica) of the NW Mediterranean coast and the study infers that the dominance of carbohydrate and lower PRT: CHO ratio in the aquatic system lead to a typical feature of detrital heterotrophic environment. Moreover, a decrease in the concentration of PRT may be due to the preferential utilisation of protein by the benthic organisms and biological activity or to the nitrogen compounds are incorporated into humic matter through various humification pathways (Bhosle and Dhople, 1988). Lipid to carbohydrate ratio(LPD:CHO) showed an average value of 3.3, 2.4, 4.2 & 1.1 in S_1, M_1, M_2 and N_1 cores respectively, which in turn reflects energetic (food) quality of the organic contents in the study area and these inferences are well supportive of the earlier literatures (Gremare et al., 1997; Fabiano and Pusceddu, 1998;Gremare et al., 2002) . Relatively low LPD: CHO ratio was observed in the core S_2 (0.27) and N_2 (0.59), may be related to the decreased in lipid inputs derived from anthropogenic sources. Percent average of BPC was in the order 2.23, 0.25, 0.42, 0.47,1.9 & 1.1 in S_1,S_2, M_1, M_2, N_1 & N_2 cores respectively.

The ratio of total organic carbon (TOC) percentages to total sulfur (TS) percentages (TOC:TS), in sediments ranges from core S_1 (1.2 to 3.0), S_2 (5 to 6.38) ,M_1 (0.7 to 3.0), M_2 (0.46 to 1.22), N_1 (1.2 to 3.0) and N_2 (5.60 to 5.8) respectively. However its ratio was highest at the sediment cores S_2 and N_2, showing the amount of metabolizable organic matter available to support sulphate reducing bacteria which increases with the total amount of organic matter arriving at the sediment water interface. As a consequence, the sedimentary pyrite sulphide content is positively correlated with the non metabolized (resistant or unused) organic matter content (TOC). Under anoxic conditions, dissolved sulfate is reduced to hydrogen sulfide gas, which reacts with iron minerals to form iron sulfides causing a qualitative redox status of the environment under deposition. Marine sediments undergoing sulfate reduction under euxinic/ inhospitable bottom conditions typically have TOC: TS ratios lower than 1.5 (Niffy Benny, 2009) and similar observation was found at bottom portions of the sediment cores (S_1, M_1, M_2 and N_1). Marine sediments undergoing sulfate reduction below the oxygenated water column exhibits TOC: TS ratios in the range 1.5 to 5 and well supports the earlier works of Berner and Raiswell, (1983). Thus sediments from the stations (S_1, M_1, M_2 & N_1) were characterized as under predominantly periodic anoxic stipulation in middle to bottom portions of the core. Increased anoxia in the study region not only increases preservation of the pigments but also excludes the benthic animal community, thereby reducing ingestion and bioturbation, which has a significant effect on the degradation of sedimentary pigments.TOC/TS ratio > 5 in the sediment cores S_2 and N_2 are considered as oxic sediment with oxygenated bottom water.

3.2.3.1 e Statistical Analysis

The correlation analysis of various biogeochemical parameters of sediment cores were discussed as follows**.** In the sediment core (S_1), Biopolymeric carbon (BPC) showed a highly significant correlation with lipid, followed by tannin & lignin and establishes them as the major contributors to BPC. A significant correlation of OM with TOC were also observed. In the case of sediment core S_2, BPC had significant positive correlations with carbohydrate and lipid; suggest that they are the major contributor of BPC. A well momentous correlation of clay with chlorophyll-a and pheo pigments was also noticed. In the sediment core (M_1), BPC had high significant correlation with lipid followed by carbohydrate. A significant correlation of clay with carbohydrate, chlorophyll-a, chlorophyll-b, carotenoid and pheophytin was also noticed. In the sediment core (M_2), BPC exhibited a significant correlation with lipid and established as the major contributor of BPC. In the sediment core (N_1), BPC had significant positive correlations with lipid, tannin &lignin, carbohydrate, protein and clay, indicating an equal contribution of all organic matter to BPC. A significant correlation was also observed between BPC and clay. In the sediment core N_2, Biopolymeric carbon (BPC) showed a high significant correlation with all OM, and establishes them as the major contributors to BPC. A well momentous correlation of clay with the OM establishes the high affinity for the fine grained sediment, which constitute clay particles with increased surface area per unit weight for the absorption of OM.

To confirm the different variable associations, and the identification of parameters controlling the organic matter distribution, factor analysis was carried out and is depicted in the Table 3.7. 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). In the sediment core S_1, four factors accounts for 71.3% of the total variance. The first factor accounted for high positive loadings on all the sedimentary parameters except sand, slit and lipid. Factor-2 exhibit significant positive loadings for all OM and BPC. Factor-3 showed significant positive loading for lipid and high negative loadings for carbohydrate, protein, pigments, clay and slit. Factor-4 shows no such significant positive loadings. In the case of sediment core S_2, four factors accounts for 89.3 % of the total variance. Factor-1 is associated with all pigments and hence can be called the “Pigment controlled factor”. Factor-2 is associated with the OM component, and hence can be called the “OM controlled factor (I)”. This factor explains the significant role of OM in binding of certain trace contaminants. Third factor can be called the “Clay controlled factor”, assuming the elements to be enriched in the clay fraction. Factor-4 is associated with the OM component and hence can be called the “Organic matter controlled factor-II”. Thus factor analysis will provide the clue for better understanding the distribution and concentrations of trace organic/inorganic contaminants that enter and get deposited in the complex, dynamic environment. In the sediment core M_1, four factors accounts for 84.5% of the total variance. The first factor shows positive loadings for all sedimentary parameters except for sand and protein, evidence to high significant loadings of pigments. Hence, this can be called the “pigment controlled factor”. High positive loadings of lipid and BPC are the features of factor-2. No such high positive loadings to the sedimentary parameters were found in factor-3, but factor-4 shows significant positive loadings to Chlorophyll-c. In the sediment core M_2, three factors accounts for 71.1% of the total variance. The first factor shows positive loadings of all sedimentary parameters except sand and resulting in significant loadings of pigments, and profoundly it could be called the “pigment controlled factor”. Factor-2 shows high positive loadings on lipid, clay & BPC. But factor-3 shows no such high positive loadings. In the sediment core N_1, three factors account for 69.1% of the total variance. The same trend as in the core M_2 was observed in the case of first factor. Though factor-2 shows no such high positive loadings, the factor-3 showed high positive loading to slit. In core N_2, four factors accounts for 89.96 % of the total variance. The first factor shows significant positive loadings on clay and good loadings on all organic matters. It establishes the high affinity for fine grained sediment, which constitute clay particles with increased surface area per unit weight for the absorption of OM. Hence this factor can be called the “Clay controlled factor”, assuming the elements to be enriched in the clay fraction. Factor-2 shows significant positive loadings of all pigments and hence can be called the “Pigment controlled factor”. Factor-3 is associated with the OM component and hence can be called the “OM controlled factor”. This factor explains the significant role of binding of OM with other trace contaminants. Factor-4 shows no such significant positive loadings.

3.2.3.2 Part B

This section details the brief description on the biogeochemical characteristics of six sediment cores collected from specific zones (same as the first sampling campaign) of CES during November 2011. Most of the earlier published research contributions were based on one-time or seasonal sampling during a year. Therefore the present research approach based on the biogeochemical analysis of sediment cores collected over a considerable time period which could provide a clue for the change in the environment and such studies are limited.

3.2.3.2 a General Sedimentary characteristics

General sedimentary characteristics like colour, pH, Eh and texture for each sediment core were discussed in the initial section and were appended in the Table 3.8 and 3.9.

Core (S_1): The whole sediment core appeared black in colour. Values of pH ranged from 6.3 at 9-12 cm depth to 7.5 at 30-33 cm depth and it was found to exhibit an increasing trend with minor fluctuations from surface to bottom. Eh value ranged from -101mV to +218 mV, and was noted as the highest negative value at the bottom portion of the core. Sand content dominated in this core and showed a variation ranging from 28 % to 86.7 %. Along the core, as depth increases, sand fraction also increases. Besides, slightly higher (35% to 49%) percentage of silt was observed at the top (0-15 cm) portion of the sediment core. Relative textural distribution was in the order; sand> silt> clay.

Core (S_2): Greyish brown colour up to 6-9 cm and uniform black colour towards the bottom section of the sediment core were observed. Values of pH ranged from 7.4 to 8 and it was found to exhibit an increasing trend with slight variations towards the bottom portion of the sediment core. Eh values ranged from -434 mV to -323mV, and noted that highest negative value existing at middle to bottom portion of the sediment core. Sand content dominated in this core, and it was found almost equal (76 % to 98 %) to the entire core. Relative textural distribution was in the order; sand> clay> silt.

Core (M_1): Greyish black colour up to 9-12 cm and uniform black colour towards the bottom portion of the sediment core. Values of pH ranged from 7.3 to 8 and it was noted to exhibit an increasing trend towards the bottom portion of the sediment core. Eh values ranged from -216 mV to -108 mV, and it was seen the highest negative value at the bottom portion of the core. Sand content dominated in the middle to bottom portion of the sediment core (41% to 81 %). Top portions of the core was slightly enriched with silt content (23% to 44%). Relative textural distribution was in the order; sand > clay > silt.

Core (M_2): The whole sediment core appeared black in colour. Values of pH ranged from 6.9 at 39-42 cm depth to 8.4 at 9-12 cm depth and it was found to exhibit a decreasing trend with minor fluctuations from surface to bottom. Eh value ranged from -211 mV to -97 mV, and it was found highest negative value at middle to bottom portion of the sediment core. Sand content was intensified in top portions of the core (31 % to 82%) and towards the bottom silt and clay fraction were dominated (~57%). The textural variation was in the order; sand> silt > clay.

Core (N_1): Black colour up to 21-24 cm portion and uniform greyish black colour were observed towards the bottom. Values of pH ranged from 6.3 to 7 and the highest value noted at 9-12 cm depth and lowest at 27-30 cm depth respectively. Eh value ranged from -86 mV to +376 mV, and it was found highest positive value at top portions of the core. Clay content varied between 35.5 % and 94.5 %. Along the core as depth increased clay content also intensified. Besides, slightly highest percentage of silt content was observed at top portions of the core. The textural variation was in the order; clay> silt> sand.

Core (N_2): The whole core appeared black in colour. Values of pH ranged from 5.2 to 8.1 and highest at middle portions of the sediment core. Eh value ranged from +64 mV to +376 mV, and it was found highest positive value at top portions of the core. Silt content was dominated in the top section of the sediment core and showed a variation ranging from 43.8 % to 89 %. As depth increased, silt fraction was decreased and increased sand content was noted at bottom portions of the sediment core. Relative textural variation was in the order; silt > clay> sand.

3.2.3.2 b Organic matter (OM)

Core (S_1): Percentage of TOC ranged from 0.85 to 3, showing the lowest and the highest at a depth of 39-42 cm and 6-9 cm respectively (Figure 3.14a). Total carbohydrate concentration ranged from 1.5 mg/g at 45-48 cm depth and 7.6 mg/g at 18-21cm, depth respectively. Towards the lower end of the core, concentration of carbohydrate was found decreased. Concentration of total protein ranged from 0.67 to 10.1 mg/g and it was slightly higher at top portions of the sediment core. The maximum concentration of protein was observed at a depth of 6-9 cm and minimum was at 42-45 cm portion of the core. Concentration of lipid was prime at top portions and lowest towards bottom. The highest concentration (6.03 mg/g) of lipid was detected at 6-9 cm portion of the core. Concentration of tannin and lignin ranged from 1.16 to 3.22 mg/g and slightly highest concentration was noticed at top and decreased towards bottom portions of the sediment core. The identification and quantification of these compounds in the aquatic environment infers the importance of land derived organic detritus. The relative OM distribution was in the order CHO>PRT>LPD>TIN (Figure 3.14b).

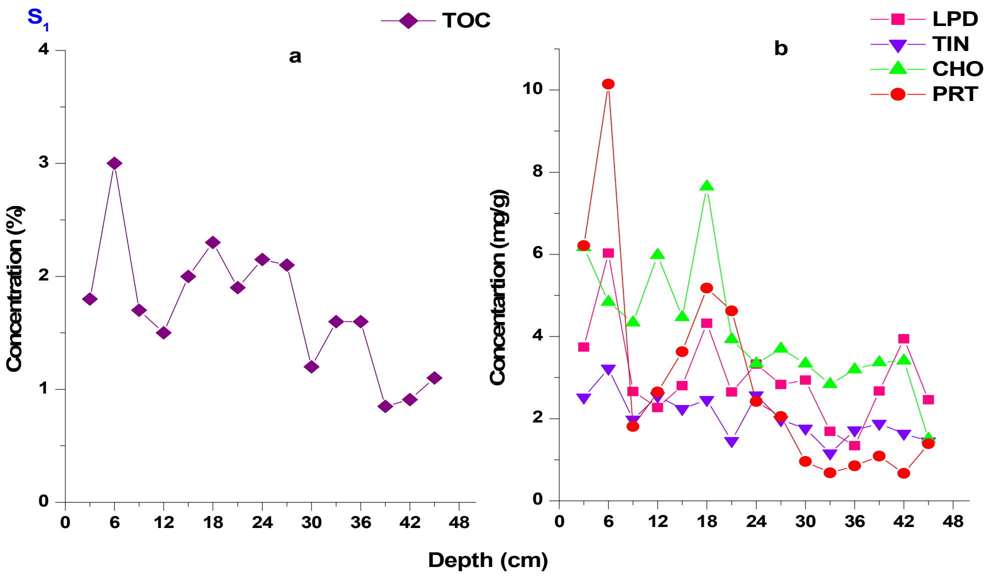

Figure 3.14 Distribution pattern of a) TOC and b) Organic matter in the sediment core S1 (2011).

Core (S_2): Percentage of TOC ranged from 0.12 to 0.29 showing the lowest and the highest at a depth of 0-3 cm and 21-24 cm respectively (Figure 3.15a). Total carbohydrate concentration ranged from 0.43 mg/g at 0-3 cm depth and the highest concentration 1.12 mg/g at 33-36 cm depth of the core. Total protein concentration ranges from 0.15 mg/g to 0.7 mg/g and its level was slightly high at top to middle portions of the core. Concentration of lipid was prime at middle portions and lowest towards bottom and the highest concentration (0.53 mg/g) was detected at 21-24 cm portion of the core. Concentration of tannin and lignin ranged from 0.1 to 0.25 mg/g. The relative OM distribution was in the order CHO>PRT>LPD>TIN (Figure 3.15b).

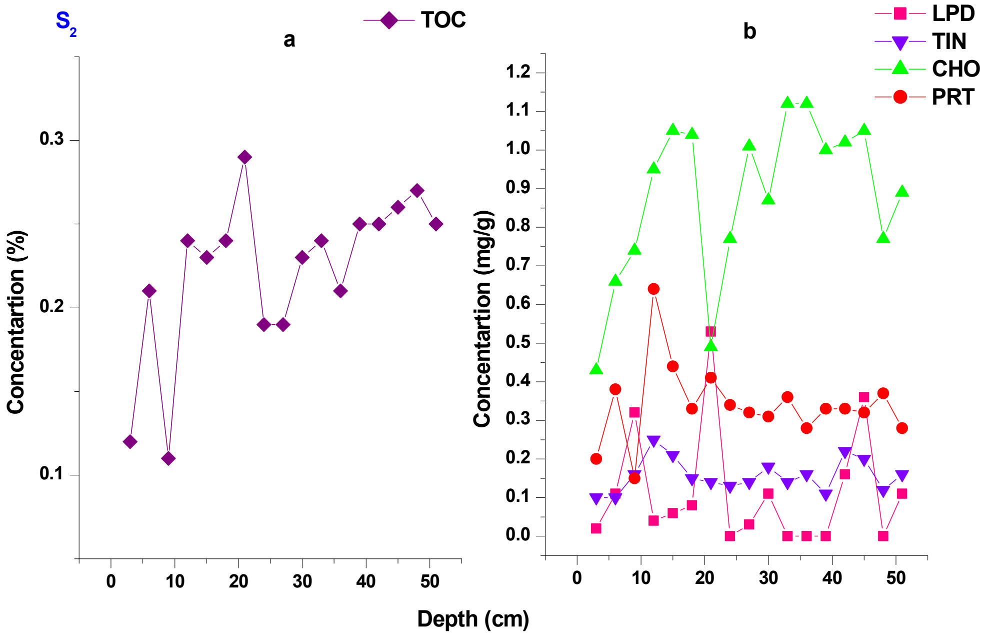

Figure 3.15 Distribution pattern of a) TOC and b) Organic matter in the sediment core S$_2$ (2011).

Core (M$_1$): Percentage of TOC ranged from 0.39 to 0.88 showing the lowest and the highest at a depth of 51-54 cm and 33-66 cm respectively (Figure 3.16a). Total carbohydrate concentration ranged from 2.66 mg/g to 11.34 mg/g and the lowest concentration was observed at the depth, 51-54 cm and the highest at 27-30 cm portion of the core respectively. Total protein concentration ranged from 1.6 mg/g to 3 mg/g at 30-33 cm and 12-15 cm depths respectively. Concentration of protein was maximum at top to middle portions of the core. Total lipid concentration ranged from 1.13 mg/g to 10.71 mg/g and lowest at 48-51 cm depth and the highest at 9-12 cm depth respectively. Concentration of lipid was enriched from the surface to the middle portions of the sediment core. The levels of tannin and lignin ranged from 0.411 mg/g to 0.96 mg/g and the lowest concentration was observed at 15-18 cm depth and the highest at 27-30 cm depth respectively.

Relative OM distribution was in the order; LPD >CHO >PRT >TIN (Figure 3.16b).

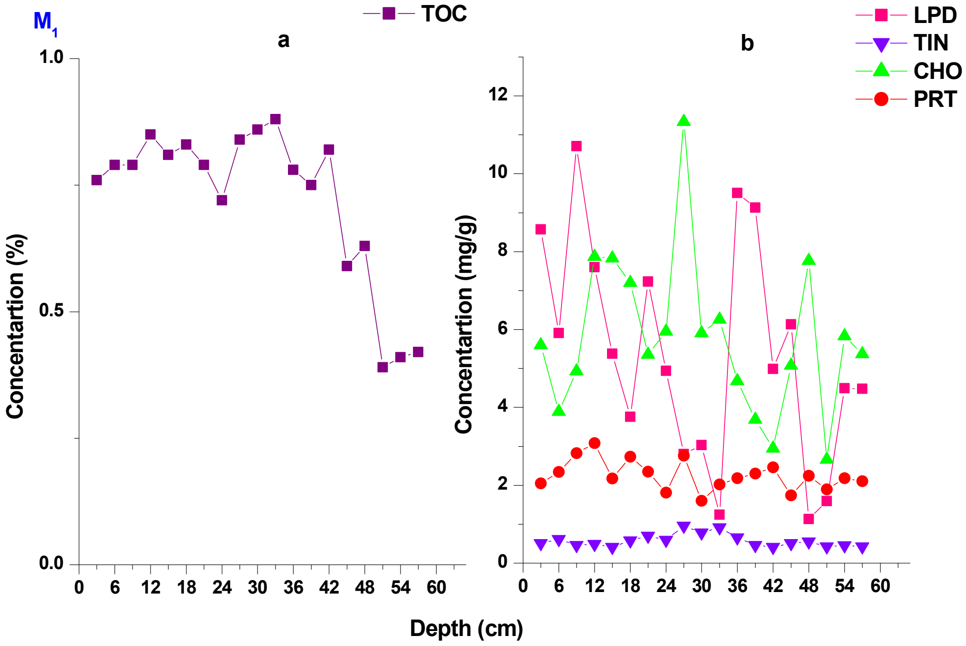

Figure 3.16 Distribution pattern of a) TOC and b) Organic matter in the sediment core M_1 (2011).

Core (M_2): Percentage of TOC ranged from 1.12 to 1.95 and the maximum value was noted at 24-27 cm depth and minimum at 15-18 cm of the sediment core. TOC values increased towards the bottom of the core (Figure 3.17a). Concentration of total carbohydrate ranged from 5 mg/g to 14.3 mg/g and the lowest concentration was observed at 15-18 cm depth and the highest at 0-3 cm depth of the core respectively. Total protein concentration ranged from 1.68 mg/g at 0-3 cm depth and the highest concentration 4.30 mg/g at 24-27 cm depth of the sediment core. Concentration of protein was highest from middle to bottom portions of the core. Total lipid concentration ranged from 3.29 mg/g to 16.37 mg/g and the lowest concentration was observed at the depth of 51-54 cm and highest at 12-15cm depth respectively. Lipid concentration was the highest in the middle portions of the core. Concentration of tannin and lignin ranged from 0.53 mg/g to 2.06 mg/g and the lowest concentration was observed at 0-3 cm depth and the highest concentration was at 18-21 cm depth. Concentrations of tannin and lignin were found increasing towards the bottom portions of the core. Relative OM distribution was in the order: LPD >CHO >PRT >TIN (Figure 3.17b).

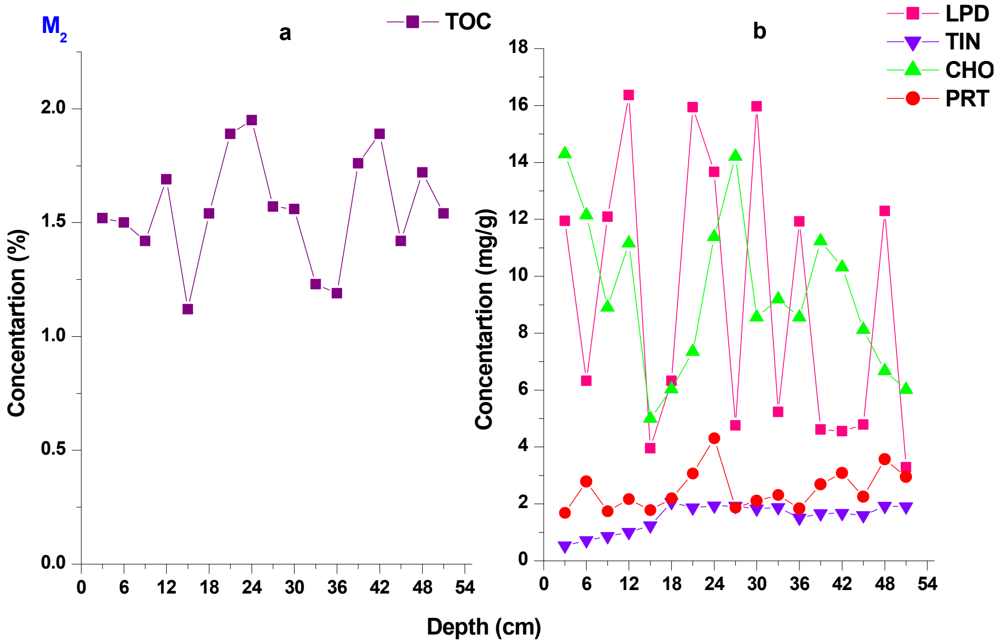

Figure 3.17 Distribution pattern of a) TOC and b) Organic matter in the sediment core M_2 (2011)

Core (N_1): Percentage of TOC ranged from 0.63 to 4.9. The maximum was noted at of 3-6 cm depth and the minimum at 39-42 cm portion of the sediment core (Figure 3.18a). In this core, the concentration of all OM was exhibited in the same manner and its level was highest at top to middle portions and decreased towards the bottom portion of the core. Concentration of the total carbohydrate ranged from 0.80 mg/g to 8.39 mg/g. Total protein concentration ranged from 0.64 mg/g to 10.25 mg/g.

Total lipids concentration ranged from 0.38 mg/g to 8.7 mg/g and finally the tannin and lignin content ranged from 0.7 mg/g to 3.31 mg/g. The relative OM distribution was in the order: LPD~PRT> CHO>TIN (Figure 3.18b).

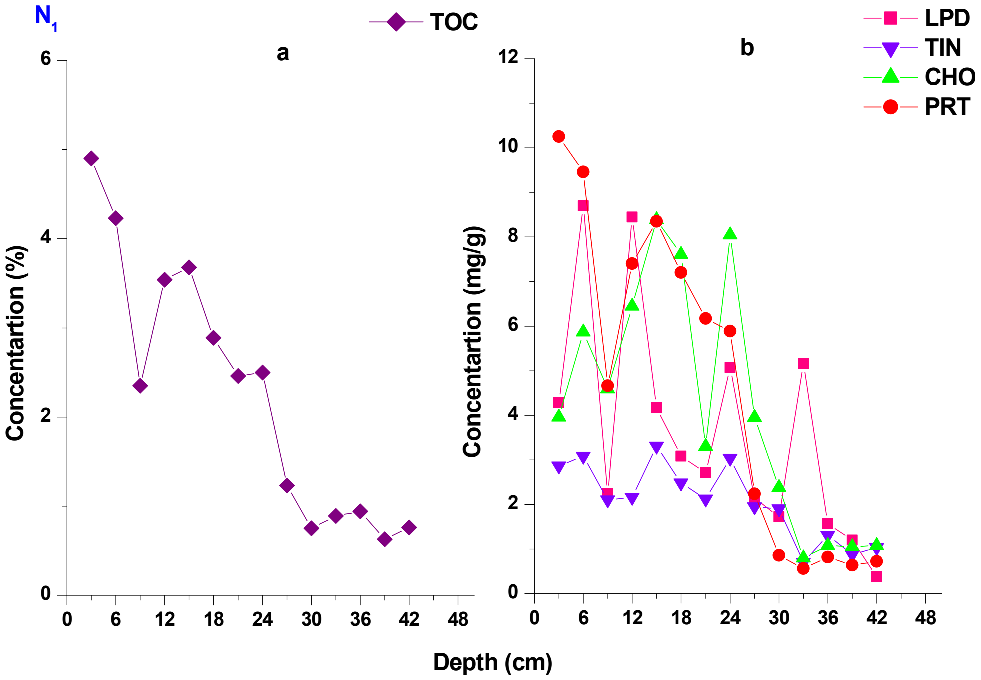

Figure 3.18 Distribution pattern of a) TOC and b) Organic matter in the sediment core N_1 (2011).

Core (N_2): Percentage of TOC ranged from 2.39 to 5.6, showing the lowest at bottom and highest at top to middle portions of the sediment core (Figure 3.19a). Total carbohydrate concentration ranged from 4.74 mg/g to 9.97 mg/g and the maximum and minimum concentrations were observed at 33-36 cm, 51-54 cm depths respectively. Towards the lower end of the core, concentration of carbohydrate was found to be decreased. Concentration of total protein ranged from 1.24 mg/g to 12.65 mg/g, and its level was highest at top portions of the sediment core. Slightly elevated concentration (13.45 mg/g) of lipid was found at the top and middle portions of the sediment core. Concentration of tannin and lignin in the core ranged from 0.73 mg/g to 3.31 mg/g. The relative organic matter (OM) distribution was in the order: LPD~ PRT > CHO> TIN (Figure 3.19b).

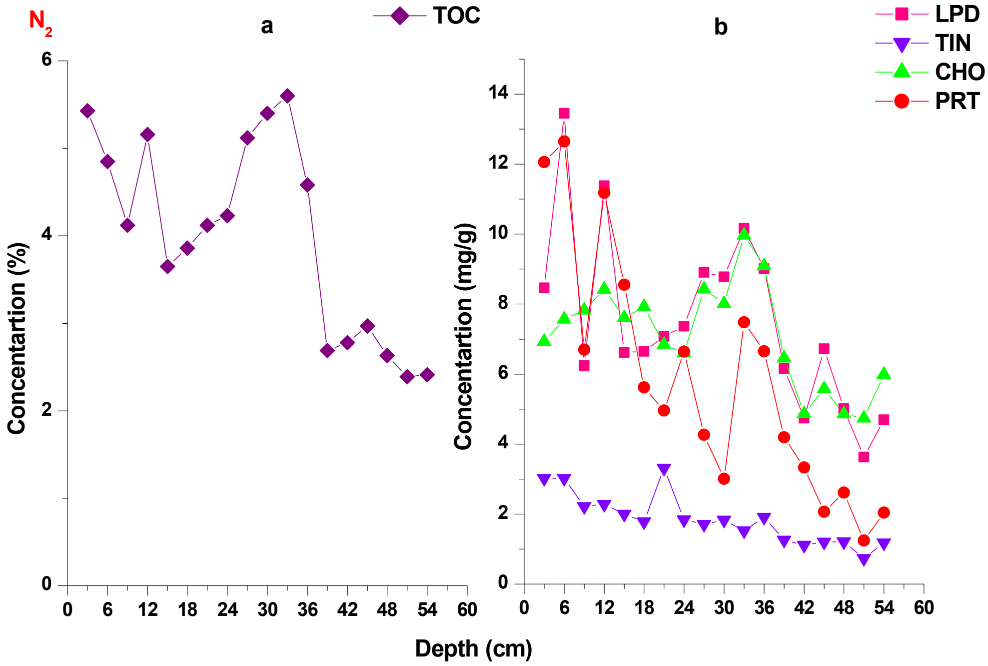

Figure 3.19 Distribution pattern of a) TOC and b) Organic matter in the sediment core N_2 (2011).

3.2.3.2 c Pigment Characteristics

Core (S_1): Amongst the phytopigments, chlorophyll-a ranged from 6.15 to 28.46 mg/Kg and it was significantly higher at middle portions of the core. The same trend was observed in the case of chlorophyll-b (45.3 mg/Kg) and chlorophyll-c (66.80 mg/Kg). Concentration of pheopigment ranged from 7.54 to 43.47 mg/Kg. Carotenoid levels were subjugated in this core and was significantly higher (76.53 mg/Kg) towards middle to bottom portions of the core (Figure 3.20).

Core (S_2): Among the phytopigments, chlorophyll-a ranged from 1.09 to 5.46 mg/Kg and was significantly high at middle portions of the core. The same trend was observed in the case of remaining pigments and the highest concentration of carotenoid (14.74 mg/Kg) was observed at 21-24 cm of the sediment core (Figure 3.20).

Core (M_1): Among the sedimentary pigments, chlorophyll-a ranged from BDL to 11.77 mg/Kg. Concentration of chlorophyll-a was BDL at bottom portions of the core. Concentration of pheophytin pigment was prime during both sampling periods and the highest concentration (79.08 mg/Kg) was observed at mid portions of the core (Figure 3.20).

Core (M_2): Amongst the phytopigments, chlorophyll-a ranged from 2.8 to 6.9 mg/Kg and it was slightly higher at bottom portions of the core. The same trend was observed in the case of chlorophyll-b, c and carotenoid. Levels of pheophytin were subjugated in this core and it was highest (7.93 mg/Kg) at bottom portions of the core (Figure 3.20).

Core (N_1): Concentration of chlorophyll-a ranged from 3.4 to 25.7 mg/Kg and it was slightly higher at top and bottom portions of the core. Concentration of pheophytin pigment was prime and the highest concentration (76.70 mg/Kg) was observed at bottom portions of the core. Levels of all pigments were subjugated in this core and it was highest at 33-36 cm portion (Figure 3.20).

Core (N_2): Concentration of chlorophyll-a ranged from 5.81 to 57.37 mg/Kg and it was highest at top and mid portions of the core. Concentration of carotenoid pigment was prime and the highest concentration (64.51 mg/Kg) was observed at 9-12 cm portion of the core. Levels of all pigments

(Chlorophyll a, b, c; Pheophytin and Carotenoid) were subjugated in top section of the core (Figure 3.20).

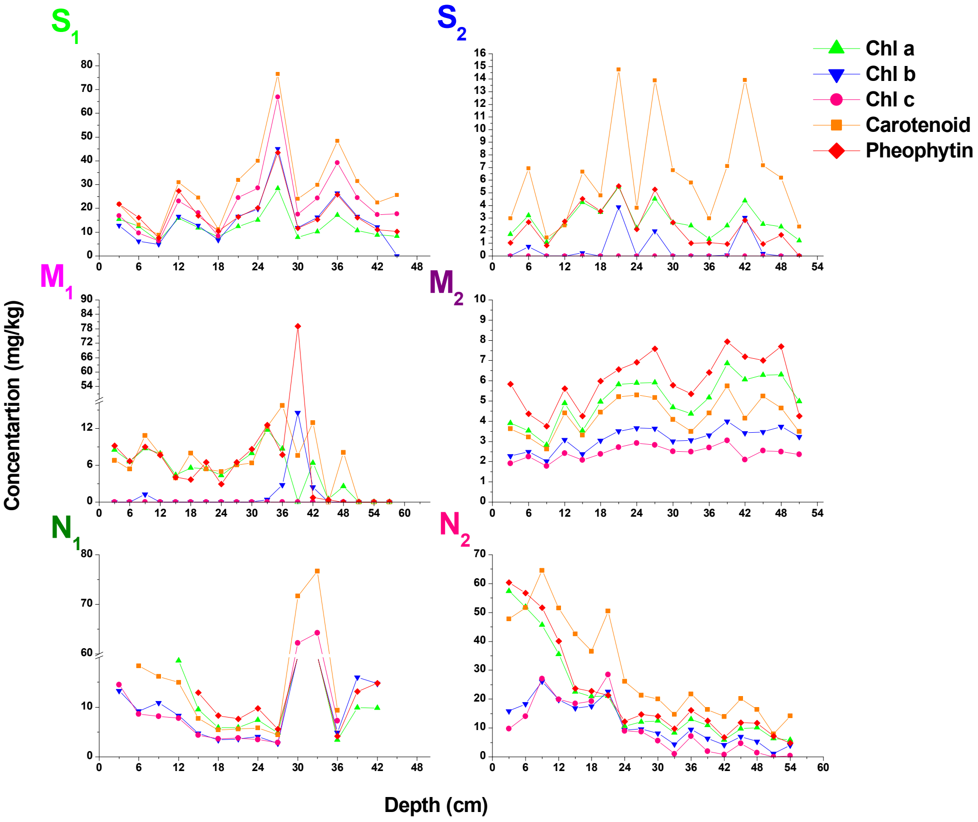

Figure 3.20 Down core variation of pigments in the sediment cores of CES (2011).

The overall results of biogeochemical analysis of sediment cores collected during 2009 and 2011 sampling periods in the CES are summarised as:

3.2.3.2 d Specific Features of Sedimentary Characteristics

- **Core S_1**
    - **pH:** Same trend with highest value was noted at bottom portions of the sediment core during both sampling periods.
    - **Eh:** Values of Eh were negative during first sampling period and it was exhibited a positive value on top portion of the sediment core during second sampling campaign.
    - **Texture:** Clay content was dominated during the first sampling campaign, besides a slightly higher sand fraction was observed at middle portion of the sediment core. During 2011 sampling period, sand content was dominated and somewhat higher percentage of silt was noted at top portion of the sediment core.
- **Core S_2**
    - **pH:** Increasing trend with minor fluctuations towards bottom section of the core during both sampling period.
    - **Eh:** Values of Eh were positive during first sampling period. During the second sampling campaign, it was exhibited a negative value in the entire sediment core.
    - **Texture:** Sand content was dominated during both sampling periods.

- **Core M_1**
    - **pH:** Increasing trend towards bottom section of the core during both sampling periods.
    - **Eh:** Values of Eh were negative during both the sampling period.
    - **Texture:** Sand content was dominated during both sampling periods. Besides, slightly higher percentage of silt was noted at top portion of the sediment core during second sampling campaign.
- **Core M_2**
    - **pH:** Decreasing trend towards bottom section of the sediment core during both sampling campaign.
    - **Eh:** Values of Eh were negative during both sampling periods.
    - **Texture:** Sand content was dominated during both sampling periods. Besides, slightly higher percentage of silt and clay fraction was noted at bottom portion of the sediment core during second sampling campaign.
- **Core N_1**
    - **pH:** Decreasing trend towards bottom section of the sediment core during both sampling periods.
    - **Eh:** Highest negative value was noted at middle to bottom portion of the sediment core during first sampling period.

During the second sampling campaign, it was found to exhibit highest positive value at top section of the sediment core.

- **Texture:** During 2009 sampling period, clay content was dominated and slightly higher sand fraction was detected at bottom section of the sediment core. During 2011 sampling period, increased clay fraction was noted towards middle to bottom section of the sediment core. Besides, slightly higher percentage of silt content was observed at top portion.

- **Core N_2**
    - **pH:** Same trend with minor fluctuations towards bottom section of the sediment core during both sampling periods.
    - **Eh:** Values of Eh were positive during both sampling campaign.
    - **Texture:** During 2009 sampling period, increased clay content was observed in the top to middle section of the sediment core. Increased silt fraction noted in the top section of the sediment core during second sampling campaign and towards bottom sand content was dominated.

Organic Matter

- **Core S_1**: Relative distribution of organic matters in the order: LPD>CHO>PRT>TIN (2009). During the second sampling campaign (2011), its order as CHO> PRT> LPD>TIN.
- **Core S_2**: Relative distribution of organic matters in the order: CHO >LPD>PRT>TIN (2009) and CHO >PRT>LPD>TIN (2011).

- **Core M_1**: Relative distribution of organic matters in the order: LPD>CHO>PRT>TIN (2009) and LPD>CHO>PRT>TIN (2011).
- **Core M_2**: Relative distribution of organic matters in the order: LPD>CHO>PRT>TIN (2009) and LPD>CHO>PRT>TIN (2011).
- **Core N_1**: Relative distribution of organic matters in the order: CHO >LPD>PRT>TIN (2009) and LPD~PRT>CHO>TIN (2011).
- **Core N_2**: Relative distribution of organic matters in the order: CHO> PRT> LPD>TIN

  (2009) and LPD~PRT>CHO>TIN (2011).

Pigment Characteristics

- **Core S_1**: During both sampling periods, concentration of carotenoid pigment was dominated.
- **Core S_2**: Compared to first sampling, concentration of all pigments were declines in second sampling campaign. Concentration of carotenoid pigment was dominated during both sampling period.
- **Core M_1**: Compared to first campaign concentration of chlorophyll-b,c and carotenoid were decreased in 2011 sampling period. Concentration of pheophytin pigment was dominated during both sampling period.
- **Core M_2**: During both sampling periods, concentration of pheophytin pigment was dominated.
- **Core N_1**: During 2009 sampling period, levels of all pigments were enriched in the top portion of the sediment core. But during second sampling period, concentration of all pigments were higher at

bottom portion of the sediment core. Concentration of pheophytin pigment dominated during both sampling period

- **Core N_2**: Concentration of pheophytin pigment was highest during first sampling period and levels of carotenoid pigment were dominated during second sampling campaign.
- During the both sampling periods, estimated chlorophyll-a to pheophytin value were <1 in all the sediment cores under this investigation, indicates the prevalence of detritus in the sediments.

3.2.3.2 e Discussion

A brief description on biogeochemical analysis of sediment cores collected during both sampling period was highlighted as follows.

- In general, the sediment cores showed a downcore decrease in organic carbon concentration. The designated cores, S_1, N_1 and N_2 (2009); N_1 and N_2 (2011), the organic carbon concentration decreased constantly whereas; in others no noticeable trend was observed. The decrease in the organic carbon contents could be very smooth, or irregular in certain sediment cores S_2, M_1 and M_2 (2009); S_1, S_2, M_1 and M_2 (2011). The downcore organic carbon contents locally may show a small sudden increase as well, which might be due to the presence of root matter. The slight decrease in trend of organic carbon in some sediment cores S_2, M_1 (2009); M_1 (2011) might be thought to result from the extensive bioturbation in those cores. Among the OM, dominance of carbohydrates over lipids and proteins in the cores S_2, N_1 and N_2 during the first sampling period, indicates lower nutritive aspect of the organic matter, and their aged and refractory nature. During the second sampling campaign, concentration of carbohydrate was highest in the cores S_1 and S_2. Higher lipid concentrations at the stations S_1, M_1& M_2 (2009) and M_1, M_2, N_1 & N_2 (2011) during both sampling periods could be attributed to the biological activity associated with the productive nature of the environment (cores from middle zone) including the anthropogenic input from the nearby industries situated in the study region (cores from north zone). Lignin like compounds may replace in large quantities from the water media by adsorption onto the microbial cell wall and also by processes like coagulation, sorption on particulates and dilution by receiving waters etc. These are readily moved about within the environment by process like tidal effect, runoff etc. Dilution effect may also be the reason for low concentration of these compounds compared to other organic matters in the study region. As compared to the first sampling campaign 2009, concentration of all OM in the sediment cores were decreased during 2011 sampling period, particularly in the southern part of the estuary.

- Among the phytopigments, distribution of pheophytin pigment in three cores ($N_{1,}$ $M_{1,}$ M_2) were highlighted. According to Dell's Anno et al., (2002), the predominance of pheopigments might be attributed to high turbidity, chemical contamination or other factors affecting photosynthetic potential of the primary producers. Besides, the higher concentration of carotenoid was detected in the fresh water augmented cores (S_1, S_2, N_2). Estimated chlorophyll-a to pheophytin value were <1 in all the sediment cores under this investigation, indicating the prevalence of detritus in the sediments. Similar observation was noted in the first sampling campaign, except in the station N_2.

- During 2011 study campaign, C/N ratio varied from 15.1 to 22.2, averaging 19.13 for core (S_1); from 17.3 to 22.2 averaging 18.5 for core (S_2); from 9.6 to 12.4, averaging 10.7 for core (M_1); from 18 to 31.7, averaging 22.6 for core (M_2) and from 13.1 to 42.2, averaging 23.6 for core (N_1); from 12.3 to 13.1 averaging 12.8 for core N_2. Among the six cores, C/N ratio was greater than 20 in four cores (S_1, S_2, M_2, & N_1) ascertaining the input of terrestrial material into the area, justifying that the source of organic matter is allochthonous also it clearly indicates the less productive and terrestrial OM could be a dominant contributor in the entire study region. Same trend was observed during the first sampling campaign. However the succession of post depositional changes may also modify the environment niche drastically. Percentage of elemental distributions (CHNS) in all the sediment cores were in the order: C> S>H>N.
- Protein to carbohydrate ratio(PRT:CHO) showed an average value of 0.67, 0.40, 0.43, 0.3, 0.84 & 0.79 in S_1, S_2, M_1, M_2, N_1 and N_2 cores respectively. Even though the middle zone is subjected to strong hydrodynamic conditions, sediments from this region also showed low PRT: CHO value. This may be due to the influence of anthropogenic inputs and rapid development activities in and around the study area. As compared to first sampling campaign, low protein to carbohydrate ratios confirms the presence of aged OM and the role of protein contribution as a potentially limiting factor for benthic consumers in the study region. Moreover, lipid to carbohydrate ratio (LPD:CHO) showed an average value of 1.66,

1.02, 1.24 and 1.05 in M_1, M_2, $N_1$and N_2 cores respectively, which in turn reflects energetic (food) quality of the organic contents in the study area and well supports the earlier literatures (Gremare et al., 2002; Gremare et al., 1997; Fabiano and Pusceddu, 1998). Relatively low LPD: CHO ratio was observed in the core S_1 (0.79) and S_2 (0.15) may be related to the decrease in lipid inputs derived from anthropogenic sources. Similar observation was noted in the first sampling campaign, except in the station S_1 and N_2. Percent average of BPC was in the order 0.53, 0.06, 0.74, 1.17, 0.66 & 1.13 in S_1,S_2, M_1, M_2, N_1 & N_2 cores respectively.

- The ratio of total organic carbon (TOC) percentages to total sulfur (TS) percentages (TOC:TS), was determined. It ranges from the sediment cores S_1 (3.35 to 5.7), S_2 (0.28 to 0.84) , M_1 (0.98 to 1.77), M_2 (0.25 to 1.21) and N_1 (2.52 to 10.14) and N_2 (4.78 to 15.5) respectively. Marine sediments undergoing sulfate reduction under euxinic/ inhospitable bottom conditions typically have TOC: TS ratios lower than 1.5 (Niffy Benny, 2009) and similar observation was found in the sediment cores S_2, M_1 and M_2 (2011). During the first sampling campaign, its value <1.5 was noted in the sediment cores (S_1, M_1, M_2, N_1) at the bottom section. Marine sediments endure sulfate reduction below an oxygenated water column exhibiting TOC: TS ratios in the range 1.5 to 5 and well corroborated earlier works conducted by Berner and Raiswell, (1983). Sediments in the stations (S_1, N_1, N_2) were characterized as under predominantly periodic anoxic stipulation in deeper portion of the core. Compared to first sampling period (2009), TOC/TS ratio in the core S_2 was below 1.5 which shows predominantly anoxic character of the aquatic niche. TOC/S ratio > 5 in the top to middle portions of the cores S_1, N_1 and N_2 are considered as oxic sediment with oxygenated bottom water. Moreover its ratio > 5 noted in the sediment cores S_2 and N_2 during the first sampling campaign, pointed out to substantial change in the nature of sedimentary environment.

3.2.3.2 f Statistical Analysis

The correlation analysis of various biogeochemical parameters of sediment cores collected during November 2011 were discussed as follows**.** In core S_1, TOC showed a high significant correlation with all OM. A significant correlation of organic matters with BPC establishes them as the major contributors to BPC. Besides, a profound correlation of clay and silt with OM was also observed. In core S_2, BPC had significant positive correlation with TIN and LPD, suggest that they are the major contributors of BPC. A significant positive correlation of fine fractions of sediment with PRT and TOC indicates their high affinity towards fine grained sediments. In core $M_{1,}$ BPC had a noticeable correlation with LPD followed by PRT was observed. This observation suggests that LPD and PRT is the major contributor of BPC. A considerable correlation of clay with chlorophyll-a also observed in this core. In core M_2, BPC showed a high significant correlation with LPD and suggest that LPD is the major contributor of BPC. TOC showed significant positive correlation with PRT, Chlorophyll-a, Chlorophyll-b, Carotenoid and Pheophytin. All pigments exhibited a significant positive correlation with clay, indicates the considerable affinity of these compounds towards fine grained sediments. In core $N_{1,}$ a very high significant correlation of TOC and BPC with all OM was observed. Besides, significant correlation of OM with silt also noted. In core $N_{2,}$ BPC showed a high significant positive correlation with all OM, indicating an equal contribution of all OM to BPC. TOC exhibited significant positive correlation with all OM. Moreover, pigments and OM exhibited significant positive correlation with clay and silt respectively. The result establishes the high affinity of these compounds into fine grained sediments.

To confirm the different variable associations, and the identification of parameters controlling the organic matter distribution, factor analysis was carried out (Table 3.10). In core $S_{1,}$ four factors accounts for 90.7 % of the total variance. The first factor shows significant positive loadings on OM and good loadings on clay and can be called the "Organic matter controlled factor". Factor-2 exhibits high positive loadings for pigments except chlorophyll-a and good loadings on clay and silt. This factor is called "Pigment controlled factor". Factor 3 and 4 shows no such significant positive loadings. In core $S_{2,}$ four factors accounts for 84% of the total variance. Factor-1 has high significant positive factor lodgings for all pigments and hence can be called the "Pigment controlled factor". Factor -2 and 3 associated with the OM component, and hence can be called the "Organic matter controlled factor". Factor-4 shows no such significant positive loadings. In core M_1, four factors accounts for 80 % of the total variance. Factor-1 shows significant positive loadings on PRT, LPD, Chlorophyll-a, Carotenoid, TOC & BPC and good loadings on clay. Thus, Factor-1 is associated with both OM component as well as pigment. This factor explains the significant binding role of these compounds in the fine grained sediments. Factor-2 exhibit significant positive loadings on chlorophyll-b and pheophytin and good loadings on LPD and BPC. This factor may be called "Pigment controlled factor-1". Factor-3 shows significant positive loadings on chlorophyll-b & pheophytin and good loadings on TIN, TOC and sand. This factor can be called the "Pigment controlled factor-2". Factor-4 with significant positive loadings on clay and good loadings on PRT, CHO, LPD and BPC, suggests the association of these OM with fine sediment fractions. This factor can be called the "Clay controlled factor", assuming the components to be enriched in the clay fraction. In core M_2, a four factor model explaining 85.7% of total variance has been adopted. Factor-1 has high significant positive factor loadings for all pigments and good loadings on Clay, Silt, TOC, TIN and PRT. This factor can be called "Pigment controlled factor". Factor-2 exhibits high positive loadings for BPC, TOC, LPD & CHO and good loadings on PRT, Carotenoid and Pheophytin. This factor can be called "Organic matter controlled factor". Factor-3 and 4 shows no such significant positive loadings. In core $N_{1,}$ four factors accounts for 96.6% of the total variance. The first factor shows significant positive loadings on PRT, CHO, TIN, TOC, BPC, Sand & Silt and good loadings on LPD. This factor may be called the "Organic matter controlled factor". Factor-2 exhibits high positive loadings for all pigments and good loadings for silt and lipid. This factor can be called the "Pigment controlled factor". Factor 3 and 4 shows no such positive loadings.

Thus, from factor analysis it is inferred that "organic matter controlled factor", has a maximum amount of total variance in all the core sediments, indicating good correlation of OM in most of the variables studied. However, combining the sedimentary record with other biological and geochemical indicators in multi-proxy studies still constitutes the most robust method for interpreting long term changes in ecosystem structure.

3.3 Conclusion

Biogeoorganics describe the entire array of organic compounds in the aquatic realm and includes the investigations on the source of organic substances, their pathways along which they enter the aquatic environment. Therefore, the studies in both the surface and core sedimentary environment will provide a deeper insight into the complexities that govern the organic load, source, fate and transformations of organics in the aquatic niche. The present study has been the first comprehensive attempt ever made to characterize the core sediment biogeoorganics in the specific zones of CES. It has served to emphasis the prominent role for regulating the complex interactive forces that operate within the estuarine system and also provides a baseline data for future research on anthropogenic impacts in this region. The distribution of biogeoorganics in the Cochin estuary is influenced by the increasing human activities, waste discharge from major industrial establishments into the Periyar and Muvattupuzha rivers, river runoff and also by the sewage through a network of large and small canals. The detrimental effects of these complex pollutants not only affect the water quality but also the quality of the sediment. An entire idea of the bottom sediment is thus a pre-requisite for future water quality management procedures.

Biogeochemical evaluation of the study region revealed that organic matter in the sediments in the CES are aged and the role of protein contribution as a potentially limiting factor for benthic consumers. Overall, C/N ratio supports the allochthonous character of the sediments in the aquatic system and it clearly indicates the terrestrial OM could be the dominant contributor in the study region and make profound influence in the biogeochemical processes.

In the case of sedimentary pigments, all the studied pigments showed the same down- core trend, indicating that there is no major change in the dominant phytoplankton groups which has occurred in the aquatic niche. Apart from these, each site represents a unique depositional environment with regard to preservation conditions. During both the sampling periods, estimated chlorophyll-a to pheophytin value were <1 in all the sediment cores, indicating the prevalence of detritus in the sediments. These detrital organic matter accumulation in sediment, degrades the quality of organic constituents; limiting the benthic ecology and acting as a potential carrier of toxic pollutants. Heterotrophy has potent green house implications and hence it is highly imperative to develop a sustainable management strategy to prevent further degradation of this fragile ecosystem. The background information on biogeoorganics is deeply authenticated in the next Chapters 4 and 5, which describes both the spatial and vertical distribution pattern of Organochlorine Insectisides (OCIs) in the CES.

The salient features discussed in the above chapter was published in the journal "***Journal of Earth System Science***" as a research article entitled "**Core Sediment Biogeochemistry in Specific Zones of Cochin Estuarine System (CES)**" by the authors P S Akhil, Nair P Manju and C H Sujatha. Vol. 122-126, pp. 1557–1570 (2013).

Table 3.3 Factor analysis matrix in the surface sediments of CES

3.3a First sampling campaign (2009)

	Component			
	1	2	3	4
PRT	.723	.550	-.288	-.056
CHO	.894	.213	-.110	-.037
TINN	.340	.343	-.217	.826
LPD	.634	.618	-.240	-.221
Chla	.865	-.446	.031	.087
Chlb	.900	-.347	.144	.083
Chlc	.896	-.161	.138	-.028
Carotenoid	.822	-.522	.139	-.025
Pheophytin	.792	-.534	.049	.074
Sand	.044	-.909	-.101	-.025
Clay	-.049	.868	-.032	-.031
Slit	.004	.598	.664	.270
TOC	.566	.482	.497	-.233
BPC	.811	.499	-.224	-.124

Extraction Method: Principal Component Analysis.
a 4 components extracted.

3.3b Second sampling campaign (2011)

	Component			
	1	2	3	4
PRT	.785	-.480	.334	-.069
CHO	.769	-.453	-.039	-.286
TINN	.768	-.547	.052	-.041
LPD	.857	-.222	.375	.115
Chla	.794	.522	-.205	.059
Chlb	.795	.566	-.139	.122
Chlc	.819	.488	.037	-.055
Carotenoid	.751	.636	-.059	.044
Pheophytin	.740	.588	-.218	.035
Sand	-.352	.457	.804	-.079
Clay	.291	-.242	-.796	-.440
Slit	.235	-.493	-.351	.758
TOC	.873	-.156	.262	.036
BPC	.868	-.412	.256	-.071

Extraction Method: Principal Component Analysis.
a 4 components extracted.

Table 3.4 Correlation between sedimentary parameters in the surface sediments of CES.

3.4a First sampling campaign (2009)

	PRT	CHO	TINN	LPD	Chla	Chlb	Chlc	Carotenoid	Pheophytin	Sand	Clay	Slit	TOC	BPC
PRT	1													
CHO	**0.805**	1												
TINN	0.446	0.34	1											
LPD	**0.878**	**0.67**	0.32	1										
Chla	0.348	**0.67**	0.19	0.20	1									
Chlb	0.394	**0.69**	0.22	0.31	**0.94**	1								
Chlc	0.461	**0.69**	0.20	0.44	**0.86**	**0.93**	1							
Carotenoid	0.237	**0.61**	0.04	0.16	**0.96**	**0.94**	**0.84**	1						
Pheophytin	0.261	**0.57**	0.12	0.12	**0.97**	**0.89**	**0.76**	**0.95**	1					
Sand	-0.362	-0.13	-0.26	-0.43	0.37	0.32	0.10	0.45	0.46	1				
Clay	0.356	0.12	0.23	0.43	-0.35	-0.33	-0.09	-0.45	-0.44	-0.98	1			
Slit	0.190	0.10	0.26	0.19	-0.25	-0.10	-0.08	-0.24	-0.28	-0.53	0.36	1		
TOC	**0.564**	**0.52**	0.12	**0.61**	0.25	0.37	0.47	0.26	0.19	-0.39	0.32	**0.51**	1	
BPC	**0.963**	**0.89**	0.39	**0.92**	0.44	**0.50**	**0.58**	0.37	0.34	-0.34	0.33	0.17	**0.62**	1

3.4b Second sampling campaign (2011)

	PRT	CHO	TINN	LPD	Chla	Chlb	Chlc	Carotenoid	Pheophytin	Sand	Clay	Slit	TOC	BPC
PRT	1													
CHO	**0.79**	1												
TINN	**0.88**	**0.86**	1											
LPD	**0.87**	**0.70**	**0.77**	1										
Chla	0.28	0.42	0.36	0.48	1									
Chlb	0.30	0.33	0.29	**0.52**	**0.96**	1								
Chlc	0.46	0.35	0.34	**0.61**	**0.84**	**0.92**	1							
Carotenoid	0.27	0.24	0.20	0.49	**0.92**	**0.96**	**0.94**	1						
Pheophytin	0.20	0.37	0.27	0.41	**0.99**	**0.95**	**0.83**	**0.92**	1					
Sand	-0.23	-0.45	-0.45	-0.12	-0.18	-0.14	-0.06	-0.04	-0.14	1				
Clay	0.12	0.44	0.30	-0.03	0.21	0.15	0.15	0.11	0.19	-0.84	1			
Slit	0.25	0.21	0.40	0.26	0.05	0.05	-0.10	-0.09	-0.01	-0.65	0.13	1		
TOC	**0.87**	**0.64**	**0.70**	**0.88**	**0.50**	**0.56**	**0.68**	**0.60**	0.43	-0.21	0.12	0.21	1	
BPC	**0.96**	**0.88**	**0.90**	**0.93**	0.42	0.41	**0.52**	0.37	0.35	-0.28	0.17	0.27	**0.87**	1

Table 3.5 Variation of pH and Eh in the sediment cores (2009 Sampling Period).

	pH						Eh (mV)					
	Sediment Cores						Sediment Cores					
Length of the core (cm)	**S1**	**S2**	**M1**	**M2**	**N1**	**N2**	**S1**	**S2**	**M1**	**M2**	**N1**	**N2**
0-3	5.4	7.5	7.0	8.6	6.6	5.7	-118	264	-267	-314	-254	284
3-6	5.8	7.6	7.0	8.6	6.5	5.8	-110	243	-264	-312	-252	283
6-9	5.6	7.6	7.1	8.7	6.4	5.8	-107	247	-266	-312	-255	280
9-12	5.4	7.6	7.1	8.6	6.6	5.8	-127	218	-263	-310	-264	276
12-15	6.1	8.1	7.0	8.4	6.6	5.6	-143	234	-263	-324	-286	270
15-18	6.4	8.1	7.4	8.0	6.4	5.5	-140	122	-263	-334	-376	266
18-21	6.4	8.4	7.6	8.1	6.3	5.6	-137	102	-270	-341	-371	270
21-24	6.4	8.7	7.6	8.0	6.3	6.6	-137	116	-274	-352	-373	280
24-27	6.7	8.6	8.0	8.0	6.1	6.7	-142	108	-279	-376	-370	281
27-30	6.8	8.7	7.7	8.0	6.1	7.1	-136	107	-301	-392	-375	266
30-33	6.7		7.8	8.2		7.2	-224		-306	-398		241
33-36	7.0		7.9	8.0		7.3	-245		-294	-402		241
36-39	7.0		7.9	8.0		7.3	-247		-297	-408		232
39-42	7.2		8.0	8.0		7.1	-263		-297	-409		218
42-45	7.0		8.0	8.2		7.1	-261		-297	-410		197
45-48			7.8	8.3		7.2			-318	-411		197
48-51			7.9	8.0		7.1			-324	-412		186
51-54			7.9	8.0		7.0			-320	-412		176
54-57				8.0		7.3				-412		174
57-60				8.0		7.4				-411		172
60-63				7.9		7.4				-411		

Table 3.6 Grain size distribution pattern in the sediment cores (2009 Sampling Period).

	S1			S2			M1			M2			N2			N1		
Sample length	Sand	Clay	Silt	Sand	Clay	Silt	Sand	Clay	Silt	Sand	Clay	Silt	Sand	Clay	Silt	Sand	Clay	Silt
(cm)	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
0-3	28.41	71.03	0.55	92.75	5.13	2.12	93.7	5.656	0.643	76.92	9.8	13.27	6.98	80.31	12.71	14.511	85.407	0.081
3-6	16.77	41.99	41.22	93.13	4.13	2.74	76.77	22.85	0.367	65.26	9.8	24.93	5.68	81.83	12.49	14.028	73.01	12.96
6-9	18.71	73.78	7.5	90.4	6.71	2.89	76.97	21.76	1.265	88.51	4.9	6.58	3.99	84.35	11.66	36.143	48.33	15.52
9-12	53.36	33.28	13.34	82.3	10.12	7.58	72.43	25.44	2.113	76.06	14.7	9.23	5.84	83.81	10.35	12.7	72.87	14.42
12-15	66.62	3.238	30.13	93.71	5.21	1.08	66.56	33.2	0.225	72.47	19.6	7.92	7.02	82.33	10.65	16.87	77.36	5.75
15-18	63.63	34.49	1.867	95.58	2.32	2.1	72.49	27.08	0.419	83.76	9.8	6.43	3.46	85.68	10.86	38.34	58.65	3
18-21	48.46	28.33	23.19	94.28	4.31	1.41	77.15	18.37	4.479	83.5	14.7	1.798	3.09	86.71	10.2	33.48	59.78	6.73
21-24	70.24	24.03	5.72	94.03	4.13	1.84	89.15	10.5	0.348	65.79	29.4	4.8	3.78	82.81	13.41	54.45	41	4.54
24-27	65.69	23.92	10.38	92.5	5.18	2.32	86.09	10.29	3.61	70.7	19.6	9.69	6.99	84.23	8.78	97.67	1.929	0.393
27-30	32.23	65.98	1.78	81.74	15.81	2.45	89.94	8.25	1.797	36.76	39.2	24.03	5.61	87.32	7.07	92.71	3.42	3.86
30-33	29.71	70.22	0.054				91.16	8.02	0.818	40.93	19.6	39.46	2.97	88.91	8.12			
33-36	0.173	97.7	2.123				84.08	10.64	5.267	73.56	14.7	11.73	6.22	87.72	6.06			
36-39	6.89	91.33	1.77				4.14	92.54	3.316	60.77	19.6	19.62	5.86	84.13	10.01			
39-42	6.26	93.61	0.114				73.59	25.99	0.412	43.33	14.7	41.96	6.49	85.82	7.69			
42-45	2.1	97.78	0.107				66.19	5.64	28.15	66.15	14.7	19.14	10.46	80.73	8.81			
45-48							73.94	7.44	18.6	55.58	19.6	24.81	12.52	70.82	16.66			
48-51							75.53	9.31	15.15	52.06	24.5	23.43	9.8	78.21	11.99			
51-54							54.63	27.25	18.11	52.77	39.2	8.02	82.01	11.31	6.68			
54-57										38.08	24.5	37.41	81.73	12.53	5.74			
57-60										34.51	19.6	45.88	96.67	2.21	1.12			
60-63										45.9	14.7	39.39	64.45	21.23	14.32			

Table 3.7 Factor analysis matrix for six sediment cores (First sampling Period 2009)

3.7a Sediment Core S_1

	Component			
	1	2	3	4
LIPID(mg/g)	-.018	.708	.670	-.187
Tanin & Lignin(mg/g)	.595	.505	.369	.232
Carbohydrate(mg/g)	.433	.318	-.611	.335
Protein(mg/g)	-.104	.557	-.583	.292
Chl-a (mg/Kg)	.932	-.007	-.040	.048
Chl-b(mg/Kg)	.869	-.303	.225	.297
Chl-c(mg/Kg)	.869	-.290	.260	.268
Carotenoid(mg/Kg)	.835	-.312	.266	.316
Pheophytin(mg/Kg)	.716	.588	-.168	-.182
Sand%	-.734	-.248	.465	.304
Clay%	.809	.022	-.310	-.484
Silt%	-.527	.447	-.168	.587
BPC%	.033	.879	.433	-.064

3.7b Sediment Core S_2

Component Matrix (a)

	Component			
	1	2	3	4
Protein	.022	.695	-.031	.607
Carbohydrate	.448	.575	-.073	-.641
Tannin	.423	.154	-.046	.818
Lipid	.634	.549	-.254	.384
Chla	.965	-.006	.136	.020
Chlb	.912	-.318	.214	.008
Chlc	.841	-.349	.394	-.001
Carotenoid	.909	-.241	.305	-.009
Pheophytin	.826	.312	.104	-.110
Sand	.464	-.531	-.690	.000
Clay	-.537	.363	.659	.006
Silt	-.105	.662	.454	-.014
TOC	.034	.510	-.724	-.093
BPC	.531	.675	-.117	-.445

Extraction Method: Principal Component Analysis.
a 4 components extracted.

3.7c Sediment Core M_1

Component Matrix[a]

	Component			
	1	2	3	4
LIPID(mg/g)	.507	.726	.316	-.182
Tanin & Lignin(mg/g)	.518	-.598	.044	-.394
Carbohydrate(mg/g)	.870	.135	.045	-.284
Protein(mg/g)	-.103	.218	-.857	.321
Chl-a (mg/Kg)	.944	-.172	.035	.232
Chl-b(mg/Kg)	.758	.086	.062	.165
Chl-c(mg/Kg)	.446	.169	.392	.754
Carotenoid(mg/Kg)	.958	-.123	-.011	.207
Pheophytin(mg/Kg)	.837	-.317	-.096	-.047
Sand%	-.881	.225	.307	.049
Clay%	.842	.145	-.433	-.096
Silt%	.127	-.858	.275	.105
BPC%	.706	.619	.177	-.215

Extraction Method: Principal Component Analysis.

a. 4 components extracted.

3.7d Sediment Core M_2

Component Matrix [a]

	Component		
	1	2	3
LIPID(mg/g)	.126	.835	.432
Tanin & Lignin(mg/g)	.843	.230	-.062
Carbohydrate(mg/g)	.077	.466	-.173
Protein(mg/g)	.633	.404	-.138
Chl-a (mg/Kg)	.909	-.280	.065
Chl-b(mg/Kg)	.773	-.374	.325
Chl-c(mg/Kg)	.566	-.382	.695
Carotenoid(mg/Kg)	.917	-.271	-.017
Pheophytin(mg/Kg)	.463	-.157	-.702
Sand%	-.814	-.311	.218
Clay%	.267	.789	-.268
Silt%	.818	-.124	-.094
BPC%	.150	.855	.407

Extraction Method: Principal Component Analysis.

a. 3 components extracted.

3.7e Sediment Core N_1

Component Matrix[a]

	Component		
	1	2	3
LIPID(mg/g)	.554	-.694	-.357
Tanin & Lignin(mg/g)	.915	-.250	.184
Carbohydrate(mg/g)	.833	-.050	.222
Protein(mg/g)	.862	-.268	.086
Chl-a (mg/Kg)	.929	.042	-.075
Chl-b(mg/Kg)	.771	.596	-.015
Chl-c(mg/Kg)	.774	.558	-.172
Carotenoid(mg/Kg)	.848	.413	-.236
Pheophytin(mg/Kg)	.550	.399	.246
Sand%	-.984	.101	.089
Clay%	.958	-.081	-.250
Silt%	.525	-.139	.801
BPC%	.860	-.423	-.052

Extraction Method: Principal Component Analysis.

a. 3 components extracted.

3.7f Sediment Core N_2

Component Matrix (a)

	Component			
	1	2	3	4
Protein	.891	.264	-.060	.130
Carbohydrate	.728	.221	.050	.285
Tannin	.867	.119	-.311	-.005
Lipid	.482	-.081	.839	.081
Chla	.214	.936	.081	-.199
Chlb	-.468	.841	-.051	.187
Chlc	-.627	.715	-.041	.218
Carotenoid	-.302	.947	.038	-.041
Pheophytin	.280	.858	.077	-.333
Sand	-.954	.041	.181	.004
Clay	.940	-.040	-.192	.089
Silt	.528	-.027	.013	-.789
TOC	.687	.262	-.267	.226
BPC	.884	.157	.379	.194

Extraction Method: Principal Component Analysis.

a 4 components extracted.

Table 3.8 Variation of pH and Eh in the sediment cores (2011 Sampling Period).

	pH						Eh (mV)					
	Sediment Cores						Sediment Cores					
Length of the core (cm)	S1	S2	M1	M2	N1	N2	S1	S2	M1	M2	N1	N2
0-3	6.5	7.5	7.4	8.3	6.8	5.3	211	-323	-109	-98	370	354
3-6	6.5	7.4	7.4	8.3	6.8	5.4	218	-326	-108	-97	376	346
6-9	6.4	7.5	7.4	8.3	6.8	5.2	217	-337	-109	-110	318	370
9-12	6.3	7.4	7.3	8.4	7.0	5.2	197	-376	-114	-118	346	376
12-15	6.7	7.4	7.3	8.5	6.8	5.8	196	-383	-124	-120	286	244
15-18	7.0	7.7	7.6	8.4	6.7	5.9	187	-393	-136	-184	218	233
18-21	7.2	7.8	7.7	7.8	6.7	6.2	188	-412	-137	-193	184	119
21-24	6.9	7.4	7.7	7.8	6.5	7.2	164	-434	-141	-201	76	84
24-27	7.4	7.5	7.7	7.9	6.5	7.6	118	-433	-147	-210	-18	83
27-30	7.4	7.5	8.0	7.7	6.3	7.8	97	-412	-166	-201	-34	76
30-33	7.5	7.5	7.9	7.7	6.5	8.1	-86	-418	-174	-208	-66	71
33-36	7.4	7.5	7.9	7.1	6.4	8.1	-96	-426	-182	-211	-74	78
36-39	7.4	7.8	7.8	7.1	6.4	7.9	-101	-433	-210	-201	-86	71
39-42	7.4	7.9	7.7	6.9	6.4	7.1	-97	-428	-211	-208	-84	66
42-45	7.4	8.0	7.9	7.0		7.1	-97	-428	-216	-211		64
45-48		8.0	8	7.0		6.8		-429	-215	-210		72
48-51		7.8	8	7.0		6.8		-429	-215	-211		76
51-54			7.8						-215			
54-57			7.9						-216			
57-60												
60-63												

Table 3.9 Grain size distribution pattern in the sediment cores (2011 Sampling Period).

	S1			S2			M1			M2			N2			N1		
Sample length	**Sand**	**Clay**	**Silt**	**Sand**	**Clay**	**Silt**	**Sand**	**Clay**	**Silt**	**Sand**	**Clay**	**Silt**	**Sand**	**Clay**	**Silt**	**Sand**	**Clay**	**Silt**
(cm)	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
0-3	28.0	23.1	48.8	98.2	1.7	0.1	51.16	14	34.84	64.22	7.19	28.59	4.4	15.2	80.4	14.2	35.5	50.3
3-6	36.2	18.4	45.3	94.4	1.5	4.1	63.28	17.6	19.12	81.71	0	18.29	5.1	21.1	73.2	13.2	45.2	41.3
6-9	41.5	12.2	46.2	96.7	2.7	0.6	46.43	44.84	8.73	77.82	4.95	17.23	8.9	85.9	78.6	8.7	62.1	28.9
9-12	40.6	19.8	38.9	76.5	11.2	12.3	40.93	15.72	43.35	75.99	8.25	15.76	12.5	19.2	68.2	15.4	66.3	18.2
12-15	52.8	11.2	35.1	95.8	2.3	1.9	72.52	17.25	10.23	72.32	5.26	22.42	10.6	23.5	65.8	14.2	71.2	14.2
15-18	54.3	15.6	29.6	83.6	10.7	5.6	68.29	8.63	23.08	54.11	5.41	40.48	7.3	20.4	72.3	9.6	80.2	10.2
18-21	58.6	11.2	30.1	94.6	4.7	0.7	57.92	22.74	19.34	53.15	11.45	35.4	5.3	16.1	78.6	7.6	84.6	7.6
21-24	61	9.6	29.4	83.0	10.1	6.9	76.34	13.84	9.82	43.1	13.02	43.88	7.2	12.3	80.3	11.0	87.6	1.5
24-27	60.9	8.3	30.8	84.0	4.0	11.9	71.81	26.83	1.36	50.99	13.18	35.83	3.6	8.9	87.3	5.7	88.9	5.3
27-30	75.6	4.3	28.7	92.5	5.2	2.3	70.13	20.74	9.13	62.49	14.14	23.37	3.0	8.0	88.9	8.2	87.6	4.2
30-33	78.3	3.1	18.6	93.0	4.5	2.5	67.47	20.76	11.77	48.25	22.76	28.99	12.3	12.2	75.3	5.8	90.2	3.8
33-36	74.3	10.4	15.3	92.0	2.0	6.0	70.2	18.6	10.2	60.91	18.98	20.11	18.2	10	71.6	5.3	92.3	2.3
36-39	68.7	16.8	14.2	94.2	1.1	4.7	71.5	14.2	14.2	56.48	32.97	10.55	17.5	14.2	68.3	8.2	90.7	1.2
39-42	86.7	3	10.3	95.6	4.3	0.1	75.3	16.4	8.1	43.68	22.99	33.33	25.6	7.1	67.2	3.6	94.5	1.9
42-45	82.7	8.8	8.5	95.3	3.7	1.0	78.6	11.8	9.5	31.05	34.25	34.7	18.6	23.1	58.3			
45-48				94.9	4.6	0.6	79.6	12.3	7.8	43.16	21.37	35.47	26.9	19.8	52.3			
48-51				96.1	3.9	0.0	74.1	10.4	15.4	57.86	15.87	26.27	36.2	15.1	48.6			
51-54							80.97	13.49	5.54				41.3	14.9	43.8			
54-57							75.68	13.84	10.48									

Table 3.10 Factor analysis matrix for six sediment cores (Second sampling Period 2011)

3.10 a Sediment Core S_1

	Component			
	1	2	3	4
PRT	.907	.018	.323	.016
CHO	.802	.052	-.357	-.023
TIN	.878	.170	.107	.048
LPD	.747	-.188	.473	-.255
Chla	.007	.989	.103	.040
Chlb	-.266	.925	-.091	-.227
Chlc	-.496	.017	.573	.614
Carotenoid	-.445	.883	.112	-.026
Pheophyitin	-.023	.987	-.005	.080
Sand	-.886	-.194	.260	-.241
Clay	.756	.125	-.194	.530
Silt	.829	.174	-.275	.037
TOC	.739	.305	.309	-.242
BPC	.949	-.041	.245	-.084

Extraction Method: Principal Component Analysis.
a 4 components extracted.

3.10b Sediment Core S_2

	Component			
	1	2	3	4
PRT	.649	-.498	.039	-.021
CHO	.209	-.485	.549	.528
TIN	.487	-.331	.585	-.229
LPD	.382	.617	.236	-.574
Chla	.875	.283	-.278	.150
Chlb	.712	.559	-.226	-.021
Carotenoid	.746	.490	-.207	.304
Pheophytin	.805	.089	-.454	.017
Sand	-.379	.833	.315	.158
Clay	.353	-.681	-.123	-.447
Silt	.306	-.753	-.390	.113
TOC	.627	.002	.404	.239
BPC	.753	.068	.582	-.118

Extraction Method: Principal Component Analysis.
a 4 components extracted.

3.10c Sediment Core M_1

	Component			
	1	2	3	4
PRT	.643	.003	-.256	.217
CHO	.181	-.594	-.067	.253
TIN	.217	-.710	.464	-.067
LPD	.656	.608	-.142	.202
Chla	.746	-.528	.083	-.240
Chlb	.190	.741	.600	-.075
Carotenoid	.695	-.158	.416	-.207
Pheophytin	.274	.649	.568	-.143
Sand	-.827	-.041	.441	.110
Clay	.612	-.187	.142	.609
Silt	.436	.189	-.605	-.597
TOC	.780	-.323	.300	-.244
BPC	.773	.382	-.187	.315

Extraction Method: Principal Component Analysis.
a 4 components extracted.

3.10d Sediment Core M_2

	Component			
	1	2	3	4
PRT	.609	.223	-.465	-.155
CHO	.026	.505	.560	-.584
TIN	.760	-.321	-.346	.254
LPD	-.031	.860	-.186	.398
Chla	.969	-.025	.142	.010
Chlb	.966	-.026	.111	.119
Chlc	.800	.077	.243	.304
Carotenoid	.900	.163	.223	.085
Pheophytin	.888	.133	.258	-.111
Sand	-.839	.287	.177	.170
Clay	.696	-.366	.365	.100
Silt	.519	-.047	-.635	-.353
TOC	.599	.554	-.200	-.280
BPC	.034	.956	-.051	.185

Extraction Method: Principal Component Analysis.
a 4 components extracted.

3.10e Sediment Core N_1

	Component			
	1	2	3	4
PRT	.975	.061	-.034	.070
CHO	.822	-.190	.434	.217
TIN	.895	-.066	.153	.354
LPD	.691	.404	.355	-.468
Chla	.078	.961	-.091	.036
Chlb	-.569	.791	.157	.135
Chlc	-.635	.723	.193	.123
Carotenoid	-.582	.784	.160	.085
Pheophytin	-.039	.977	-.025	-.053
Sand	.877	.265	.178	.041
Clay	-.804	-.431	.404	-.013
Silt	.730	.440	-.515	.006
TOC	.966	.158	-.100	.026
BPC	.940	.161	.263	-.124

Extraction Method: Principal Component Analysis.
a 4 components extracted.

3.10f Sediment Core N_2

	Component			
	1	2	3	4
PRT	.863	-.085	.418	.003
CHO	.652	-.501	-.209	.461
TIN	.892	.087	.020	-.336
LPD	.759	-.507	.251	.099
Chla	.847	.329	.332	-.057
Chlb	.854	.445	-.186	-.026
Chlc	.750	.455	-.346	-.045
Carotenoid	.877	.465	-.017	-.029
Pheophytin	.854	.319	.321	-.020
Sand	-.823	.252	.382	.194
Clay	.342	.720	-.202	.496
Silt	.684	-.391	-.498	-.159
TOC	.788	-.538	-.093	.075
BPC	.868	-.370	.278	.125

Extraction Method: Principal Component Analysis.
a 4 components extracted.

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4

SPATIAL BUDGETARY EVALUATION OF ORGANOCHLORINE CONTAMINANTS IN THE CES

4.1 Introduction

Estuarine sediments act both as a short or long term reservoir for many type of organic/inorganic contaminants (OCIs, PAHs, PCBs, trace metals etc). Diffusion, advection, mixing and resuspension of the sediment will affect the distribution of these trace contaminants in the estuarine niche. Therefore, a comprehensive idea on these disciplines will contribute a major role for the assessment of water quality and their management procedures in the aquatic system. Hence, the present chapter elucidate the spatial trend pattern of OCI residues in the surface sediments of CES. The main theme and objective of the study is to account the contaminant levels, distribution pattern and other contributing sources for assessing the environmental impact in the ecosystem.

As per the review of literature discussed in the Chapter-1 pointed out that, the data on residual levels of pesticide accumulation in the marine sediments is limited (Sarkar and SenGupta, 1987, 1988, 1991; Takeoka et al., 1991; Sarkar et al., 1997; Pandit et al., 2001; Pandit et al., 2002; Guzzella et al., 2005; Sarkar, et al., 2008) especially in the coastal belt of India, indicating the presence of their major emission sources in these regions. A few reports are available on the residual levels of conservative pesticides in CES (Sujatha et al., 1991, 1993, 1994 and 1999) but no systematic and scientific studies concerning these persistent contaminants in sediment were reported. The applied and direct dumping of industrial wastes of these persistent contaminants can be transported through surface run-off, leaching, ultimately accumulating and getting settled into the bottom sediments. Hence these bottom sediments represent an integrated conspicuous level of particle bound contaminants that have deposited over a longer period of time. Most of the earlier research contributions were based on one-time or seasonal sampling during a year, from the areas known for environmental pollution (Barakat, 2003; Khaled et al., 2004; Said et al., 2008). An approach based on the analysis of OCI residues in sediments collected over a considerable time period could provide any specific changes in the pollution status of the CES and such studies are limited. For the assignment, surface sediments (top 0-5 cm) were collected from seventeen locations of CES during November 2009 and November 2011 (post monsoon season) for performing OCI residual analysis. Details regarding the sampling and analytical procedure of these trace organics were mentioned in the Chaper-2. Seventeen surface sediment samples were grouped into three zones - South, Middle and North based on environmental variability such as the physicochemical and sediment characteristics. The results discussed hither are on the basis of three zones. The following organochlorine insecticides were quantified: α-hexachlorocyclohexane (α-HCH), β-HCH, γ-HCH, heptachlor, heptachlor epoxide (B), aldrin, dieldrin, endrin, 4,4’-DDE, 2,4’-DDD, 4,4’-DDD, 2,4’-DDT, 4,4’-DDT, α-endosulfan, and β-endosulfan. The findings will constitute the base line data set for the OCI residues in the sediments of CES.

4.2 Results and Discussion

The residual concentrations of OCIs in the surface sediments of CES during 2009 and 2011 sampling periods are summarized in the Tables.4.1 and 4.2. These OCIs are grouped as ∑Cyclodienes (aldrin, dieldrin, endrin and α,β-endosulfan), ∑HCH (α-HCH, β-HCH and γ-HCH), ∑DDT (4,4’-DDE, 2,4’-DDD, 4,4’-DDD, 2,4’-DDT and 4,4’-DDT) and Chlordane (heptachlor and heptachlor epoxide (B)) in this research work. Varying concentrations of OCIs in the environmentally divergent 17 sampling locations of CES (**South Zone:** Station No:1-6; **Middle Zone**: Station No:7 -11; **North Zone**: Station No: 12 -17) are independently described.

Among these contaminants, residual levels of cyclodienes are discussed as follows:

Aldrin the probable carcinogen, is mainly used as an insecticide for the underground control of termites in many areas of the world and is quickly converted to a more toxic persistent dieldrin, through microbial oxidation or epoxidative degradation processes. In the present study, residual level of aldrin ranging from BDL to 33.2 ng/g in 30% of the samples collected during 2009 sampling period and the highest concentration detected at Station No: 9 (33.2 ng/g) followed by Station No: 5 (21.1 ng/g). The abundance of aldrin relative to dieldrin implies that, it is widely used in this region without converting to the dieldrin form during the year 2009. The highest concentration of dieldrin (BDL to 142.4 ng/g), with maximum value at Station No: 13 was detected in 2011. In 2009, the residue levels of endosulfan (α) ranged from BDL to 43.2 ng/g and its level was highest at Station No: 13 (43.2 ng/g) followed by Station No: 4 (36.8 ng/g). During 2011 sampling period, contamination by endosulfan (α) was abnormally increased in the Station No:16 (350.5 ng/g) situated close to the industrial hub. The elevated concentration of α-isomer may be due to the recent input of these pesticides in the study area. Moreover, the result shows that instead of restriction in usage, excessive and indiscriminative adoptions of these are still continuing due to the low cost and popularity of the insecticide formulations among the local people.

Across the world, HCH is the most extensively used insecticide, particularly in Asia due to their large scale production in China and India. Among the HCH isomers, α-HCH is more likely to diffuse into the air and get transported for a long distance, while β-HCH is more resistant to hydrolysis and environmental degradation, and is the predominant isomer in the water, fluids, animal tissues and sediments (Sujatha et al., 1993; Walker et al., 1999; Lee et al., 2001). During 2009, the highest concentration of β-HCH detected in the Station No: 5 (76.2 ng/g) followed by Station No:14

(38.2 ng/g), and its level dominated at southern zone followed by north and middle zones. The residual level of β-HCH was BDL at entire sampling stations during 2011. The residual levels of γ-HCH was highest (138 ng/g) at Station No: 9 (Middle Zone) followed by south zone at Station No:2 (15 ng/g) during 2009 sampling period and its level was BDL during 2011, except at the Station No:13 (18.3 ng/g) situated in the north zone. The residual levels of α-HCH was detected at Station No: 2 (28.9 ng/g) and Station No: 3 (2 ng/g) during the sampling periods 2009 and 2011 respectively. The total HCH (α-HCH, β-HCH and γ-HCH) concentration was 423 ng/g detected in the entire study area during 2009 and its level decreased to 23.7 ng/g in the year 2011. Concentrations and compositions of HCH isomers were found to be in the order β-HCH>γ-HCH>α-HCH in 2009, which implies that HCH contamination in the sediments of CES might have originated from a relatively remote source or long-term accumulation from prolonged usage or discharge from industries. In 2011, residual levels of these isomers were in the order γ-HCH>α-HCH>β-HCH showing the recent input of these contaminants in the study area (Figure 4.2). In industrial HCHs, the constituent distribution of the four isomers is α -HCH (65–70%)>ẟ-HCH (12– 14%)> β -HCH (5–6%), while γ -HCH is 99% in lindane and it confirm the use of lindane as insecticide in the study region.

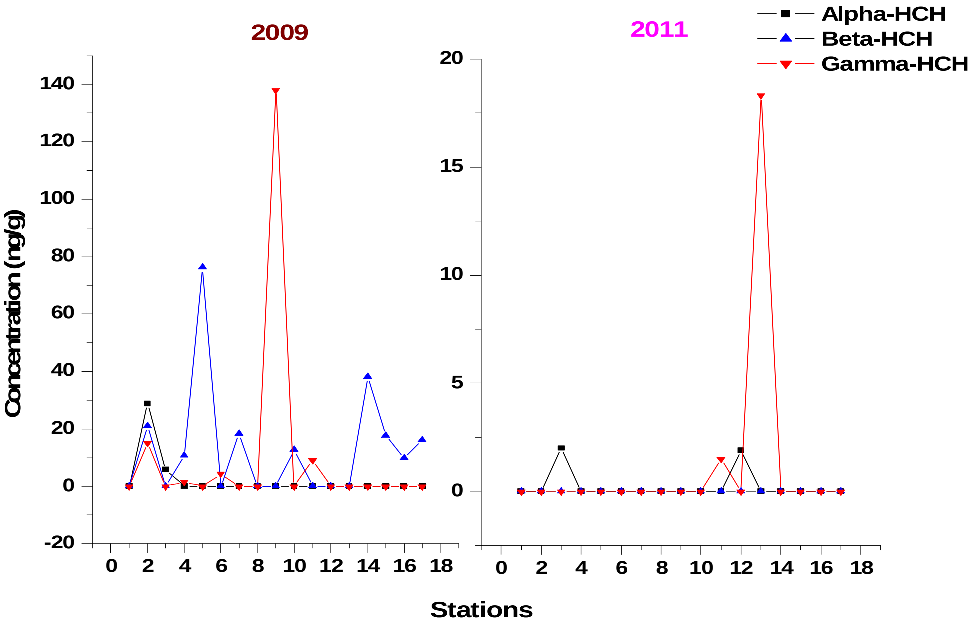

Figure 4.2 The levels of HCH isomers in surface sediments of Cochin Estuary (2009-2011).

Previously, Mathur (1993), reported that, around 25,000 MT (metric tons) of chlorinated pesticides were used annually in India and DDT accounted for 40% of this group. Being as an inexpensive industrial product, they have been commercially available for decades for varying purposes (malaria eradication, termite control, agriculture etc). Concentration of DDT and its metabolites detected in the CES varied significantly in both the sampling periods. The highest concentration (162.5 ng/g) of 4,4'-DDT was detected in the Station No:11 during the second sampling campaign, and substantiate with the accumulation or sorption behaviour of clay content (61.17%) with the metabolite in this station. As compared to 2009 sampling period, contamination by DDT and its metabolites were conspicuously higher in 2011 sampling period and its level was highest at middle zone. These results pointed out that the slow degradation pattern of DDT, atmospheric transport and fallout, influence tides/water currents and heavy discharge of untreated or partially treated effluents from nearby industries which could contribute higher level of these contaminants into the aquatic niche.

Among the chlordane compounds, the highest contamination level of heptachlor epoxide (69.4 ng/g) was detected at Station No:8 during 2009 sampling campaign and is the major persistent degradation product of the synthetic OCI heptachlor. Because of the rapid conversion process, heptachlor epoxide is more abundant in the environment than its parent compound. Adverse biological effects for heptachlor in the aquatic BEDS (Biological Effects Database for Sediments) results decreased diversity, reduced abundance, increased mortality, and behavioural changes in the benthic organisms (CCME, 1999). During 2011, residual level of heptachlor epoxide is highest at the Station No. 13 (21.8 ng/g) followed by the Station No.10 (12.6 ng/g) and Station No. 15 (12 ng/g) respectively.

Levels of ∑HCH (α-HCH, β-HCH and γ-HCH) in sediments from CES were found generally higher than those of ∑DDT (4,4'-DDE, 2,4'-DDD, 4,4'-DDD, 2,4'-DDT and 4,4'-DDT) during 2009. However, the ∑HCH concentrations in sediments collected in 2011 is lower than that of ∑DDT, while the levels of ∑Cyclodienes (aldrin, dieldrin, endrin and α,β-endosulfan) were still higher in both the sampling periods, 2009 and 2011 (Table 4.1 and 4.2). These results reflect the fact that the contamination sources and environmental fate of degradation in these HCH's and cyclodienes are different, this clearly depict that ∑Cyclodienes followed by ∑HCH and ∑DDT compounds were the predominant OCIs in the sediments of CES.

The relative concentrations of the parent compound DDT and its metabolite can also provide a useful information on the pollution source in the context of pesticides in the environmental niche. DDT can be biodegraded by microorganisms to DDE and DDD under aerobic and anaerobic conditions. Therefore, ratios of (DDE+DDD)/∑DDT and DDE/DDD can be used as predictive indices, for assessing the long term weathering and biotransformation of DDT under various redox conditions (Zhang et al., 1999; Doong et al., 2002; Yang et al., 2005). Mostly DDE/DDD ratio shows in the average value as >0.5 which indicates that the collected samples were mainly under anaerobic conditions. General sedimentary parameters detailed in the Chapter-3, showed that Eh value ranged between -109 mV to +274 mV in the study region and the highest negative value noted at middle zone, indicating the periodic anoxic nature of the sediments in the study region with minor fluctuations during both the sampling periods. Moreover, low value of TOC/TS in most of the surface sediment samples from the study region also supports the present findings (shown in Figure 3.4, Chapter-3). The observed pattern of DDT and its metabolites in most of the sediment samples were in the order of DDD>DDE>DDT. The ratio of (DDE+DDD)/∑DDT >1 in majority of the stations infers that the contaminant levels of DDT's in the sediments of CES may have been derived from the aged and weathered agricultural soil and retained under anaerobic conditions within the sediment phase. During both the sampling periods, biochemical composition of sedimentary organic matter revealed that the dominance of carbohydrate and low PRT/CHO suggest the presence of aged OM and the role of protein as a potentially limiting factor for benthic consumers in the aquatic niche also substantiate with the present result (shown in Figure 3.3, Chapter-3). The dominance of DDD's over DDE's clearly supports the reductive dechlorination of DDT's to DDD under anaerobic conditions and similar observations reported earlier (Barakat et al., 2002).

Table 4.1 Concentrations (ng/g, dry wt.) of selected chlorinated insecticides in the sediments of Cochin Estuary, November 2009.

Station	Heptachlor	Heptachlor Epoxide (B)	4,4'-DDE	2,4'-DDD	4,4'-DDD	Aldrin	Endrin	α-Endosulfan
	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g
1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
2	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
3	63.6	BDL	BDL	BDL	BDL	11.8	BDL	BDL
4	BDL	BDL	12.2	11.9	BDL	BDL	BDL	36.8
5	BDL	BDL	BDL	BDL	BDL	21.1	BDL	BDL
6	BDL	BDL	BDL	BDL	33.1	BDL	BDL	BDL
7	BDL	BDL	16	41	BDL	BDL	BDL	BDL
8	BDL	69.4	BDL	BDL	BDL	BDL	BDL	BDL
9	43.6	BDL	BDL	BDL	BDL	33.2	BDL	BDL
10	BDL	BDL	6	BDL	BDL	BDL	BDL	BDL
11	2.7	BDL	BDL	BDL	BDL	BDL	BDL	BDL
12	BDL	22.2	21.5	BDL	BDL	BDL	24.1	BDL
13	BDL	BDL	BDL	BDL	34.7	BDL	BDL	43.2
14	BDL	BDL	BDL	BDL	BDL	BDL	103.1	BDL
15	BDL	BDL	4.5	12.2	BDL	7.2	BDL	BDL
16	BDL	BDL	BDL	BDL	BDL	BDL	30.4	BDL
17	BDL	BDL	BDL	BDL	35.9	6.1	BDL	BDL

Notes: BDL: below detection limits

Table 4. 2 Concentrations (ng/g, dry wt.) of selected chlorinated insecticides in the sediments of Cochin Estuary, November 2011.

Station	Heptachlor Epoxide (B)	4,4'-DDT	4,4'-DDE	2,4'-DDD	4,4'-DDD	Aldrin	Dieldrin	Endrin	α-Endosulfan
	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g
1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
2	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
3	BDL	BDL	BDL	BDL	33	BDL	BDL	BDL	BDL
4	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
5	BDL	BDL	BDL	BDL	33	BDL	BDL	BDL	BDL
6	BDL	BDL	14	BDL	BDL	BDL	BDL	BDL	BDL
7	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
8	BDL	BDL	BDL	BDL	33	BDL	18.7	BDL	BDL
9	BDL	BDL	14.2	BDL	BDL	BDL	BDL	BDL	BDL
10	12.6	BDL	BDL	42.7	BDL	BDL	BDL	59.4	6
11	BDL	162.5	BDL	BDL	33.1	BDL	18.8	BDL	BDL
12	BDL	BDL	13.8	BDL	BDL	3.1	BDL	BDL	BDL
13	21.8	BDL	BDL	BDL	BDL	BDL	142.4	BDL	BDL
14	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
15	12	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
16	BDL	BDL	BDL	38.7	BDL	BDL	BDL	BDL	350.5
17	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

Notes: BDL: below detection limits

The total ∑OCI contamination in sediment was 1170 ng/g (2009) and 1087 ng/g (2011) in the entire study region. Maximum concentrations of ∑OCI were found in the stations situated at the north zone (industrial hub) followed by middle and south zone of the estuary (Figure.4.3).

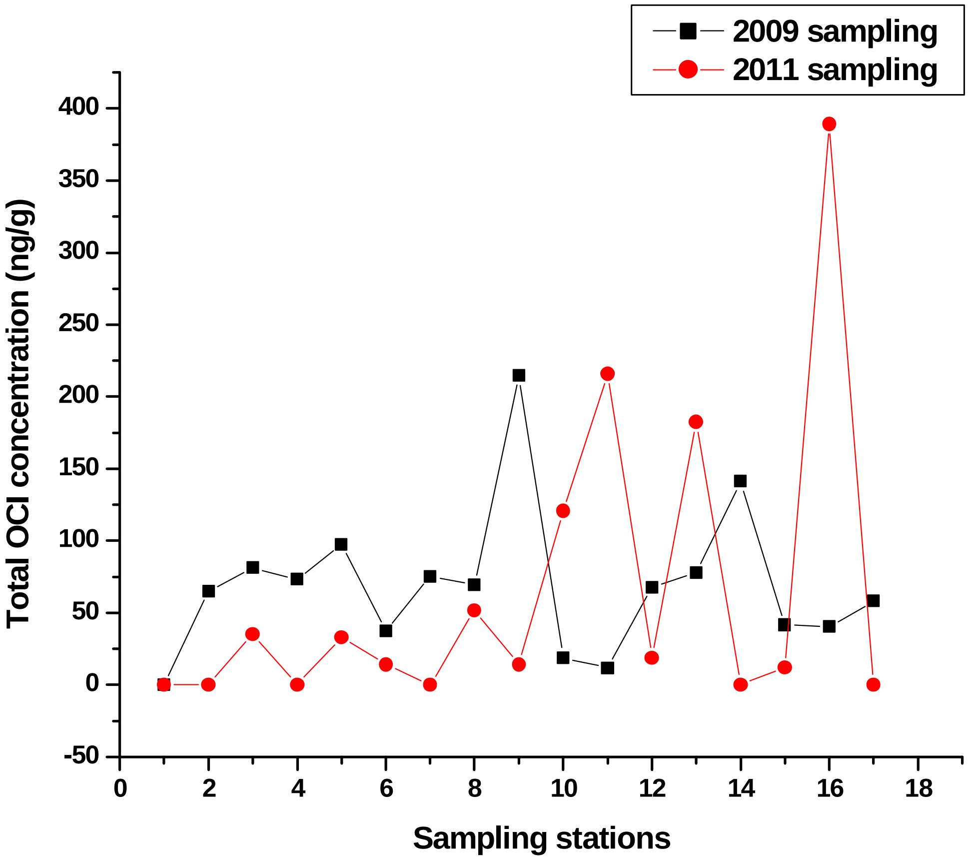

Figure 4.3 Total OCl concentrations in surface sediments of Cochin Estuary (2009-2011).

As described in Chapter-3, the textural characteristics of the sediment sampled from the southern and northern part of the estuary showed fine fractions of the sediment with significant amounts of TOC contents. This can be a reason for elevated organic input in this area. Moreover, the weak flow and the huge input of industrial waste in the northern part of the estuary also results in high organic/inorganic input in this region (Manju et al., 2014; Dsikowitzky et al., 2014). During both the sampling periods (November 2009 and November 2011), moderately rich organic contaminant residues were detected in the middle zone of the estuary indicates their spatial transport behaviour by the influence of tides and water currents. Frequent dredging of sediments from this region (The Hindu, 2014) also leads to resuspension and redistribution of sediment bound contaminants in this region. Furthermore, bioaccumulation by sediment dwelling organisms and plants can reintroduce these contaminants into the food web. However the successive post depositional changes may also modify the environment niche drastically.

4.3 Ecological Risk Assessment

To determine the potential of organochlorine contaminants that cause adverse effects to biota, concentration ranges of selected analytes from the sampling location were compared to the sediment quality guidelines (SQG) sited in Table.4.3.

Sediment quality guideline values from NOAA’s National status and trends program (Long et al., 1995) designate an effects range low ERL and an effects range medium ERM. ERL’s represent chemical concentrations below which adverse effect would be rarely observed; ERM’s represents the chemical concentration above which adverse effects would frequently occur. The Canadian sediment quality guideline (CCME, 1999), probable effect level (PEL) defines the level above which adverse effects on aquatic biota are expected to occur frequently.

Table 4.3 Comparison of OC concentrations in the study area (ng/g dry wt.) with toxicity guidelines.

Compound	SQGs, ng/g d.w.			Study area	Stations (S)		
	ERL	ERM	PEL		S of ERL ~ ERM	S of >ERM	S of >PEL
				2009-2011	2009-2011	2009-2011	2009-2011
$\sum$DDTs	1.58	46.1	NA	229-418	3,4,5,6,8,9,10,12,13,15,16,17	7,11	
o,p'- and p,p'-DDD	NA	NA	8.51	168.8-213.5			3,5,6,8,11,13,17
o,p'- and p,p'-DDE	NA	NA	6.75	60.2-42			4,6,7,9,12
o,p'- and p,p'-DDT	NA	NA	4.77	BDL-162.5			11
p,p'-DDD	2	20	NA	103.7-132.1	None	3,5,6,8,11,17	
p,p'-DDE	2.2	27	NA	60.2-42	4,6,7,9,10,12,15	None	
p,p'-DDT	1	7	NA	BDL-162.5	None	11	
Endrin	0.02	45	62.4	157.6-59.4	12,16	10,14	14
Dieldrin	NA	NA	6.67	BDL-179.9			8,11,13
Lindane	NA	NA	1.38	167.8-19.8			2,4,6,9,11,13
Heptachlor Epoxide	NA	NA	2.74	91.6-BDL			8,10,12,13,15
CHLs	0.5	6	8.87	201.5-46.4	11	3,9,10,13,15	3,9,10,13,15

NA: Not available, BDL: Below detection limit

Most of the pesticide residues detected from the study area were above SQG. The highest concentrations of OCs were detected at stations near the discharge point of sewage and close to the industrial areas. Based on earlier reported values of OCI residual concentrations in various aquatic systems, the present study infers that sediment from CES is comprised of higher toxicants than those from other worldwide locations (Table.4.4).

Table 4.4 Comparison of organochlorine concentrations (ng/g dry wt.) in the sediments from other locations.

Area	Year	$\sum$ DDTs	$\sum$ HCHs	References
Eastern coast of India	NA	0.10—0.97	0.008—0.02	Sarkar, (1994)
Rhone prodelta, France	1987—1991	62—675	NA	Tolosa et al., (1995)
Barcelona Offshore	1987—1991	4.4—76.2	NA	Tolosa et al., (1995)
Ebro Prodelta, Spain	1987—1991	0.8—89.2	NA	Tolosa et al., (1995)
Arabian Sea	1997	1.14—25.17	NA	Sarkar et al., (1997)
Ebro River, Spain	1995—1996	0.4—52	0.001—0.038	Fernandez et al., (1999)
Manzala Lake	1993	5—640	0.97—16.1	Yamashita et al., (2000)
West and east coast of India	1995—1997	ND—364	1.5—1053	Pandit et al., (2001)
Alexandria harbour, Egypt	1998	<0.25—885	0.25—6.0	Barakat et al., (2002)
Mumbai	NA	0.5—9.6	3.8—16.2	Pandit et al., (2002)
Masan Bay, Korea	1997	0.27—89.2	NA	Hong et al., (2003)
Northeastern coast of India	2003	0.18—1.93	0.11—0.40	Guzzella et al., (2005)
Bahrain	2000	0.088—0.430	0.004—0.013	de Mora et al., (2005)
Bay of Bengal, India	1998	0.04—4.79	0.17—1.56	Babu Rajendran et al., (2005)
Gulf of Aden, Yemen	2005	ND—0.74	ND—0.06	Mostafa et al., (2007)
Estuarine and marine sediments, Vietnam	2003—2004	0.31—274	ND—1.00	Hong et al., (2008)
Remote lakes and coastal areas, Norwegian Arctic	2005	0.23—5.4	0.21—7.0	Jiao et al.,(2009)
Baiyangdian Lake, North China	2007—2008	1.3—51.3	4.7—679	Hu et al.,(2010)
Lower Mekong River Basin, Laos and Thailand	2005	0.027—52	0.005—9.9	Sudaryanto et al.,(2011)
Lake Victoria, Uganda.	2003—2007	4.24 ± 3.83	2.80 ± 2.00	Wasswa et al.,(2011)
Maryut Lake, Egypt	2005	0.07—105.6	ND—2.20	Barakat et al., (2012a)
Manzala Lake, Egypt	2005	ND- 3.42	ND-7.25	Barakat et al., (2012b)
Cochin Estuary	2009-2011	229-418	423-23.7	This study

ND: Not Detected, NA: Not available

4.4 Conclusion

The research work allowed a comprehensive evaluation of OCIs content in the sediments of CES. Due to the excessive agriculture application, industrial pollutant discharge, atmospheric transport and the OCIs persistent nature, obviously there still exist a variety of these residues in the sediments of CES. Among these contaminants, cyclodienes followed by HCH and DDT compounds are the predominant OCIs in the study area. The high concentration of biological metabolite p,p'-DDD from the parent DDTs depict that OCIs contamination was mainly from aged and weathered agricultural soils and was retained under anaerobic conditions in the sediment. The results also indicate that there exists a certain potential health risk to the habitat in study area. The baseline data obtained from the present investigation can be used for regular ecological monitoring, considering the tremendous industrial activities and agricultural practices around this important estuarine system. To strengthen and to have a detailed picture of the spatial OCIs distribution pattern in the CES, the depth profile contaminant pattern in the sediment core samples collected from specific areas of CES are important. Therefore, attempted on these aspects and detailed in Chapter-5.

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5

ORGANOCHLORINE INSECTICIDES IN SPECIFIC CORE SEDIMENTS OF A TROPICAL ESTUARY

5.1 Introduction

Aquatic environment comprises three main compartments: water, sediment and suspended matter. The influence of the latter two compartments contributes in the accumulation and concentrations of contaminants (POPs, trace metals etc) in these deposits were increasingly recognised previously (Westrich and Forstner, 2007). The hydrophobic nature of many contaminants is known to associate strongly with particulate matter or dissolved organic matter respectively (Warren et al., 2003). High concentrations of pesticides and heavy metals are frequently found in the sediment phase of both in fresh water deposits and coastal marine sedimentary systems (Pandit et al., 2002; Guzzella et al., 2005; Sarkar et al., 2008; Manju et al., 2014; Dsikowitzky et al., 2014). All these studies pointed out that adverse effect on the benthic communities are the net result of these environments.

Ecotoxicological assessments on surface sediments as well as deep sediment deposits are used to understand the complex relationship between contamination flux and fate of the pollutants in different compartments of the aquatic system. Estuarine core sediment geochemistry allows extrapolating pollution histories to be studied and judged and is an extremely useful tool used in conjunction with environmental monitoring assessments. Moreover, sediment core analysis is interesting because of the bottoms water body are records of the objects and materials which have fallen into the aquatic system over a period of time. They are unique and closely linked with the geochemical history of the earth. Therefore, the sequential monitoring studies of aquatic sediment records are valuable to assess the extent and effect of human inputs in the present and the past and it can predict variances in the contaminant inventory over a broad interval of time (Vink et al., 1999; Brandengerger et al., 2008; Schwarzbauer, 2010). However, based on a catchment-wide assessment of the historical load of soil and sediment is able to provide detailed information about the:

- Variety of sediment contaminants, which can be classified according to their ecotoxicological relevance.
- Sphere of direct or indirect influence of an emission source, regarding the specific conditions within the aquatic system (transport, flow, morphological and geological setting).
- Classification of polluted areas, for instance in areas of low/high/significant pollution.
- Significance of regulatory intervention for the areas of high and significantly high contamination.

Generally, the major contamination sources include industrial and municipal discharges, surface and stormwater runoff, diagenetic processes in sediments, ground water, and atmospheric deposition (Eganhouse, 1997; Warren et al., 2003; Breivik et al., 2004; Schwarzbauer, 2010; Akhil and Sujatha, 2012). Furthermore, the sedimentological record in the dynamic marine (coastal and estuarine) environments is often obscured mainly by the sediment reworking process as a result of biological activity and erosion (Smith and Walton, 1980; Alderton, 1985; Smith and Levy, 1990). Hydrodynamic phenomena such as wave action, storm surges, or seasonal variability in sedimentation rate and texture, also leads to discontinuities in the sedimentary sequence. Moreover, the sediment archives of coastal and estuarine areas are often influenced by mixing processes and the occurrence of undisturbed sediment records which are rather scarce (Gocht et al., 2001).

Several studies on trace organic contaminants (OCIs, PCBs, PAHs etc) present in the core sediments were reported in all over the world (Hong et al., 2003; Frignani et al., 2005; Hem et al., 2005; Evenset et al., 2007; Kim et al., 2007; Francu et al., 2010) and have successfully elucidated as a pollution records to restore the historical changes in the levels and pattern of POPs in the aquatic environments, but limited data were obtained in the Indian coastal environments were concerned (Sarkar et al., 2008). Only a few reports were published relating to the budgetary status on conservative pesticides in CES (Sujatha and Chacko, 1991; Sujatha et al., 1993, 1994a and 1999; Dsikowitzky et al., 2014) and all these research works were focussed on their spatial distribution trends.

5.2 Results and Discussion

The results of the distribution pattern of analysed OCIs in the sediment cores collected from different zones of CES are presented hereunder as: Tables 5.1, 5.2, 5.3, 5.4, 5.5 & 5.6 and the illustrations are discussed separately in two sections as Part-A (First sampling campaign, November- 2009) and Part-B (Second sampling campaign, November-2011).

The spatial distribution pattern of OCIs in the surface sediments of CES detailed in the Chapter-4 conclude that cyclodienes followed by HCH and DDT compounds are the major entities in the aquatic niche. To acquire more information about the transport pathways and occurrence of these contaminants in the study region, the vertical distribution pattern in the sediment cores collected from specific areas of CES are essential. Therefore the study conducted accordingly and the samples are grouped into South, Middle and North zones as discussed previously in the Chapter-2.

5.2.1 Part-A

Among the analyzed OCIs, the distribution pattern of HCH isomers in most of the sediment core samples showed a wide range of fluctuation as delineated in these regions. From the literatures, it was found that α-HCH is more likely to diffuse into the air and traverse to a long distance, while β-HCH is more resistant to hydrolysis and environmental degradation; therefore it exists as the predominant isomer in the water, animal tissues and sediments (Sujatha et al., 1993; Walker et al., 1999; Lee et al., 2001). Highest concentration (247.1 ng/g) of β-HCH was detected at 25-30 cm portion of the sediment core (S_1) bearing length (45 cm) which was collected from the southern zone of the estuary and its residual level decreased towards the bottom section of the core. In the sediment core S_2 (length 30 cm), contamination by α-HCH was detected (2.168 ng/g) at the bottom and γ-HCH residues (4.34 ng/g) were found at top 5 cm portion of the core. The residue level of HCH isomers were BDL in the sediment core M_1 of total length 55 cm, whereas in core M_2 (length 63 cm) the concentration of β-HCH were highest at both the top and middle portions. Isomers of HCH (α and γ) were present in the bottom segment of the sediment core M_2. β-HCH content was highest (65.23 ng/g) at 30-35 cm depth in the sediment core N_2 bearing length 63 cm, collected from the northern zone of the estuary. The higher concentration of the β-isomer confirms its stability and resistance to microbial degradation over other HCH isomers and earlier literatures also support this inference (Willett et al., 1998; Walker et al., 1999). A ratio of β-HCH to γ- HCH is generally being used to predict the past application of HCH as a pesticide (Li et al., 2008) and the value > 1 obtained from the sediment core S_1 confirms the past use of HCH and its persistent character. This point towards the occurrence of HCH and links to either the use of a technical HCH mixture (combination of α-(67%), β-(10%), γ-(15%) and (8%) in general) or the use of lindane as the pesticide (Covaci et al., 2002). The residual levels of HCH isomers were identified in the order β-HCH>γ-HCH>α-HCH, which implies their contamination in the surface sediments as well as sediment cores of CES which might have originated from a prolonged usage or discharge from industries and might have concentrated and accumulated in the aquatic niche. The spatial distribution pattern of these toxicants in the CES as already described in the Chapter-4, also substantiate the present result.

The study extends to the analysis of other xenobiotics and their metabolites/isomers, to provide more information about the source and transport path ways in the aquatic realm. Concentration of DDT and its metabolites varied significantly in all the six sediment cores under investigation. Highest concentration (114.28 ng/g) of 2,4'-DDT was detected at 30-35 cm section of the sediment core N_2 bearing length 63 cm and its level was BDL at top section of the core. Relatively higher concentration of DDT and its metabolites were detected in the sediment cores collected from northern part of the study region. These results confirm the slow degradation pattern of DDT and heavy discharge of untreated or partially treated effluents from nearby industries into the aquatic niche. Contamination by 4,4'-DDD was highest (39.02 ng/g) at 30-35 cm portion in the sediment core N_2 of length 63 cm, followed by cores S_2 and N_1. The ratios (DDE+DDD)/∑DDT and DDE/DDD can be used as indices for assessing the long term weathering and biotransformation of DDT under various redox conditions (Zhang et al., 1999; Doong et al., 2002; Yang et al., 2005). Presence of both 4,4'-DDE and 4,4'-DDD residues in the sediment cores S_2 and N_1 collected from southern and northern region of the estuary, indicates significant anaerobic degradation having occurred in addition to aerobic metabolisation of DDT. One possibly anomalous point (maximum of 62.71 ng/g) in the profile for 4,4'-DDE in the sediment core N_1 at 15-20 cm section, may be owing to large effluent discharge carried out by nearby industries in the CES as endorsed by Dsikowitzky et al., (2014).

Moreover, biodegradation of DDT into its metabolites in the riverine ecosystem may be another reason for a higher concentration of its metabolites in these sediment cores as previously endorsed by Zhang et al., 1999 and Peris et al., 2005 elsewhere.

A relatively high concentration of heptachlor and its isomer was detected in both the surface sediment samples (detailed in Chapter-4) and the sediment cores (M_1 and M_2 at the top and middle portions) collected from middle zone of the CES (Table 5.3 and 5.4). The residual level of aldrin ranges from BDL to 33.7 ng/g in core M_2 and the highest concentration (33.7 ng/g) was profoundly observed in the 35-40 cm section. The persistent nature of heptachlor and aldrin in these regions indicate its direct input to the aquatic environment from nearby point sources, followed by rapid burial and preservation under anaerobic sediments. As already discussed in the Chapter-3, sediment cores collected from the stations S_1, $M_{1,}$ M_2 & N_1 were characterized as under predominantly periodic anoxic stipulation in middle to bottom portions of the core. Marine sediments undergoing sulfate reduction below the oxygenated water column exhibits TOC: TS ratios in the range 1.5 to 5 and well supports the earlier works of Berner and Raiswell (1983) and justifies the present result. Moreover, the abundance of aldrin relative to dieldrin implies that it is widely used in this region, without converting to the dieldrin form through microbial oxidation or epoxidative degradation processes.

The highest concentration of endosulfan isomers was detected in the sampling station situated near to the industrial zone (core N_2) followed by sediment cores M_1 and M_2 which were collected from middle zone (Tables

5.3, 5.4, 5.5 & 5.6). The residue levels of endosulfan-α in the surface sediments of CES (detailed in Chapter-4) ranging from BDL to 43.2 ng/g during 2009 in the northern part of the study area, supports the present findings. These variations observed in the concentration level of OCIs and their metabolites in the estuarine sediments may be due to the high influx rate of contaminants into the estuaries through the rivers, agricultural runoff, microbial activities and various physico-chemical characteristics of the sediments which inturn influence the abiotic degradation of insecticides (Sarkar, 1994).

5.2.2 Part-B

During 2011 sampling, elevated levels of DDT and its metabolites were noted in the sediment cores M_1 and M_2 as compared to first sampling campaign. Highest concentration of 4, 4'DDE (278.5 ng/g) was detected in 15-20 cm portion of the sediment core M_2 bearing length (51 cm) collected from middle zone of the estuary, followed by core M_1 (124 ng/g) at 50-55 cm length. The high concentration levels of DDT metabolites and higher sand percentage (~80 %) in these stations confirms that, the residual levels of OCIs in the middle zone of the estuary significantly controlled by continuous regional inputs rather than natural sorption process on particulate organic carbon. Moreover, the weathered agricultural and industrial runoff was the major input of DDTs and they were retained under anaerobic conditions within the sediment in the CES. It could also be interpreted that the usage of dicofol and DDT-containing antifouling paints are still widely used in the agricultural and ship/boat painting purposes in India and China (Jaward et al., 2005; Lin et al., 2009; Qiu et al., 2004; Taylor et al., 2003) contribute higher input of these contaminants in the aquatic niche. The contamination by DDT metabolites in the sediment cores during both sampling campaigns was in the order as: north zone > south zone > middle zone (2009); middle zone> north zone>south zone (2011).

As compared to first sampling campaign, contamination by HCH isomers were very low and only 1.53 ng/g of γ-HCH were detected in the core M_2 at top 5 cm portion. The residual level of aldrin, endrin and endosulfan were BDL in all the sediment core samples. The presence of dieldrin in the sediment cores collected from middle zone, pointed out that the transformation of aldrin to a more toxic persistent dieldrin, through microbial oxidation or epoxidative degradation processes, and it provide insight for the aged character of aldrin in the study region.

5.2.3 Overall Significance

Different opinions exist regarding the relationship between the concentration of POP's and the respective sedimentary characteristics. Several earlier researchers have observed that OCIs in the sediments are mainly associated with the organic matter (Knezovich et al., 1987; Doong et al., 2002; Barakat et al., 2012b) and their total content depends on the grain size distribution (Law and Andrule wicz, 1983; Doong et al., 2002). Though the present study fails to correlate sediment characteristics (TOC and Texture) and the residual levels of OCIs, especially in certain sediment cores (M_1 and M_2), they are in conformity with the results of de Mora et al., 2004 and Guzzella et al., 2005 reported elsewhere. The typical feature OCI residues in the middle zone of CES may be more prominently controlled by the direct continuous regional inputs rather than the natural sorption process on particulate organic carbon. Furthermore, the productive and varying benthic communities at the collection sites (Menon et al., 2000) contribute to the higher level of organic carbon in the sediment, masking any relationships which may exist between POPs and TOC.

Moreover, accurate reconstructions using sediment core profile data can often be challenging due to site specific environmental contributing factors which may not support a stable depositional environment. Physical processes such as sediment entrainment induce mixing, winnowing and erosion which may disturb the sediment record. Previously Sarkar et al., (2008) reported the occurrence of DDT and its metabolites in all core sediment samples collected from Sunderban wetland ecosystem and the study revealed that there is an irregular pattern, either top to bottom or vice versa, reflecting non-homogenous input of these compounds in the aquatic niche. Similar trend was observed in the residual levels of OCIs in the sediment cores of CES. The erratic distribution of these contaminants might be due to particular hydrological characteristics of both CES and Sundarban wetland being severely controlled by the monsoon, tidal characteristics and nonhomogeneous inputs from point and nonpoint sources of these xenobiotics. The dispersion process is also influenced by estuarine mixing and resuspension processes in this typical environment. In the Mississippi river delta, Santschi et al., (2001) asserted that the presence of DDTs in the sediments might be controlled by a combination of riverine erosion processes and other sedimentary deposits during floods. In the case of CES, sediment mixing by either natural disturbances such as tidal and water currents, as well as anthropogenic activities such as land reclamation (The

Hindu, 2014) interferes the interpretation of chronological pollution status in this ecosystem. In addition to these, bioturbation of the sediment by benthic organisms is commonly found to be an issue (Menon et al., 2000) affecting accurate interpretation of sediment core profiles in many sites.

The characteristic morphology of Cochin estuary impart that it has a settling environment and the sediments are shown to exhibit a low to moderate energy regime in areas away from the river mouths (Priju and Narayana, 2007). The 2D hydrodynamic model data in CES reported previously by Balachandran et al., 2008, reasonably conceptualised that the northern and southern zones are sensitive to environmental stress. Besides, the feeble flow and the bulk industrial waste thrown out into the northern part of the estuary leads to high organic input in this area which makes the estuary a copious contaminant zone. The distinction in residual levels among the analysed sediment cores may be explained by the possible change in pattern of local economic development practices and waste disposal methods. The elevated C/N ratio in the sediment cores (S_1, S_2, M_2, N_1) indicates a higher contribution of terrigenous material in the study region also corroborate with the present result. Recently Dsikowitzky et al., (2014) reported that the highest contamination by HCH isomers and DDT-metabolites in the water and surface sediment samples collected from the industrial area of CES. The study confirms the ongoing production of these contaminants in the nearby industries of CES, contributes the elevated concentration of these compounds detected in the drainage channel samples. Furthermore, present research reveals that instead of restriction in usage, excessive and indiscriminative adoptions of OCIs are still continuing due to the low cost and popularity of the insecticide formulations among the local people.

5.3 Ecological Risk Assessment

To determine the potential adverse effects of organochlorine contaminants that cause adverse effects to biota, concentration ranges of selected analytes from the sampling location was compared to the sediment quality guidelines (SQG) cited in Table 5.7 and 5.8. Since India presently has no established SQGs, the US National Oceanic and Atmospheric Administration (NOAA) guidelines were used as interim measures to assess whether the concentrations of contaminants in sediments could relate to adverse biological impacts. These guidelines were developed based on the analysis of benthic invertebrate communities combined with chemical data from numerous modelling, laboratory and field studies, including several hazardous elements and well known organochlorine contaminants (Long et al., 1995). Potential environmental risk of OCI residues in the CES was evaluated by two widely used SQGs, ie. the effects range low value (ERL) and an effects range medium value (ERM) guidelines and probable effects level (PEL) guidelines from Canadian Council of Ministers of the Environment (CCME, 1999; Mechdonald et al., 2000). ERLs represent chemical concentrations below which adverse effect would be rarely observed; ERMs represents the chemical concentration above which adverse effects would frequently occur in the benthic communities. Probable effect level (PEL) defines the level above which adverse effects on aquatic biota are expected to occur frequently. The comparison of the present data with these guidelines shows that organic contaminants have exceeded the threshold limit. Therefore, adverse effects on benthic species can be expected at all stations. Based on earlier reported values from other regions in the world, the present study infers that sediment from CES is of higher toxicity than those from other locations (Table 5.9).

5.4 Conclusion

The elevated concentration of OCIs in the CES is due to the direct discharge of partially treated or untreated industrial effluents into the river Periyar. Despite the restriction in use, the widespread nature of OCI residues in the sediment cores reflects the illegal use, runoff from the tributaries, the persistent nature and the lipophilic character of these contaminants. The vertical distribution of these trace contaminants in the CES reveals an erratic pattern in all the sampling stations due to the varying environmental conditions existing in the CES. The concentration of three isomers of HCHs disclose a heterogenic distribution where γ-HCH (lindane) and β-HCH shared the dominant part. The current sequence of DDT metabolites indicates slow degradation pattern of the parent compound in the sediments and heavy discharge of untreated or partially treated effluents from nearby industries into the aquatic niche. As per the sediment quality guidelines infers that, the peak concentrations of HCH isomers and DDT metabolites have the potential to induce ecotoxicological impact to the bottom dwelling consumers in the CES.

As compared to first sampling campaign, residual levels of OCIs and the concentration of organic matter was decreased in the sediment cores collected during 2011 sampling, particularly in the southern part of the estuary. Depletion in the contamination might probably not reflect lower emission rates but might be the result of rather higher flow rates washing away the fine grained and normally polluted particles/ organics. Besides, frequent dredging and sand mining in the CES leads to resuspension and redistribution of sediment bound contaminants, may also be one of the reason for reduction OCIs in the aquatic niche.

The present zone wise analysis would provide a better understanding of these trace organics in the environment and could develop more effective strategies for protecting this vulnerable ecosystem from further pollution. Besides, this study would provide the valuable information to understand the behaviour of POPs caused from OCIs in the environment from the environmental pollution point of view in this tropical estuary. Further, using sediment screening bioassays can also be conducted for both sediment quality evaluation and to identify the existing potent toxicants.

Table 5.1 Concentration of OCls in the sediment core S_1

	2009			2011
Depth	**α-HCH**	**β-HCH**	**γ-HCH**	**All OCls**
cm	**ng/g**	**ng/g**	**ng/g**	**ng/g**
0-5	< 0.10	< 0.13	< 0.09	BDL
5-10	4.32	< 0.13	< 0.09	BDL
10-15	1.81	< 0.13	< 0.09	BDL
15-20	< 0.10	46.4	< 0.09	BDL
20-25	12.2	184.2	0.18	BDL
25-30	20.82	247.1	0.29	BDL
30-35	< 0.10	34.1	< 0.09	BDL
35-40	< 0.10	16.2	14.2	BDL
40-45	11.34	47.4	32.5	BDL

BDL: Below Detection limit

Table 5.2 Concentration of OCls in the sediment core S_2

	2009						2011
Depth	**α-HCH**	**γ-HCH**	**4,4'-DDE**	**4,4'-DDD**	**Aldrin**	**Heptachlor**	**4,4'-DDE**
cm	**ng/g**	**ng/g**	**ng/g**	**ng/g**	**ng/g**	**ng/g**	**ng/g**
0-5	< 0.10	4.34	< 0.06	33.17	< 0.04	< 0.18	14
5-10	< 0.10	2.12	< 0.06	16.4	< 0.04	< 0.18	8.12
10-15	< 0.10	0.81	< 0.06	32.1	1.8	0.92	2.16
15-20	< 0.10	< 0.09	2.82	6.4	3.5	2.95	9.28
20-25	1.8	< 0.09	8.12	< 0.16	0.92	< 0.18	< 0.06
25-30	2.168	< 0.09	14.8	< 0.16	1.2	< 0.18	< 0.06
30-35	NA	NA	NA	NA	NA	NA	< 0.06
35-40	NA	NA	NA	NA	NA	NA	< 0.06
40-45	NA	NA	NA	NA	NA	NA	< 0.06

BDL: Below Detection limit NA: Not Available

Table 5.3 Concentration of OCls in the sediment core M_1

		2009		2011		
Depth	**Heptachlor Epoxide (B)**	**Endrin**	**Endosulfan (α)**	**4,4'-DDD**	**4,4'-DDE**	**Dieldrin**
cm	**ng/g**	**ng/g**	**ng/g**	**ng/g**	**ng/g**	**ng/g**
0-5	69.45	< 0.19	< 0.18	33	< 0.06	18.7
5-10	44.8	31.2	< 0.18	18.4	< 0.06	14.2
10-15	18.2	55.2	< 0.18	19.9	< 0.06	8.1
15-20	32.1	32.1	< 0.18	24.1	< 0.06	0.28
20-25	0.84	18.4	< 0.18	0.92	< 0.06	< 0.06
25-30	1.82	0.29	< 0.18	2.81	24.2	< 0.06
30-35	< 0.18	< 0.19	21.2	< 0.16	61.53	< 0.06
35-40	< 0.18	< 0.19	2.9	< 0.16	36.4	< 0.06
40-45	< 0.18	< 0.19	16.4	< 0.16	48.9	< 0.06
45-50	< 0.18	< 0.19	42.3	< 0.16	54.3	< 0.06
50-55	< 0.18	< 0.19	68.6	< 0.16	124	< 0.06

BDL: Below Detection limit

Table 5.4 Concentration of OCIs in the sediment core M_2

	2009								2011				
Depth	α-HCH	β-HCH	γ-HCH	4,4'-DDE	Aldrin	Heptachlor	Endrin	Endosulfan (α)	γ-HCH	4,4'-DDD	4,4'-DDE	4,4'-DDT	Dieldrin
cm	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g
0-5	< 0.10	12.78	< 0.09	6.06	< 0.04	< 0.18	< 0.19	< 0.18	1.53	33.16	< 0.06	162.5	18.8
5-10	< 0.10	10.2	< 0.09	1.26	< 0.04	< 0.18	< 0.19	< 0.18	< 0.09	18.4	76.4	54.6	4.26
10-15	< 0.10	7.4	< 0.09	3.17	< 0.04	< 0.18	< 0.19	< 0.18	< 0.09	12.1	104.2	44.1	2.18
15-20	< 0.10	< 0.13	< 0.09	0.86	< 0.04	< 0.18	< 0.19	< 0.18	< 0.09	1.22	278.5	9.4	8.21
20-25	< 0.10	< 0.13	< 0.09	< 0.06	11.2	2.94	24.3	< 0.18	< 0.09	< 0.16	44.3	< 0.19	< 0.06
25-30	< 0.10	8.3	< 0.09	2.81	8.4	8.41	16.8	< 0.18	< 0.09	< 0.16	8.6	< 0.19	< 0.06
30-35	0.89	23.4	< 0.09	< 0.06	22.2	12.5	63.4	< 0.18	< 0.09	< 0.16	< 0.06	< 0.19	< 0.06
35-40	3.1	36.97	< 0.09	< 0.06	33.7	23.41	82.12	< 0.18	< 0.09	< 0.16	< 0.06	< 0.19	< 0.06
40-45	1.2	18.4	< 0.09	< 0.06	18.9	4.86	46.3	< 0.18	< 0.09	< 0.16	< 0.06	< 0.19	< 0.06
45-50	4.8	16.3	2.81	< 0.06	1.28	< 0.18	8.6	8.46	< 0.09	< 0.16	< 0.06	< 0.19	< 0.06
50-55	2.1	0.81	4.23	< 0.06	< 0.04	< 0.18	< 0.19	16.3	NA	NA	NA	NA	NA
55-60	8.82	<0.13	6.38	< 0.06	< 0.04	< 0.18	< 0.19	65.2	NA	NA	NA	NA	NA

BDL: Below Detection limit   NA: Not Available

Table 5.5 Concentration of OCIs in the sediment core N_1

	2009					2011
Depth	**α-HCH**	**β-HCH**	**4,4'-DDE**	**4,4'-DDD**	**Aldrin**	**4,4'-DDE**
cm	**ng/g**	**ng/g**	**ng/g**	**ng/g**	**ng/g**	**ng/g**
0-5	< 0.10	< 0.13	< 0.06	35.9	6.08	< 0.06
5-10	< 0.10	16.1	< 0.06	18.41	1.28	< 0.06
10-15	1.2	4.8	8.42	8.1	< 0.04	8.42
15-20	4.6	1.8	62.71	< 0.16	< 0.04	88.14
20-25	6.06	< 0.13	4.34	< 0.16	< 0.04	123.5
25-30	< 0.10	< 0.13	< 0.06	< 0.16	< 0.04	4.3
30-35	NA	NA	NA	NA	NA	< 0.06
35-40	NA	NA	NA	NA	NA	< 0.06

BDL: Below Detection limit NA: Not Available

Table 5.6 Concentration of OCIs in the sediment core N_2

	2009						2011	
Depth	**β-HCH**	**2,4'-DDT**	**4,4'-DDD**	**Endrin**	**Endosulfan (α)**	**Endosulfan (β)**	**Heptachlor Epoxide (B)**	**4,4'-DDE**
cm	**ng/g**	**ng/g**	**ng/g**	**ng/g**	**ng/g**	**ng/g**	**ng/g**	**ng/g**
0-5	38.26	< 0.15	< 0.16	103.15	< 0.18	< 0.13	< 0.18	< 0.06
5-10	18.4	< 0.15	< 0.16	48.2	< 0.18	< 0.13	< 0.18	< 0.06
10-15	9.81	< 0.15	2.1	16.4	< 0.18	< 0.13	< 0.18	< 0.06
15-20	43.1	26.4	12.1	72.6	< 0.18	< 0.13	< 0.18	< 0.06
20-25	16.2	84.1	< 0.16	7.3	42.1	8.26	4.82	< 0.06
25-30	4.26	63.2	14.1	< 0.19	18.6	12.3	1.36	< 0.06
30-35	65.23	114.28	39.02	< 0.19	88.17	41.2	20.45	< 0.06
35-40	0.84	9.4	8.2	< 0.19	8.9	4.21	0.94	7.41
40-45	< 0.13	< 0.15	< 0.16	< 0.19	< 0.18	6.34	< 0.18	44.3
45-50	< 0.13	< 0.15	< 0.16	< 0.19	< 0.18	17.2	< 0.18	77.94
50-55	< 0.13	7.6	< 0.16	< 0.19	14.2	64.3	< 0.18	2.93
55-60	< 0.13	63	< 0.16	< 0.19	62.3	154	NA	NA

BDL: Below Detection limit NA: Not Available

Table 5.7 Comparison of OCI concentrations in the sediment cores of CES (ng/g dry wt.) with toxicity guidelines (First sampling campaign 2009).

Compound	SQGs, ng/g d.w.			Stations (S)		
	ERL	ERM	PEL	S of ERL ~ ERM	S of >ERM	S of >PEL
$\sum$DDTs	1.58	46.1	51.7	M_2	N_1,N_2,S_2	N_1,N_2,S_2
o,p'- and p,p'-DDD	NA	NA	8.51			N_1,N_2,S_2
o,p'- and p,p'-DDE	NA	NA	6.75			N_1,S_2,M_2
o,p'- and p,p'-DDT	NA	NA	4.77			N_2
p,p'-DDD	2	20	7.81	None	N_1,N_2,S_2	N_1,N_2,S_2
p,p'-DDE	2.2	27	374	M_2,S_2	N_1	None
p,p'-DDT	1	7	4.77	None	None	None
Endrin	0.02	45	62.4	None	M_1,M_2,N_2	M_1,M_2,N_2
Dieldrin	NA	8	6.67		None	None
Lindane	NA	NA	1.38			M_2,S_1,S_2
Heptachlor Epoxide (B)	NA	NA	2.74			M_1

NA: Not available

Table 5.8 Comparison of OCI concentrations in the sediment cores of CES (ng/g dry wt.) with toxicity guidelines (Second sampling campaign 2011).

Compound	SQGs, ng/g d.w.			Stations (S)		
	ERL	ERM	PEL	S of ERL ~ ERM	S of >ERM	S of >PEL
$\sum$DDTs	1.58	46.1	51.7	S_2	M_1,M_2,N_1,N_2	M_1,M_2,N_1,N_2
o,p'- and p,p'-DDD	NA	NA	8.51			M_1,M_2,N_1,N_2
o,p'- and p,p'-DDE	NA	NA	6.75			M_1,M_2,N_1,N_2,S_2
o,p'- and p,p'-DDT	NA	NA	4.77			M_2
p,p'-DDD	2	20	7.81	None	M_1,M_2	M_1,M_2
p,p'-DDE	2.2	27	374	S_2	M_1,M_2,N_1,N_2	M_2
p,p'-DDT	1	7	4.77	None	M_2	M_2
Endrin	0.02	45	62.4	None	None	None
Dieldrin	NA	8	6.67		M_1,M_2	M_1, M_2
Lindane	NA	NA	1.38			M_2
Heptachlor Epoxide (B)	NA	NA	2.74			N_2

NA: Not available

Table 5.9 Distribution pattern of OCIs (ng/g dry wt.) in the surface sediment samples from various ecosystems.

Location	∑DDT	∑HCH	Aldrin	Dieldrin	Endrin	References
Xiamen Harbour	4.5-311	0.14-1.12	NA	NA	NA	Hong et al (1995)
River Wuchuan, Southeast China	0.47-2.14	0.21-3.85	0.02-0.87	0.03-0.24	0.02-0.13	Zhang et al (2002)
Minjiang River Estuary, Southeast China	1.57-13.06	2.99-16.21	0.47-2.23	0.67-1.79	0.27--2.43	Zhang et al (2003)
Qiantan River, East China	8.64-100.2	19.74-152.1	0.36-19.56	< 0.15-28.40	< 0.1652.37	Zhou et al (2006)
Northeastern Part of Sao Paulo State, Brazil	0.05-0.92	0.12-11.01	< 0.04-0.23	0.05-0.96	< 0.05-0.25	Rissato et al (2006)
Sunderban wetland, India	0.05—11.5	0.05—12	NA	NA	NA	Sarkar et al (2008)
Bosomtwi Lake, Ghana	15.06-31.92	2.03-13.94	0.30-0.46	0.20-0.46	NA	Darko et al (2008)
Gomti River , India	1.63-368.7	BDL-155.17	< 0.11-0.89	< 0.05-1.65	< 0.05-11.96	Malik et al (2009)
Tamiraparani River, India	< 0.01-857	< 0.01-472	< 0.02-562	< 0.03-1693	NA	Kumarasamy et al (2012)
Maryut Lake, Egypt	0.07105.6	BDL-2.20	NA	NA	NA	Barakat et al (2012a)

NA: Not available, BDL: Below detection limits

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6

CONCLUDING REMARKS

Since time immemorial, Man has started living and building up his activities around the estuaries, which are the most dynamic and productive environments on earth. With the increasing population and consequent industrial and agricultural developments, besides programmes like deforestation, the ecosystem and the environment of the estuaries got deteriorated. Disposal of sewage and industrial effluents have not only polluted the estuaries but also biologically affected the marine life. Almost all marine coastal ecosystems have complex structural and dynamic characteristics that can be easily modified by anthropogenic influences. Thus, the delicate balance maintained between human settlements and estuarine environment has got affected and destroyed. Any change in chemical properties of the water and the sediment can affect benthic communities, including their survival. Contaminated marine sediments have been recognized as a very important repository for persistent toxic substances (Xenobiotic organic compounds, Heavy metals etc.) released from various point and non point sources and finally enter reside into the water bay. Sediment toxicity to marine organisms and their risk posed to the environment have arouse growing interest to both the researchers and Environment Development Authorities.

As estuaries are geochemical barriers regulating the export of materials, emerging metropolises like Cochin, necessitates information on the fate of pollutants in the coastal environment. CES comprises one of the most important harbour and industrial centres in the West coast of India. Moreover, it receives large inputs of terrigenous materials exported from land and autochthonous marine materials from the ocean. Therefore, understanding the nature and origin of organic matter could provide valuable information regarding the anthropogenic pressures in this estuarine niche.

Seventeen surface sediments and six core sediment samples from regionally important locations of CES were collected during November 2009 and November 2011 (post monsoon season) for performing the analysis of biogeochemical constituents and OCIs. These 17 surface sediment samples were grouped into three zones - South, Middle and North based on environmental variability such as the physicochemical and sedimentary characteristics. Two core sediment samples from each of these three zones were grouped as (S_1 and S_2) south, (M_1 and M_2) middle and (N_1 and N_2) north. The results discussed on the basis of three zones.

Biogeochemical evaluation of the study region revealed that organic matter in the sediments of CES is aged and the role of protein contribution as a potentially limiting factor for benthic consumers. Besides, the C/N ratio supports the allochthonous character of the sediments in the aquatic niche during the entire sampling periods and attributes a profound influence in the biogeochemical processes. In both the sampling periods, estimated chlorophyll-a to pheophytin value shows <1 in all the sediment cores, which indicates the prevalence of detritus matter in the sediments. The accumulation of detrital organic matter in sediment degrades the quality of organic constituents; limiting the benthic ecology and act as a potential carrier of toxic pollutants.

Distribution of various organochlorine insecticides presented in this research work will constitute the first judicious baseline data set in the sediment cores of CES. For this assignment, the following organochlorine insecticides were quantified: α-hexachlorocyclohexane (α-HCH), β-HCH, γ-HCH, heptachlor, aldrin, heptachlor epoxide (B), 4,4'-DDE, dieldrin, endrin, 2,4'-DDD, 4,4'-DDD, 2,4'-DDT, 4,4'-DDT, α-endosulfan, and β-endosulfan. Among these contaminants, cyclodienes followed by HCH and DDT compounds are the predominant OCIs in the study area. The high concentration of biologically degraded metabolite - p,p'-DDD from the parent DDTs depict that OCIs contamination was mainly from aged and weathered agricultural soils and was retained under anaerobic conditions in the sediment. The results also indicate that there exists a certain potential health risk to the habitat in the study area. The elevated concentration of OCIs in the CES is due to the direct discharge of partially treated or untreated industrial effluents into the river Periyar. Despite the restriction in use, the prevalent nature of OCIs in the core sediment reflects the illegal use, runoff from the tributaries, the persistent nature and the lipophilic character of these insecticides. The vertical distribution of these trace contaminants in the CES reveals an erratic pattern in all the sampling stations due to the varying environmental conditions exists in the CES. The study reveals that absolute comparability is difficult to achieve between the sediment cores taken within the same profundal zone in the estuary. Accumulation pattern cannot be expected to be uniform over the aquatic bed. As compared to first sampling campaign, residual levels of OCIs and the concentration of organic matter were decreased during 2011 sampling period, particularly in the southern part of the estuary. Frequent dredging and sand mining in the CES leads to resuspension and redistribution of sediment bound contaminants, may be the reason for reduction OCIs in the aquatic niche. The present zone wise analysis would provide a better understanding of trace organics in the environment and could develop more effective strategies for protecting this vulnerable ecosystem from further pollution. There is also an urgent need to bring into notice the attention of researchers and technologists to the hitherto neglected estuarine ecosystem. Further, using sediment screening bioassays can also be conducted for both sediment quality evaluation and to identify the existing potent toxicants.

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Career Achievements and Publications

CAREER ACHIEVEMENTS

- Participated in the **First Indian GEOTRACES Cruise 2013** in the Indian Ocean water mass onboard **ORV Sagar Kanya,** carried out from March-2 to May-10. Organized by Physical research Laboratory (PRL), Ahmadabad, India, under the aegis of Ministry of Earth Science, Govt of India.
- Training facilities in the latest analytical methods of environmental chemistry obtained from **RWTH Aachen University, Aachen** and **Leibniz Center for Tropical Marine Ecology**, **Bremen, Germany** during October 17 to November 09' 2012.
- Participated and successfully completed the Short Term training on **"Isotope Tracer Techniques for Water Resources Development and Management"** organized by Centre for Water Resources Development and Management (CWRDM) at Kunnamangalam, Kozhikode, under the aegis of Department of Science and Technology, Government of India during 21-26 June 2010.
- Participated in the **"IVth Indian Scientific Expedition to Southern Ocean 2010"** carried out from January-11 to March-25, onboard **ORV Sagar Nidhi**, and reached up to **66^{o}35' S** at the coastal regions of **Antarctica**. Organized by National Centre for Antarctic and Ocean Research (NCAOR), Goa, India, under the aegis of Ministry of Earth Science, Govt of India.

LIST OF PUBLICATIONS

A. Research Articles

1. **Akhil P S** and Sujatha C H (2014) “Residual Archives on Organochlorine Insecticides in the Core Sediment of A Tropical Estuary, India”. ***Journal of Toxicology and Environmental Health, Part -A.*** **(Under Review).**
2. **Akhil P S** and Sujatha C H (2014) “Spatial Budgetary Evaluation of Organochlorine Contaminants in the Sediments of Cochin Estuary, India”. ***Marine Pollution Bulletin***. 174(1-4), 299-312.
3. Manju P Nair, **Akhil P S** and Sujatha C H (2014) “Toxic Metal Distribution in the Core Sediment of Cochin Estuarine System (CES)”. ***International Journal of Environmental Research***. 8(1): 133-138, Winter 2014.
4. Larissa Dsikowitzky, Inga Nordhaus, Sujatha C H, **Akhil P S**, Kunjupilai Soman, Jan Schwarzbauer (2014) “A combined chemical-biological assessment of industrial contamination in an estuarine system in Kerala, India” ***Science of the Total Environment***, 485–486 (2014) 348–362.
5. **Akhil P S**, Manju P Nair and Sujatha C H (2013) “Core Sediment Biogeochemistry in Specific Zones of Cochin Estuarine System (CES)”. ***Journal of Earth System Science***. 122, No. 6, pp. 1557–1570.
6. Manju P Nair, **Akhil P S** and Sujatha C H (2013) “Geochemistry of Core Sediment from Antarctic Region”. ***Research journal of Chemistry and Environment*** 17(2),8-12.

7. **Akhil P S**, Sumangala K N and Sujatha C H (2013) "Groundwater Hydrochemistry in the Crystalline Laterites/ Forest Loams of Kasargod District, Kerala, India". ***Water Science and Technology: Water Supply***, 13.2, 486-498.
8. Sumangala K N, **Akhil P S** and Sujatha C H (2013) "Hydrogeochemical Quality Assessment of Ground Waters in Ernakulam District, Kerala, India". ***Journal of Environmental Science, Computer Science and Engineering & Technology***, Vol.2. No.4, 1353-1368.
9. **Akhil P S** and Sujatha C H (2012) "Prevalence of Organochlorine Pesticide Residues in Groundwaters of Kasargod District,India". ***Toxicological and Environmental Chemistry,*** Vol. 94, No. 9.1718–1725.

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Baseline

Spatial budgetary evaluation of organochlorine contaminants in the sediments of Cochin Estuary, India

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A R T I C L E I N F O

Keywords:
Organochlorine insecticide
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Ecotoxicological factor

A B S T R A C T

This paper presents the first detailed investigation on the residual levels of organochlorine insecticide (OCI) concentrations in the Cochin estuarine sediment. It aims in elucidate their distribution and ecological impact on the aquatic system. Concentrations of persistent organochlorine compound (OC) were determined for 17 surface sediment samples which were collected from specific sites of Cochin Estuarine System (CES) over a period of November 2009 and November 2011. The contaminant levels in the CES were compared with other worldwide ecosystems. The sites bearing high concentration of organochlorine compounds are well associated with the complexities and low energy environment. Evaluation of ecotoxicological factors suggests that adverse biological effects are expected in certain areas of CES.

Pesticides are synthetic organic chemicals used to control unwanted or harmful pests, such as insects and mites that feed on crops. The environmental pollution by organochlorine insecticides are one of the most important Persistent Organic Pollutants (POPs) and have been of great concern around the world owing to their chronic toxicity, persistence and bioaccumulation. They have been extensively studied over the last 30 years, because of their resistance to degradation which has resulted in its being an almost universal contaminant of the environment (Jones and Voogt, 1999; Laabs et al., 2002; Monirith et al., 2003; Mudiam et al., 2012; Akhil and Sujatha, 2012). Due to the careless disposal practices, they have become a major pollutant in many parts of the world. In aquatic environments, OCs get removed from the water column and adsorb onto the particulate matter, and finally deposit on to sediments. The persistent nature of these compounds in soil and water, can adversely affect the health of pedospheric (Kammenga et al., 2000) and aquatic biocoenoses and the quality of drinking water (Kumar et al., 1995; Akhil and Sujatha, 2012). A greater tendency shown by OCIs for bioaccumulation and biomagnification in the food chains is due to their resistance to chemical and biological decay (Badawy and Wahaab, 1997; Yamashita et al., 2000; Abbassy et al., 2003). Although the applications of OCIs have been banned in many developed countries, some developing countries are still producing and using these persistent pesticides because of their low cost and versatility in controlling various insects (Tanabe et al., 1994; Monirith et al., 2003).

The main objective of the study is to survey the contaminant levels, distributions and other sources of these OCIs in surface sediments from CES and to assess their environmental impact in the ecosystem. Most of the earlier research contributions were based on one-time or seasonal sampling during a year, from the areas known for environmental pollution (Barakat, 2003; Khaled et al., 2004; Said et al., 2008). An approach based on the analysis of OCI residues in sediments collected over a considerable time period can provide a clue for a change in environment and such studies are limited. A few reports are available on the residue analysis of conservative pesticides in CES (Sujatha and Chacko, 1991; Sujatha et al., 1993, 1994, 1999) but no studies concerning these persistent contaminants in sediment were reported. A broad spectrum of pesticides is used in India for agriculture as well as vector control programs and hence the impact of residues of these OCs on Indian coastal environments is of considerable interest.

Cochin Estuary, one of the largest tropical estuaries of India, is facing gross pollution problems due to the release of untreated effluents from industries and domestic sectors. The major polluting industries in the region include fertilizer plant, oil refinery, rare earth processing plant, minerals and rutiles plant, zinc smelter plant, insecticide manufacturing unit and organic chemical plant. Reclamations over the past several decades have resulted in considerable shrinkage (40%) of the Cochin Estuary (Gopalan et al., 1983). Further, the construction of hydraulic barriers on the northern and southern limbs of the estuary to prevent saline intrusion into the upstream agricultural fields has imposed severe flow restrictions and increased sedimentation rate in the estuary (Menon et al., 2000). The development activities in and around Cochin Backwater System have added to the complexities and environmental dilemmas in this coastal niche. For a long period, there were no pollution control regulations and the untreated effluents continuously discharged into the backwaters.

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Study area is divided into three zones viz South, Middle, and North (Fig. 1). The south zone is situated in the fresh water region and it originates from southern bough of Moovattupuzha. Major source of pollution is from agriculture runoff and it is less affected by industrial effluents (Station No 1–6). The middle zone is well regulated by a bund (namely Thannirmukham), which was constructed in order to prevent the salt water intrusion into the paddy fields. The bund remains open during monsoon season. This zone has a perennial connection with the Arabian Sea and experiences an irregular encroachment of saline water intrusion there by making cradle grounds for diverse types of flora and fauna. With the advent of ICTT project, this area has become a backbone for the economy of State of Kerala. Due to enhanced containerization, resulting in improved trade and economic growth, widespread activities like dredging, piling, along with anthropogenic inputs are increasing frequently (Station No 7–11). Finally north zone originates from the industrial locale of Periyar – the life line of Kerala. Large scale industries on the river bank discharge effluents directly into these waterways resulting in the accumulation of varying amounts of nutrients in the Periyar River (Station No 12–17).

Surface sediments (top 0–5 cm) were collected from seventeen locations of CES over a period of November 2009 and November 2011. This was performed using a stainless steel grab sampler used repeatedly (three to five times) at each station, followed by thorough mixing of collected sediment on an aluminum tray in order to obtain a more representative sediment sample. All samples were then transferred into well labeled hexane-rinsed glass jars and kept it in the ice chest boxes on board and during transportation. The samples were then stored at −20 °C until the analysis.

About 5 gm of the sediment sample was accurately weighed and then extracted twice with 50 mL portions of 1:1 hexane-acetone mixture (HPLC grade, Glaxo, Mumbai, India). The combined extract was subjected to a cleanup procedure involving elution through a Florisil column (60 cm × 22 mm i.d) with 50 mL 1:1 hexane–acetone mixture. The extract was concentrated to about 5–6 mL by means of a rotary evaporator at 50–60 °C for further analysis. Separation and analysis of the OCIs were performed on a gas chromatograph (GC) (model 7890A, Agilent, Waldbronn, Germany) with a Ni-63 ECD and equipped with capillary column (HP-35, 30 m × 0.320 mm × 0.5 mm) using nitrogen as carrier gas (1.5 mL min^{-1}). The GC was calibrated with a standard solution of a pesticide mixture (Supelco, USA) prepared in HPLC grade n-hexane. Solvent blanks were used to confirm the absence of any pesticide residues. Analytical reproducibility was checked by replicate measurements. Identification and quantification of OCIs were accomplished by using reference solutions supplied by EPA (USA) and Supelco (USA). The following GC conditions were maintained: injection port temperature 250 °C, detector temperature 350 °C, oven temperature program: 110 °C (5 min) at 5 °C min^{-1} to 190 °C (2 min) at 15°C min^{-1} to 280 °C (10 min). 1 μL of aliquot samples were injected onto the column. All data were subjected to strict quality control procedures, including the analysis of procedural blanks and spiked samples with each set of samples analyzed. None of the target compounds were detected in the procedural blanks for sediment samples. Spiked samples (10 ng of pesticide mix standard) were determined with good precision and high recoveries. Limit of detection (LOD) and relative standard deviation (RSD) of the analytical method for OCIs is as follows. The detection limit was lowest for aldrin (0.04 ng/g) and highest for endrin and 4,4′-DDT (0.19 ng/g), while the detection limit of other analytes lies within the range. The average recoveries ($n = 3$) for OCIs revealed an efficiency of 87–103%. The relative standard deviations (RSD) were below 5.0% and fall within the requirement criteria of US-EPA (Recovery: 70–130%, RSD is <30%). The following organochlorine

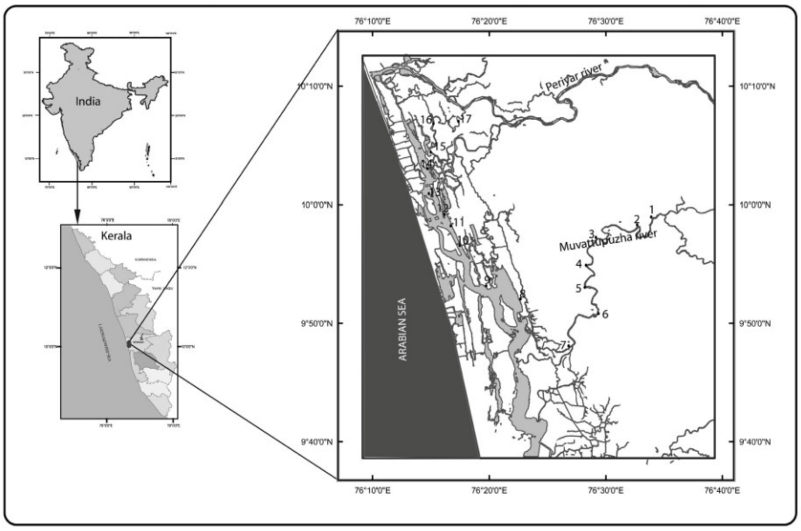

Fig. 1. Map of the study area and sampling sites.

pesticides were quantified. α-hexachlorocyclohexane (α-HCH), β-HCH, γ-HCH, heptachlor, aldrin, heptachlor epoxide (B), 4,4′-DDE, dieldrin, endrin, 2,4′-DDD, 4,4′-DDD, 2,4′-DDT, 4,4′-DDT, α-endosulfan, and β-endosulfan.

Data on the residual levels of pesticide accumulation in the marine sediments is limited, especially in the coastal belt of India. Coastal sediments serve both as temporary and long-term sink for many classes of anthropogenic contaminants and consequently act as the source of these xenobiotics into the aquatic realm. The applied and direct dumping of industrial wastes of these persistent contaminants can be transported through surface run-off, leaching ultimately accumulating and getting settled into the bottom sediments. Hence these bottom sediments represent an integrated conspicuous level of particle bound contaminants that have deposited over a longer period of time. A few studies have been reported on these contamination of OCs in the sediments from Indian coastal regions (Sarkar and SenGupta, 1987, 1988, 1991; Takeoka et al., 1991; Sarkar et al., 1997; Pandit et al., 2001) indicating the presence of their major emission sources in these regions. The findings of this research work constitute the first judicious base line data set for the OCl residues in the sediments of CES (Tables 1 and 2). Across the world, HCH is the most extensively used insecticide, particularly in Asia due to their large scale production in China and India. Being as an inexpensive industrial product, it has been commercially available for decades for varying purposes in these regions. Previously, Mathur (1993), reported that, around 25,000 MT (metric tons) of chlorinated pesticides were used annually in India and DDT accounted for 40% of this group. Among the HCH isomers, α-HCH is more likely to diffuse into the air and get transported for a long distance, while β-HCH is more resistant to hydrolysis and environmental degradation, and is the predominant isomer in the water, fluids, animal tissues and sediments (Sujatha et al., 1993; Walker et al., 1999; Lee et al., 2001). In the present research work, total HCH concentration of 423 ng/g was detected in the entire study area during 2009. Levels decreased to 23.7 ng/g in 2011. Concentrations and compositions of HCH isomers were found to be in the order β-HCH > γ-HCH > α-HCH in 2009, which implies that HCH contamination in the sediments of CES might have originated from a relatively remote source or long-term accumulation from prolonged usage or discharge from industries. In 2011, residual levels of these isomers was in the order γ-HCH > α-HCH > β-HCH showing the recent input of these isomers in the study area (Fig. 2). Levels of ∑HCH in sediments from CES were found generally higher than those of ∑DDT during 2009. However, the ∑HCH concentrations in sediments collected in 2011 is lower than that of ∑DDT, while the levels of ∑Cyclodienes were still higher in both the sampling periods, 2009 and 2011. These results reflect the fact that the contamination sources and environmental fate of degradation in these HCH's and cyclodienes are different, this clearly depict that ∑Cyclodienes followed by ∑HCH and ∑DDT compounds were the predominant OCls in the sediments of CES. In 2009, the residue levels of endosulfan (α) ranged from BDL to 43.2 ng/g. Contamination level of endosulfan (α) was highest at Station No:16 (350.5 ng/g) during 2011. The elevated concentration of α-isomer may be due to the recent input of these pesticides in the study area.

Aldrin, the probable carcinogen is mainly used as an insecticide for the underground control of termites. The residue level of aldrin was BDL to 33.2 ng/g in 30% of the samples collected in 2009 and is quickly transferred to a more toxic persistent dieldrin, through microbial oxidation or epoxidative degradation. The abundance of aldrin relative to dieldrin implies that it is widely used in this region during the year 2009. Dieldrin concentration was high (BDL to 142.4 ng/g), with maximum value at Station No:13 in 2011. The result shows that instead of restriction in usage, excessive and indiscriminative adoptions of these are still continuing due to the low cost and popularity of the insecticide formulations among the local people. Among the chlordane compounds, heptachlor epoxide is relatively abundant with the highest contamination level (69.4 ng/g) at Station No:8 during 2009 and BDL during 2011 in the entire study region.

The relative concentrations of the parent compound and its metabolite can provide useful information on the pollution source. DDT can be biodegraded by microorganisms to DDE and DDD under aerobic and anaerobic conditions. Therefore, ratios of (DDE + DDD)/∑DDT and DDE/DDD can be used as indicative indices for assessing the long term weathering and biotransformation of DDT under various redox conditions (Zhang et al., 1999; Doong et al., 2002; Yang et al., 2005). Mostly DDE/DDD ratio were in the average value >0.5 which indicates that the collected samples were mainly under anaerobic conditions. The observed pattern of DDT and its metabolites in most sediment samples were in the order of DDD > DDE > DDT. The ratio of (DDE + DDD)/∑DDT > 1 in majority of the stations infers that the contaminant levels of DDT's in the sediments of CES may have been derived from the aged and weathered agricultural soil and retained under anaerobic conditions within the sediment phase. The dominance of DDD's over DDE's clearly supports the reductive dechlorination of DDT's to DDD

Table 1
Concentrations (ng/g, dry wt.) of selected chlorinated pesticides in the sediments of Cochin Estuary, November 2009.

Station	Heptachlor (ng/g)	Heptachlor epoxide (B) (ng/g)	4,4′-DDE (ng/g)	2,4′-DDD (ng/g)	4,4′-DDD (ng/g)	Aldrin (ng/g)	Endrin (ng/g)	α-Endosulfan (ng/g)
1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
2	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
3	63.6	BDL	BDL	BDL	BDL	11.8	BDL	BDL
4	BDL	BDL	12.2	11.9	BDL	BDL	BDL	36.8
5	BDL	BDL	BDL	BDL	BDL	21.1	BDL	BDL
6	BDL	BDL	BDL	BDL	33.1	BDL	BDL	BDL
7	BDL	BDL	16	41	BDL	BDL	BDL	BDL
8	BDL	69.4	BDL	BDL	BDL	BDL	BDL	BDL
9	43.6	BDL	BDL	BDL	BDL	33.2	BDL	BDL
10	BDL	BDL	6	BDL	BDL	BDL	BDL	BDL
11	2.7	BDL	BDL	BDL	BDL	BDL	BDL	BDL
12	BDL	22.2	21.5	BDL	BDL	BDL	24.1	BDL
13	BDL	BDL	BDL	BDL	34.7	BDL	BDL	43.2
14	BDL	BDL	BDL	BDL	BDL	BDL	103.1	BDL
15	BDL	BDL	4.5	12.2	BDL	7.2	BDL	BDL
16	BDL	BDL	BDL	BDL	BDL	BDL	30.4	BDL
17	BDL	BDL	BDL	BDL	35.9	6.1	BDL	BDL

Notes: BDL, below detection limits.

Table 2
Concentrations (ng/g, dry wt.) of selected chlorinated pesticides in the sediments of Cochin Estuary, November 2011.

Station	Heptachlor epoxide (B) (ng/g)	4,4′-DDT (ng/g)	4,4′-DDE (ng/g)	2,4′-DDD (ng/g)	4,4′-DDD (ng/g)	Aldrin (ng/g)	Dieldrin (ng/g)	Endrin (ng/g)	α-Endosulfan (ng/g)
1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
2	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
3	BDL	BDL	BDL	BDL	33	BDL	BDL	BDL	BDL
4	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
5	BDL	BDL	BDL	BDL	33	BDL	BDL	BDL	BDL
6	BDL	BDL	14	BDL	BDL	BDL	BDL	BDL	BDL
7	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
8	BDL	BDL	BDL	BDL	33	BDL	18.7	BDL	BDL
9	BDL	BDL	14.2	BDL	BDL	BDL	BDL	BDL	BDL
10	12.6	BDL	BDL	42.7	BDL	BDL	BDL	59.4	6
11	BDL	162.5	BDL	BDL	33.1	BDL	18.8	BDL	BDL
12	BDL	BDL	13.8	BDL	BDL	3.1	BDL	BDL	BDL
13	21.8	BDL	BDL	BDL	BDL	BDL	142.4	BDL	BDL
14	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
15	12	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
16	BDL	BDL	BDL	38.7	BDL	BDL	BDL	BDL	350.5
17	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

Notes: BDL, below detection limits.

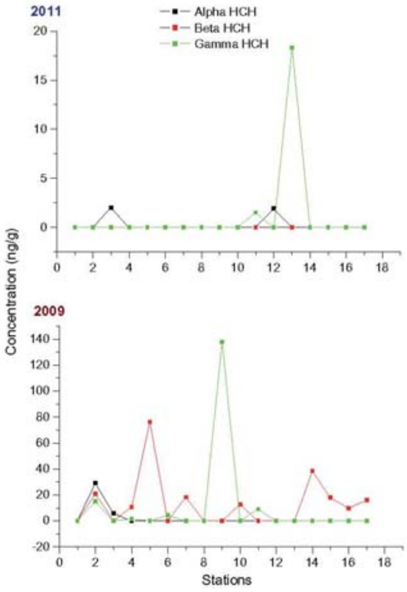

Fig. 2. The levels of HCH isomers in surface sediments of Cochin Estuary (2009–2011).

under anaerobic conditions and similar observations reported earlier (Barakat et al., 2002). The results of anoxic behavior of sediments from the study area was in good concurrence with the previous work of Akhil et al., 2013 and Manju et al., 2013.

The total ∑OCl contamination in sediment was 1170 ng/g (2009) and 1087 ng/g (2011) in the entire study region. Maximum concentration of ∑OCl were found in the northern part of the estuary (Fig. 3). Enrichment of organic carbon in association with the greater clay contents is attributed to the enhanced adsorption of organic carbon onto the clay minerals in the low salinity regimes. The weak flow and the huge input of industrial waste in the northern part of the estuary also results in high organic input in this area (Akhil et al., 2013). However the successive post depositional changes may also modify the environment niche drastically.

To determine the potential of organochlorine contaminants that cause adverse effects to biota, concentration ranges of selected analytes from the sampling location were compared to the sediment quality guidelines (SQG) sited in Table 3. Sediment quality guideline values from NOAA's National status and trends program (Long et al., 1995) designate an effects range low (ERL) and an effects range medium (ERM). ERL's represent chemical concentrations below which adverse effect would be rarely observed; ERM's represents the chemical concentration above which adverse effects would frequently occur. The Canadian sediment quality guideline (CCME, 1999), probable effect level (PEL) defines the level above

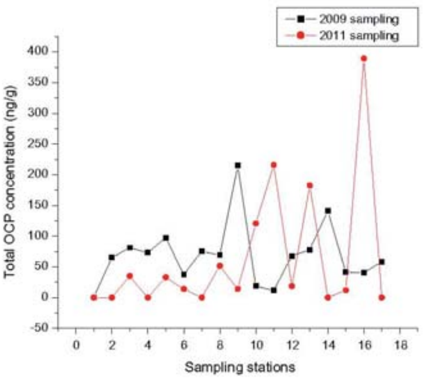

Fig. 3. Total OCP concentrations in surface sediments of Cochin Estuary (2009–2011).

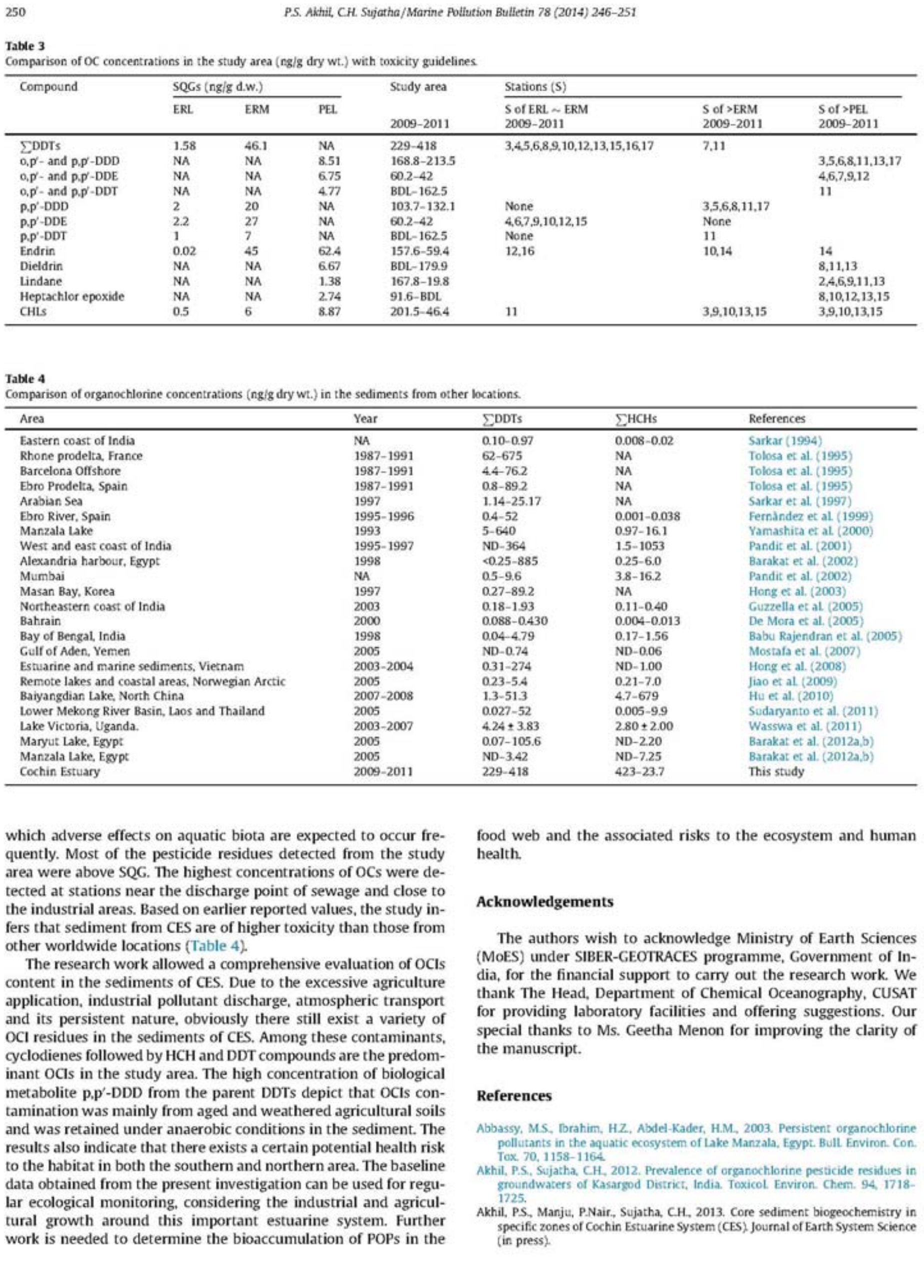

Table 3
Comparison of OC concentrations in the study area (ng/g dry wt.) with toxicity guidelines.

Compound	SQGs (ng/g d.w.)			Study area	Stations (S)		
	ERL	ERM	PEL	2009–2011	S of ERL ∼ ERM 2009–2011	S of >ERM 2009–2011	S of >PEL 2009–2011
∑DDTs	1.58	46.1	NA	229–418	3,4,5,6,8,9,10,12,13,15,16,17	7,11	
o,p′- and p,p′-DDD	NA	NA	8.51	168.8–213.5			3,5,6,8,11,13,17
o,p′- and p,p′-DDE	NA	NA	6.75	60.2–42			4,6,7,9,12
o,p′- and p,p′-DDT	NA	NA	4.77	BDL–162.5			11
p,p′-DDD	2	20	NA	103.7–132.1	None	3,5,6,8,11,17	
p,p′-DDE	2.2	27	NA	60.2–42	4,6,7,9,10,12,15	None	
p,p′-DDT	1	7	NA	BDL–162.5	None	11	
Endrin	0.02	45	62.4	157.6–59.4	12,16	10,14	14
Dieldrin	NA	NA	6.67	BDL–179.9			8,11,13
Lindane	NA	NA	1.38	167.8–19.8			2,4,6,9,11,13
Heptachlor epoxide	NA	NA	2.74	91.6–BDL			8,10,12,13,15
CHLs	0.5	6	8.87	201.5–46.4	11	3,9,10,13,15	3,9,10,13,15

Table 4
Comparison of organochlorine concentrations (ng/g dry wt.) in the sediments from other locations.

Area	Year	∑DDTs	∑HCHs	References
Eastern coast of India	NA	0.10–0.97	0.008–0.02	Sarkar (1994)
Rhone prodelta, France	1987–1991	62–675	NA	Tolosa et al. (1995)
Barcelona Offshore	1987–1991	4.4–76.2	NA	Tolosa et al. (1995)
Ebro Prodelta, Spain	1987–1991	0.8–89.2	NA	Tolosa et al. (1995)
Arabian Sea	1997	1.14–25.17	NA	Sarkar et al. (1997)
Ebro River, Spain	1995–1996	0.4–52	0.001–0.038	Fernàndez et al. (1999)
Manzala Lake	1993	5–640	0.97–16.1	Yamashita et al. (2000)
West and east coast of India	1995–1997	ND–364	1.5–1053	Pandit et al. (2001)
Alexandria harbour, Egypt	1998	<0.25–885	0.25–6.0	Barakat et al. (2002)
Mumbai	NA	0.5–9.6	3.8–16.2	Pandit et al. (2002)
Masan Bay, Korea	1997	0.27–89.2	NA	Hong et al. (2003)
Northeastern coast of India	2003	0.18–1.93	0.11–0.40	Guzzella et al. (2005)
Bahrain	2000	0.088–0.430	0.004–0.013	De Mora et al. (2005)
Bay of Bengal, India	1998	0.04–4.79	0.17–1.56	Babu Rajendran et al. (2005)
Gulf of Aden, Yemen	2005	ND–0.74	ND–0.06	Mostafa et al. (2007)
Estuarine and marine sediments, Vietnam	2003–2004	0.31–274	ND–1.00	Hong et al. (2008)
Remote lakes and coastal areas, Norwegian Arctic	2005	0.23–5.4	0.21–7.0	Jiao et al. (2009)
Baiyangdian Lake, North China	2007–2008	1.3–51.3	4.7–679	Hu et al. (2010)
Lower Mekong River Basin, Laos and Thailand	2005	0.027–52	0.005–9.9	Sudaryanto et al. (2011)
Lake Victoria, Uganda.	2003–2007	4.24 ± 3.83	2.80 ± 2.00	Wasswa et al. (2011)
Maryut Lake, Egypt	2005	0.07–105.6	ND–2.20	Barakat et al. (2012a,b)
Manzala Lake, Egypt	2005	ND–3.42	ND–7.25	Barakat et al. (2012a,b)
Cochin Estuary	2009–2011	229–418	423–23.7	This study

which adverse effects on aquatic biota are expected to occur frequently. Most of the pesticide residues detected from the study area were above SQG. The highest concentrations of OCs were detected at stations near the discharge point of sewage and close to the industrial areas. Based on earlier reported values, the study infers that sediment from CES are of higher toxicity than those from other worldwide locations (Table 4).

The research work allowed a comprehensive evaluation of OCIs content in the sediments of CES. Due to the excessive agriculture application, industrial pollutant discharge, atmospheric transport and its persistent nature, obviously there still exist a variety of OCI residues in the sediments of CES. Among these contaminants, cyclodienes followed by HCH and DDT compounds are the predominant OCIs in the study area. The high concentration of biological metabolite p,p′-DDD from the parent DDTs depict that OCIs contamination was mainly from aged and weathered agricultural soils and was retained under anaerobic conditions in the sediment. The results also indicate that there exists a certain potential health risk to the habitat in both the southern and northern area. The baseline data obtained from the present investigation can be used for regular ecological monitoring, considering the industrial and agricultural growth around this important estuarine system. Further work is needed to determine the bioaccumulation of POPs in the food web and the associated risks to the ecosystem and human health.

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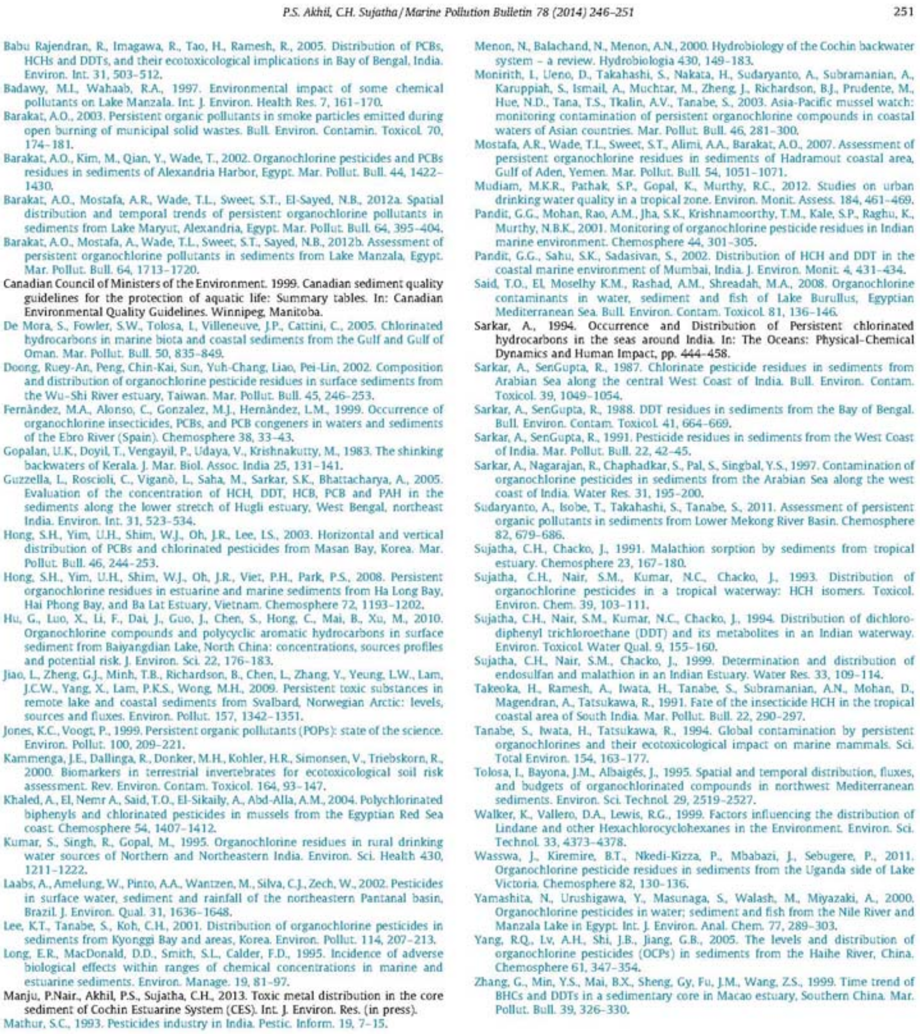

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Toxic Metal Distribution in the Core Sediment of Cochin Estuarine System (CES)

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ABSTRACT: This article present the result from a study of two sediment cores collected from the environmentally distinct zones of CES. Accumulation status of five toxic metals: Cadmium (Cd), Chromium (Cr), Cobalt (Co), Copper (Cu) and Lead (Pb) were analyzed. Besides texture and CHNS were determined to understand the composition of the sediment. Enrichment Factor (EF) and Anthropogenic Factor (AF) were used to differentiate the typical metal sources. Metal enrichment in the cores revealed heavy load at the northern (NS$_1$) region compared with the southern zone (SS$_1$) Elevation of metal content in core NS$_1$ showed the industrial input. Statistical analyses were employed to understand the origin of metals in the sediment samples. Principal Component Analysis (PCA) distinguishes the two zones with different metal accumulation capacity: highest at NS$_1$ and lowest at SS$_1$. Correlation analysis revealed positive significant relation only in core NS$_1$, adhering to the exposition of the intensified industrial pollution.

Key words: Toxic metal, Core sediment, CES, Enrichment Factor, Anthropogenic Factor

INTRODUCTION

Cochin Estuarine System (CES) situated at the tip of the northern Vembanad lake is a tropical positive estuarine system with its northern boundary at Azheekode and southern boundary at Thannirmukham bund. The lake has 80 km length and the width varies between 500 and 4000 m. The depth of the estuary often varies considerably, the major portion of the estuary has a depth range of 2–7 m. Water from two major rivers - Periyar and Muvattupuzha drains into this estuary. The nutrients and pollutants introduced into the estuary control to a great extent in the distribution and abundance of less tolerant species in ecologically sensitive areas in the backwaters. CES, widely regarded as one of the polluted estuaries in India (CPCB, 1996), entails contaminated freshwater inputs and discharges of effluents and partially treated sewage from many points throughout its tidally mixed zone. Recently, changes brought about in the estuary like reclamation and consequent shrinkage of the backwaters (Harikumar *et al.*,2009). Furthermore, the discharge of pollutants has made an adverse impact on the potential of aquatic ecosystems that used to support high levels of bio productivity and biodiversity.

Heavy metal concentration in the estuarine and coastal sediments is usually quiet high due to significant anthropogenic metal loading carried by tributary rivers (Muniz *et al.*, 2004; Guerra Gracia Jose & Gracia Gomez 2005). Thus sediments may serve as a metal pool that can release metals to the aquatic system and ultimately create toxic effect on the ecosystem due to bioaccumulation and persistent nature (Graham-Evans *et al.*, 2003; Mc Cready *et al.*, 2006). In recent years, increasing attention was given in the level of heavy metals in the sediment band (Carral *et al.*, 1992, 1995; Carballeira *et al.*, 1997; Harikumar *et al.*, 2009; Ratheesh Kumar *et al.*, 2010; Paneer Selvam *et al.*, 2012).

Geochemical study of core sediment is a helpful tool in the assessment of pollution settled in the aquatic systems. For a long period there were no pollution control regulation in the Cochin estuary, consequently partially or untreated effluents from the industries were discharged in to the water body and getting accumulated in the bottom sediment phase. Therefore the present study is to understand the characteristics of toxic metals in the core sediments of CES. Two sediment cores were collected from two prominent fresh water areas of the system. One has the industrial origin and other has domestic effluent. Toxic metal (Cd, Co, Cr, Cu, Pb) distribution, grain size

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*Corresponding author E-mail: drchsujatha@yahoo.co.in parameters and CHNS were determined to pinpoint a clear cut idea on the quality of the CES. This is the first detailed baseline dataset on toxic metal description of the core sediment in the CES.

MATERIALS & METHODS

The study area includes the CES (Fig. 1) and systematically described into two zones the South and the North in view of the environmental variability. SS_1 comprises the sampling station situated in the fresh water region and originate from the southern bough of Muvattupuzha. Many people living aside to it consider the aquatic body as their water source for various aesthetic and domestic purposes other than drinking uses. The NS_1 station situated near the vicinity of the industrial region and originates from the locality of River Periyar, which is known as the life line of Kerala. The cores were collected during low tide by pushing a hand held PVC pipe (150-300 cm long and 6.3 cm diameter) in November 2009 by a diver at the above mentioned zones of the CES. Water depth in the area was found to be 1.5m for both NS_1 and SS_1. The different length of the core obtained were 45 cm (SS_1) and 23 cm (NS_1). Sediment cores were sliced into 3 cm segments, transferred to plastic vessels and frozen at 4°C till further analysis. These sub samples were air dried, finely powdered (< 63 micro meter) separated using 230 ASTM sieve and used for further chemical analysis. Texture was determined using pipette analysis by Lewis 1984. For metal analysis, 0.5g samples were treated with 5:1 mixture of concentrated HNO_3 and $HClO_4$ (Loring & Rantala 1992) and concentration was analyzed by AAS (Perkin Elmer 3110) method. Accuracy of the analytical procedure was checked using a triplicate analysis of a certified reference material (BCSS-1) from the National Research Council of Canada (Table 1).

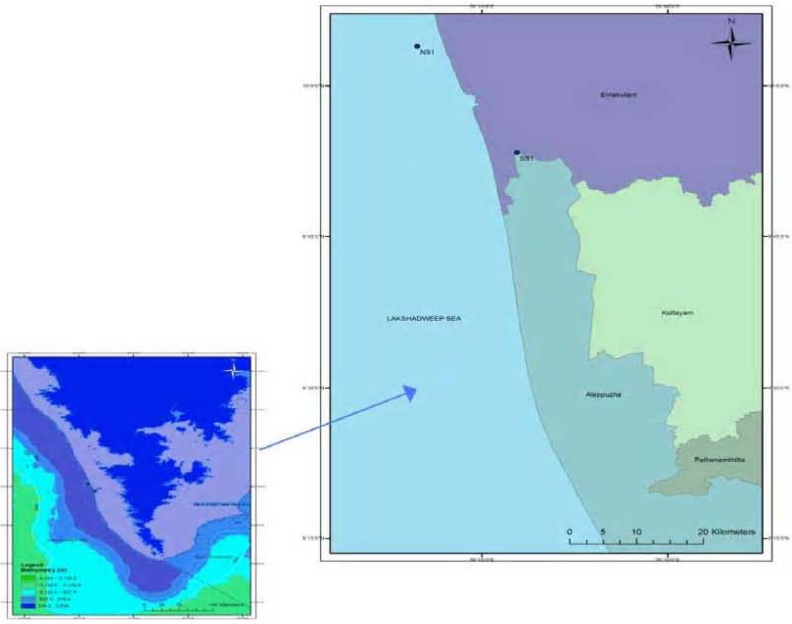


Fig. 1. Location map of sampling stations

Table 1.Comparitive values of BCSS-1 in the present study

Concentration (ppm)	Cd	Cr	Co	Cu	Pb
Metal extracted[a]	0.3	123	11.4	18.5	22.7
Metal extracted[b]	0.291	133	9.2	18.2	19.6
Accuracy (± %)	3	9	10	2	20

[a] Certified values corresponding to the total extraction of trace metals from the standard reference material BCSS-1.

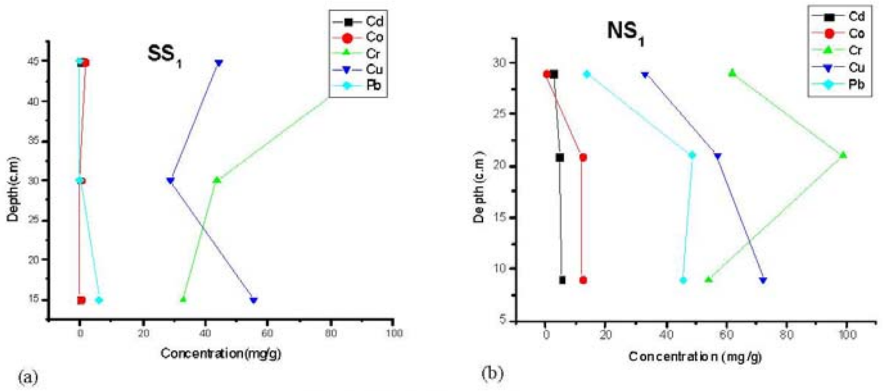
[b] Values of the metals extracted from the standard reference material BCSS-1 in the present study.

RESULTS & DISCUSSION

Increased human activities such as industrialization, coupled with over-population and raise in ambient temperature amongst other factors, have become major environmental issues in recent years. Despite, intensive agriculture and other anthropogenic activities have led to land degradation, environmental pollution and decline in crop productivity and sustainability. These adverse effects have been of great concern to human and animal health. Toxic heavy metal analyses is an important part of environmental pollution impact assessment (Narin *et al.*,1998; Loska *et al.,* 2000; Chiboski 2000; Solecki & Chibowski 2000, Ratheesh Kumar *et al.,* 2010; Paneer Selvam *et al.,* 2012 Manju P Nair & Sujatha C.H 2012; Manju P Nair *et al.,* 2012). Determination of the heavy metal contents in various environmental segments such as soil, natural waters, plants, dusts, etc (Ranjbar 1998; Macias Zamora *et al.*,1999; Soylak *et al.,* 2000) have been continuously performed by earlier researchers.

Much concern has been focused on the investigation of the total metal concentration levels in sediments of different estuarine waters. Sediments contribute a complex mixture of inorganic and organic components and are in built indicator of pollutants in the aquatic system, (Sujatha & Jacob Chacko1991; 1992; Sujatha & Jacob Chacko 1994; Soylak *et al.*,1996; Loska *et al.,* 2000; Kut *et al.,* 2000; Paneer Selvam *et al.,* 2012) , especially trace heavy metal levels of the sediment samples have been widely determined by various researchers. (Narin *et al.,* 1998; Balram *et al.,* 1999; Perezcid *et al.,* 1999). Trace metals are undergoing various physico chemical processes and recycled randomly via both biological and chemical constituents within the sedimentary compartment and water column. A number of investigations in recent years on surface sediment trace metal were carried out in CES (Shajan 2001; Balachandran *et al.,* 2005, 2006; Renjith & Chandramohanakumar 2009; Harikumar *et al.,* 2009; Ratheesh Kumar *et al.,* 2010; Paneer Selvam *et al.,* 2012). The present research attempt was carried out to compile a systematic data set to the toxic metal distribution (Cd, Co, Cr,Cu and Pb) in the core sediments of two diverse zones in the CES (Fig. 2).

Concentration of toxic metal in core SS_1 given in Table 2. Cadmium concentration was below detectable level in this core .Cobalt concentration ranges between 0-1.49mg/g. Highest level was found at the bottom of the core. Chromium content was intensified as depth increased. It was varied from 32.98 to 94.55 mg/g. Highest concentration Cu was observed in the top layers of the core and assorted between 29.01 to 55.57 mg/g. Lead showed an increased trend towards the surface of the core. Table 3 represent concentration of toxic metal in core NS_1 . Cadmium content ranged from 2.47 to 5.29 mg/g and was decreased with increase in depth. The load of Cd is comparatively high in this core reveals that the loading of Cd is mainly through industries. Human exposures to environmental cadmium are primarily the result of fossil fuel combustion, phosphate fertilizers, natural sources, iron and steel production, cement production, nonferrous metals production and municipal solid waste incineration. Cobalt concentration was intensified towards the middle part and then diminished.It showed a variation between 0 to 12.04 mg/g. The greater Co content is due to sewage or industrial runoff. Chromium was increased to the middle then lowered. Sources of Cr in the study area were from industrial or sewage effluents. Copper was varied between 33.10 to 72.51 mg/g and



(a) (b)

Fig. 2. Distribution of Toxic metal

showed an intensification to the top. Lead concentration was increased at the middle then lowered toward the bottom of the core NS_1. Lead content greater at NS_1 core originates mainly from industrial activity. In cores SS_1 and NS_1 the sediments were enriched with clay, so the adsorption is greater and metal content is high. SS_1 core is from the fresh water region the metal content intensified due to inputs from domestic and agricultural activities. Core NS_1 is also a fresh water area but it is situated in the industrial field .All the metals analyzed were present here; this may be from the industrial effluent.

Enrichment factor (EF) was interpreted for metal studied with respect to natural background concentration. EF< 1 indicates no enrichment, EF< 3 is minor enrichment, EF = 3-5 is moderate enrichment, EF=5-10 moderately severe enrichment, EF=10-25 severe enrichment, EF= 25-50 is very severe enrichment and EF >50 is extremely severe enrichment. The metal analysed showed a speckled enrichment . EF distributions for cores SS_1 and NS_1 were given in Table 4 and Table 5 respectively. Cadmium showed severe enrichment in core NS_1 but the SS_1 core behaved as a "Cd free zone". Cobalt had no enrichment in the studied area. Chromium had minor enrichment, in SS_1 bottom , at NS_1 middle and bottom portion of the core . Copper showed minor enrichment in the two cores. Lead had minor enrichment at the top and bottom and moderate enrichment in the middle, for NS_1 . In all the sites showed metal enrichment because of the antropogenic inputs and heavier load at NS_1 core due to industrial activities. The enrichment was normalized relative to depth in the sediment core was expressed using anthropogenic factor. In the studied cores metal contamination level was identified for Cu (SS_1) and; Cd, Cu, Pb (NS_1). C/N ratio also indicated the same allothonous input in the core. Elemental distributions (CHNS) in all the four sediment cores were in the order as follows C> S>H>N.

Principal Component Analysis (PCA) and correlation analysis was done to understand the interrelationship between the parameters. The factor loading matrixes generated by using sediment variables. The first factor shows the strong loading of Cr,Cu along with fine fractions of the sediment reveals the association of metals with fine fractions. This revealed the granulametric dependence of the metals.In the second factor metal load showed the geogenic mineral association in these sediments. Second factor gave good load of Cu again revealed the geogenic source. Third factor again revealed the granulametric dependence with clay.The fourth factor (Pb) exposed

Table 2. Concentration of toxic metal in core SS_1

Sections	Cd(mg/g)	Co(mg/g)	Cr(mg/g)	Cu(mg/g)	Pb(mg/g)
Top	0	0	32.98	55.57	6.21
Middle	0	0	43.63	29.01	0
Bottom	0	1.49	94.55	44.25	0

Table 3. Concentration of toxic metal in core NS_1

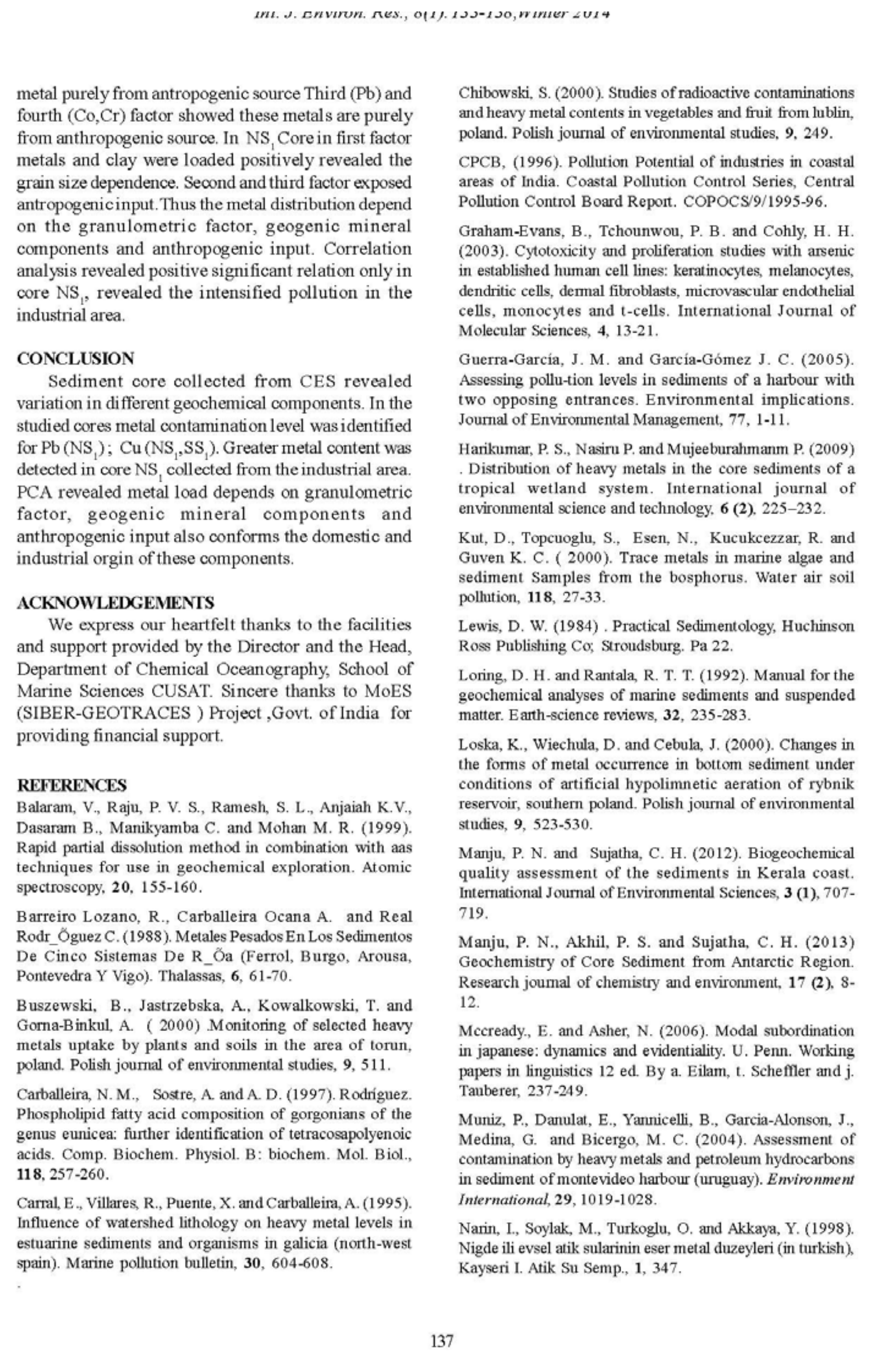
Sections	Cd(mg/g)	Co(mg/g)	Cr(mg/g)	Cu(mg/g)	Pb(mg/g)
Top	5.29	11.99	54.152	72.51	45.68
Middle	4.46	12.04	98.77	56.97	48.79
Bottom	2.47	0	61.99	33.10	13.89

Table 4. Enrichment factor of toxic metal in core SS_1

Sections	Cd	Co	Cr	Cu	Pb
Top	0	0	0.61	2.08	0.53
Middle	0	0	0.85	1.13	0
Bottom	0	0.092	1.23	1.16	0

Table 5. Enrichment factor of toxic metal in core NS_1

Sections	Cd	Co	Cr	Cu	Pb
Top	21.58	0.77	0.74	1.98	2.82
Middle	19.71	0.84	1.45	1.69	3.265
Bottom	18.07	0	1.51	1.62	1.54



metal purely from antropogenic source Third (Pb) and fourth (Co,Cr) factor showed these metals are purely from anthropogenic source. In NS_1 Core in first factor metals and clay were loaded positively revealed the grain size dependence. Second and third factor exposed antropogenic input. Thus the metal distribution depend on the granulometric factor, geogenic mineral components and anthropogenic input. Correlation analysis revealed positive significant relation only in core NS_1, revealed the intensified pollution in the industrial area.

CONCLUSION

Sediment core collected from CES revealed variation in different geochemical components. In the studied cores metal contamination level was identified for Pb (NS_1) ; Cu (NS_1,SS_1). Greater metal content was detected in core NS_1 collected from the industrial area. PCA revealed metal load depends on granulometric factor, geogenic mineral components and anthropogenic input also conforms the domestic and industrial orgin of these components.

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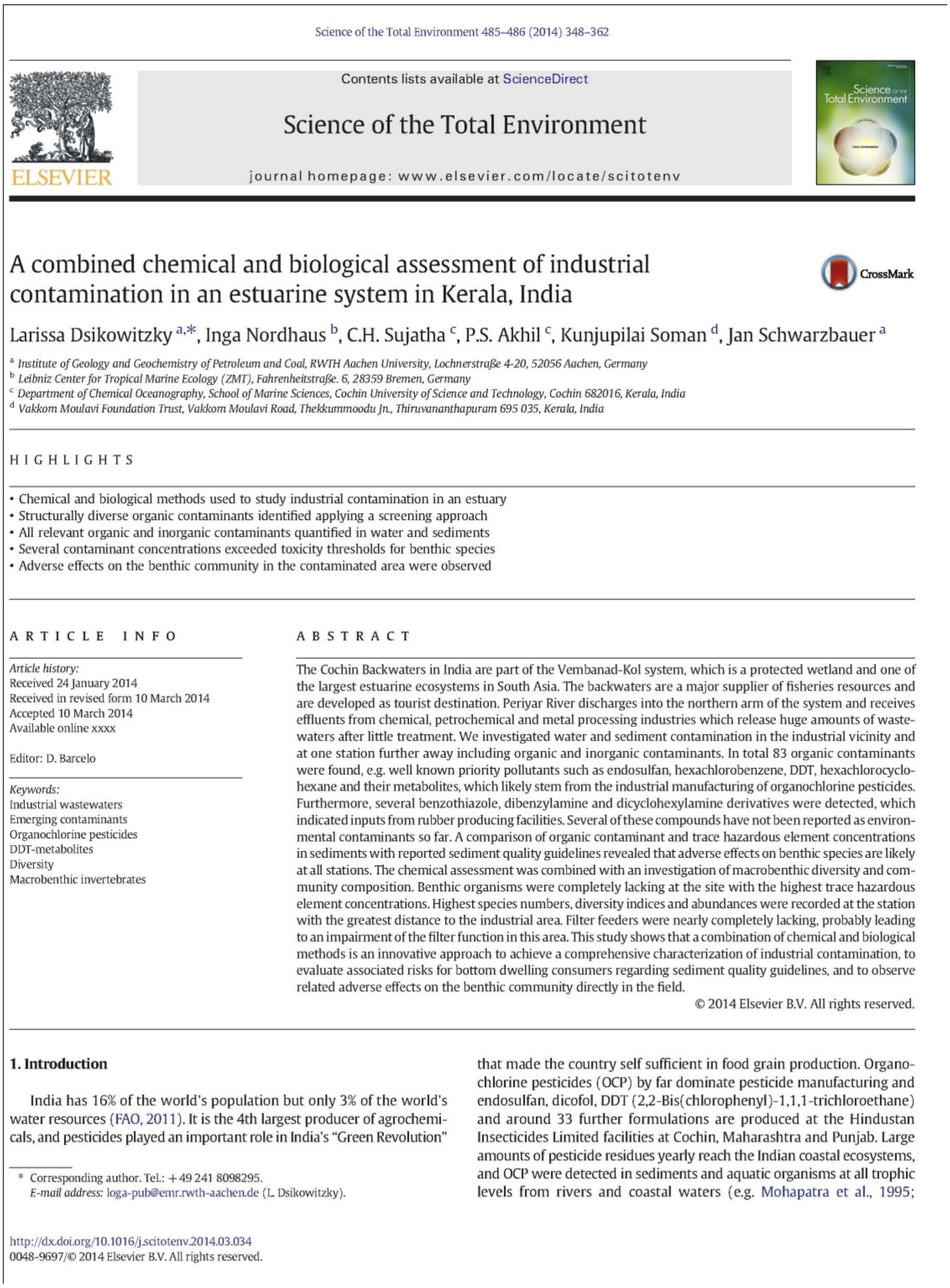

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A combined chemical and biological assessment of industrial contamination in an estuarine system in Kerala, India

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HIGHLIGHTS

- Chemical and biological methods used to study industrial contamination in an estuary
- Structurally diverse organic contaminants identified applying a screening approach
- All relevant organic and inorganic contaminants quantified in water and sediments
- Several contaminant concentrations exceeded toxicity thresholds for benthic species
- Adverse effects on the benthic community in the contaminated area were observed

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ABSTRACT

The Cochin Backwaters in India are part of the Vembanad-Kol system, which is a protected wetland and one of the largest estuarine ecosystems in South Asia. The backwaters are a major supplier of fisheries resources and are developed as tourist destination. Periyar River discharges into the northern arm of the system and receives effluents from chemical, petrochemical and metal processing industries which release huge amounts of wastewaters after little treatment. We investigated water and sediment contamination in the industrial vicinity and at one station further away including organic and inorganic contaminants. In total 83 organic contaminants were found, e.g. well known priority pollutants such as endosulfan, hexachlorobenzene, DDT, hexachlorocyclohexane and their metabolites, which likely stem from the industrial manufacturing of organochlorine pesticides. Furthermore, several benzothiazole, dibenzylamine and dicyclohexylamine derivatives were detected, which indicated inputs from rubber producing facilities. Several of these compounds have not been reported as environmental contaminants so far. A comparison of organic contaminant and trace hazardous element concentrations in sediments with reported sediment quality guidelines revealed that adverse effects on benthic species are likely at all stations. The chemical assessment was combined with an investigation of macrobenthic diversity and community composition. Benthic organisms were completely lacking at the site with the highest trace hazardous element concentrations. Highest species numbers, diversity indices and abundances were recorded at the station with the greatest distance to the industrial area. Filter feeders were nearly completely lacking, probably leading to an impairment of the filter function in this area. This study shows that a combination of chemical and biological methods is an innovative approach to achieve a comprehensive characterization of industrial contamination, to evaluate associated risks for bottom dwelling consumers regarding sediment quality guidelines, and to observe related adverse effects on the benthic community directly in the field.

1. Introduction

India has 16% of the world's population but only 3% of the world's water resources (FAO, 2011). It is the 4th largest producer of agrochemicals, and pesticides played an important role in India's "Green Revolution" that made the country self sufficient in food grain production. Organochlorine pesticides (OCP) by far dominate pesticide manufacturing and endosulfan, dicofol, DDT (2,2-Bis(chlorophenyl)-1,1,1-trichloroethane) and around 33 further formulations are produced at the Hindustan Insecticides Limited facilities at Cochin, Maharashtra and Punjab. Large amounts of pesticide residues yearly reach the Indian coastal ecosystems, and OCP were detected in sediments and aquatic organisms at all trophic levels from rivers and coastal waters (e.g. Mohapatra et al., 1995;

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Senthilkumar et al., 2001). Increased levels of β-hexachlorocyclohexane and dieldrin in blood were attributed to the higher incidence of Parkinson's disease among the North Indian population (Chhillar et al., 2013). Recently, genetic disorders in children and new borns from the vicinity of cashew plantations sprayed with endosulfan in the northern part of Kerala, a state at the southern tip of India, were reported in the newspapers and discussed by the public (e.g. Akhil and Sujatha, 2012).

The principal chemical industries of the Kerala state (~70%) are located near Cochin City at the Chitrapuzha River and the Periyar River banks (at Eloor). The two rivers discharge into the Cochin Backwaters (Fig. 1), a large estuarine system (256 km^2), which are part of the Vembanad-Kol wetlands, a RAMSAR protective area of international importance. The human intervention in the backwaters dates back to 1836 but has accelerated during the last five decades. The booming city of Cochin has a high population density and is one of the 17 major industrial cities of India. There are ~250 industries situated at the Periyar River banks, including Fertilizers and Chemicals Travancore Limited (FACT), Travancore Cochin Chemicals, Travancore Rayon's, Indian Rare Earths Limited, Hindustan Insecticides Limited (HIL), Cochin Refineries, Hindustan Organic Chemicals Limited, Periyar Chemicals, United Catalysts, and Cominco Binani Zinc manufacture. A wide range of chemical products is synthesized including organochlorine pesticides, rubber processing chemicals, paints, pigments, solvents, acids and greases. Furthermore, mercury, zinc, chrome and rare earth elements are manufactured. The processes in the factories include leather tanning, rubber production, production of batteries, and crude oil refining. The industrial facilities take large amounts of water from the Periyar River and in turn discharge concentrated toxic effluents after little treatment (trickling filter technique followed by a clarifier for the removal of sludge or removal of organic matter by anaerobic eubacteria and archaea) (e.g. Nasir, 2010). The Cochin Backwaters also receive untreated effluents (104 billion liters per day) from domestic sectors (CPCB, 1996). In addition, wastes from aquaculture fields (62 km^2), agricultural fields (80 km^2), coconut husk retting yards, fish processing plants, and animal bone processing units have increased the organic pollution of the system (Thomson, 2002).

The continuous discharge of effluents from both domestic and economic sectors that caused eutrophication of the estuarine waters significantly increased the organic carbon content in sediments (four fold in last 4 decades) and affected the distribution of the benthic fauna (e.g. Martin et al., 2011; Akhil et al., 2013). Hazardous element concentrations in sediments increased, especially in the Eloor area (e.g. Priju and Narayana, 2007; Deepulal et al., 2012). Similar areas were reported by previous researchers (e.g. Silva et al., 2011; Ribeiro et al., 2013). Studies on the occurrence of organic contaminants in the Cochin Backwaters are sparse. However, hexachlorocyclohexane, malathion and endosulfan were detected in water and sediment samples which was attributed to their agricultural usage and to direct inputs from a pesticide manufacturing plant at Eloor (Sujatha et al., 1991, 1999; Akhil and Sujatha, 2014).

Until 15 to 30 years ago, the Cochin Backwaters supported a well established endemic fauna with over 90 macrobenthic species and acted as nursery grounds of commercially important prawns and fish (e.g. Menon et al., 2000). In 2005, an inventory recorded 47 species with a decrease of molluscs and an increase of polychaetes compared to earlier studies (Martin et al., 2011). Macrobenthic species numbers and abundances in the industrial vicinity at Eloor were substantially lower compared to downstream stations (Sarala Devi and Venugopal, 1989; Sarala Devi et al., 1991).

Industrial wastewaters may contain very diverse organic compound groups (e.g. Castillo et al., 1999a,b), many of them formerly not known as environmental contaminants as well as trace hazardous elements. The aim of this study was therefore a first comprehensive survey of relevant organic and inorganic contaminants in water and sediments from

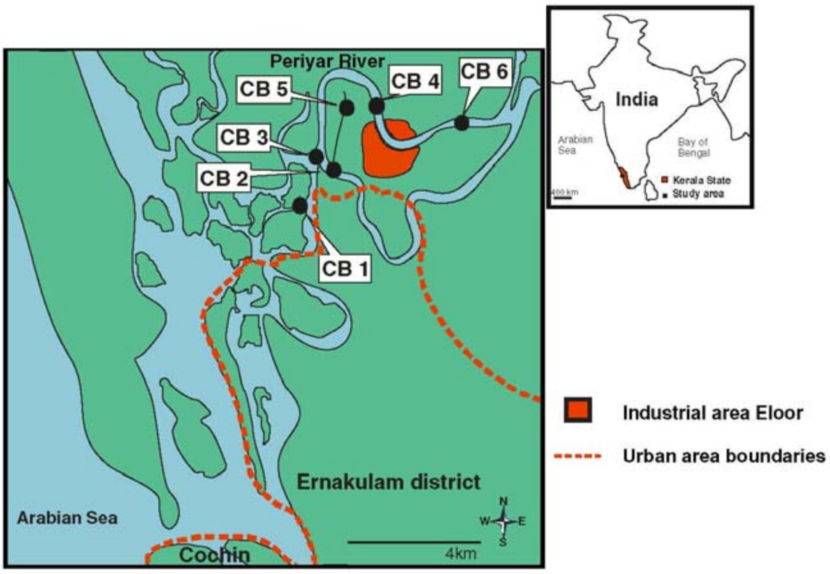

Fig. 1. Schematic overview of the working area which is located in the Cochin Backwaters at the lower reaches of the Periyar River in Kerala State, India. Chemical industries discharge their wastewaters into the Periyar River around the Eloor area.

the industrial area Eloor and the receiving aqueous system, the Periyar River, and a source apportionment of the identified contaminants. For organic contaminant analysis, a gas chromatography–mass spectrometry (GC–MS) non-target screening was executed, which allows for the detection of well known organic pollutants *and* of emerging contaminants, for which the risk potential for the environment has not been investigated yet. This chemical assessment was combined with an investigation of macrobenthic invertebrates in the sediments to get an impression on the related biological response to the industrial contamination.

In detail, the objectives were i) to determine trace hazardous element concentrations in the sediments, ii) to identify and to quantify organic contaminants in water and sediments, iii) to identify organic marker compounds which allow a characterization of the specific industrial sources, and iv) to investigate the distribution, diversity and community composition of macrobenthic invertebrates in relation to contaminant concentrations and the sediment type.

2. Experimental

2.1. Study area

Cochin Backwaters (9°40′ N–10°08′ N, 76°11′ E–76°25′ E) are situated in the northern part of the Vembanad-Kol wetlands, which are a RAMSAR protective area. They form a bar-built estuary with a permanent connection to the Arabian Sea at Cochin harbor and another opening at Azhikode (Fig. 1). Water from six major rivers, including Periyar, are discharging into the Vembanad-Kol system (Menon et al., 2000). The climate is tropical and surface water temperatures range between 29 and 34 °C. The annual rainfall at Cochin is around 3200 mm, nearly 75% of which occurring during the summer monsoon (Qasim, 2003). During monsoon, the brackish water system is converted into a freshwater system even in the area around the bar mouth (Menon et al., 2000). Annual water discharge from Periyar was 8329.14 million m^3 in 1970 and declined substantially after commissioning of dams upstream. The flow pattern at the peak of the tide is towards the estuary during the three seasons (Sankaranarayanan et al., 1986). The Cochin Backwaters are a settling environment, as the sediments are shown to exhibit a low to moderate energy regime in areas away from the river mouths (e.g. Priju and Narayana, 2007). The backwaters provide ideal breeding grounds for fish and shellfish and for completing the life cycle of many commercially important species including prawns. Total fish landings at Cochin constitute ~8% of the fish landings of Kerala state (Quasim, 2003). The Vembanad-Kol wetlands are developed as tourist destination with ~2.5 million foreign and domestic visitors of the Ernakulam district in the year 2011 (Government of Kerala, 2011).

2.2. Sampling

The industrial effluents at Eloor are collected in a drainage channel which flows into the lower reaches of the Periyar River. Water was taken at one station at the drainage channel (CB5) and at two stations at Periyar River downstream (CB3) and upstream (CB6) Eloor on March 3, 2008, during high tide (Fig. 1). During the second sampling campaign, water and surface sediments were sampled at four stations at Periyar River downstream Eloor (CB1, CB2, CB3, CB4) on February 25, 2011, during low tide. Station CB2 is located at Periyar River in striking distance to the drainage channel. Additionally, water was taken from the drainage channel outlet (CB2CH), in order to sample inputs from the channel to Periyar River. Salinity ranged between 0 (CB4) and 4 (CB1). During the second sampling, CB5 and CB6 could not be sampled due to the restricted access to the industrial area.

Water was scooped up from below the water surface and bottled in pre-cleaned aluminum flasks. Surface sediment samples were collected with a Van Veen grab in the subtidal zone and stored in pre-cleaned glass flasks. Additional two sediment samples per station were taken for the investigation of macrobenthic invertebrates. Sub-samples of 2 L were immediately sieved using sieves with nylon gauze and 0.5 mm mesh size. The samples were then fixed in 4% borax-buffered formaldehyde. Samples were transported cooled to the ZMT for trace hazardous element analysis and species identification and to RWTH Aachen University for organic-geochemical analysis and stored dark at 4 °C.

2.3. Grain size distribution

The grain size distribution of the sediment (three replicates at each station) was analyzed with a Laser Particle Analyzer (HORIBA LA-300) allowing a determination of 92 sediment classes between 0.38 and 2000 µm. The results were summarized using seven main classes (clay, fine silt, medium silt, coarse silt, fine sand, medium sand, coarse sand) (Table 1).

2.4. Trace hazardous elements

In order to minimize contamination, before usage all glass and plastic ware was soaked in 10% HNO_3 for 24 h. 500 mg of freeze-dried and powdered sample was weighed into PTFE jars and 12 mL aqua regia [1:3 nitric acid (HNO_3/hydrochloric acid (HCl)] was added. This acid mixture is not able to attack the silicate lattice of the solid matter and is therefore only a partial extraction method which has to be taken into account as these data are not comparable with total metal data (Loring and Rantala, 1992). Digestion took place for 20 min at 170 °C in the microwave (Mars Xpress, CEM, Germany). After cooling, 50 µL internal standard was added (yttrium ICP standard, 1000 ppm, Merck chemicals, Darmstadt, Germany) and the sample volume was filled up to 50 mL. For the removal of suspended matter, samples were centrifuged with 3000 rcf for 10 min.

The concentrations of the elements As, Bi, Co, Cr, Cu, Mn, Mo, Ni, Pb, V, W and Zn for which reliable results could be produced using an inductively coupled plasma-optical emission spectrometer (ICP-OES, side-on plasma, Ciros Vision, Spectro Ametek) were determined. The system was equipped with a Crossflow nebulizer and a Scott spray chamber. Operating RF power was 1.4 kW. Ar gas flow rate (L min^{-1}) was: cool gas 12, auxiliary 0.8, and nebulizer 0.9. Calibration was performed using standard solutions with defined concentrations. Yttrium was used as internal standard element. Analytical wavelengths and the lower limit of determination for each element are given in Table 2. Recovery rates were determined by performing two replicate extractions of the certified reference material PACS-2 (harbor sediment, National Research council, Canada) and are given with relative standard deviation (RSD) (Table 2). PACS-2 is a certified material for total digestion, therefore recovery rates <100% were obtained due to partial extraction of the trace hazardous elements with aqua regia (see above). No recovery rates were determined for tungsten and bismuth.

Trace hazardous element concentrations in surface sediment samples from the Cochin Backwaters were analyzed by performing three replicated extractions. If measurements were performed with more than one wavelength for an element, mean values of the different individual signals were calculated. Mean element concentrations in the samples and standard deviation (s) are shown in Table 4. Trace element concentrations in procedural blanks were negligible.

2.5. Organic contaminants

2.5.1. Chemicals, recoveries and blank experiments

Reference materials of the identified compounds were purchased from Sigma-Aldrich, Germany. Recoveries for water samples ($n = 3$) were determined by spiking 1 L high-purity water (Lichrosolv, Merck, Germany) with concentrations of 5 µg of the respective reference compounds and subsequent execution of the analytical procedure as described in Section 2.5.2. Recoveries for sediment samples ($n = 4$)

Table 1
Mean grain size distribution of the sediment samples (given in %). The grain size distribution was significantly different between sites (ANOSIM, global R = 0.89, p = 0.001). Due to the high fraction of coarse sand and low contribution of silt, the sediment at CB2 differed highly from that of all other sites (ANOSIM, R = 1, p = 0.1 each).

Site	Clay	Fine silt	Medium silt	Coarse silt	Fine sand	Medium sand	Coarse sand
	<2 μm	2–6.3 μm	6.3–20 μm	20–63 μm	63–200 μm	200–630 μm	630–2000 μm
CB1	5.25	12.52	20.76	17.03	27.37	14.77	2.29
CB2	0.22	0.64	0.93	0.76	1.84	36.18	59.43
CB3	3.21	8.24	16.06	16.02	14.52	21.75	20.23
CB4	3.97	8.82	15.87	20.58	25.70	16.60	8.48

were assessed by spiking 6 g of a pre-extracted fine-grained sediment with 5 μg of each reference compound and subsequent extraction as described in Section 2.5.2. Varying compositions of particulate matter, which probably lead to varying recovery rates, were not taken into account. The results of the recovery experiments are summarized in Table 3.

In order to minimize sample contamination, only glass, metal and PTFE equipment was used. The equipment was rinsed with high-purity acetone and *n*-hexane before usage. All solvents were distilled over a 0.5 m packed column and their purity was tested by gas chromatographic analyses. Na_2SO_4 and HCl, which were needed for the analytical procedures, were cleaned with *n*-hexane. Blank analyses ($n = 3$) revealed that none of the investigated compounds were detected in the blank.

2.5.2. Extraction procedures

Prior to extraction, 1 L aliquots of the water samples were decanted in order to remove suspended particulate matter from the aqueous phase. Samples were treated by sequential liquid–liquid extraction with organic solvents of different polarity (Dsikowitzky et al., 2002). The first two fractions were spiked with 50 μL surrogate standard solution A containing 6.12 ng μL^{-1} d_{34}-hexadecane and 7.10 ng μL^{-1} decafluorobenzophenone. The third fraction was spiked with 200 μL surrogate standard solution B containing 7.17 ng μL^{-1} fluoroacetophenone, 6.96 ng μL^{-1} decafluorobenzophenone and 4.87 ng μL^{-1} difluorophenylacetic acid. All fractions were concentrated by rotary evaporation and dried with anhydrous granulated Na_2SO_4. Prior to analysis, acidic compounds in the third fraction were methylated by addition of a methanolic diazomethane solution. The first two fractions were evaporated to final volumes of 50 μL, and the third fractions to 200 μL.

The analytical procedure used for the extraction of sediments and subsequent fractionation of organic compounds was described elsewhere (Schwarzbauer et al., 2000). Briefly, sediments were treated by extraction with a high-speed dispersion tool using mixtures of acetone and *n*-hexane. After volume reduction by rotary evaporation and drying over anhydrous granulated Na_2SO_4, elemental sulfur was removed by addition of activated copper powder. Thereafter, the raw extract was separated into six fractions by column chromatography with activated silica gel using solvent mixtures of *n*-pentane, dichloromethane and methanol. Fractions 1 to 5 were spiked with 50 μL surrogate standard A and fraction 6 with 200 μL surrogate standard B. Prior to analysis, fractions 1 to 5 were evaporated to a volume of 50 μL. Acidic compounds in fraction 6 were methylated by addition of a methanolic diazomethane solution and the volume was reduced to 200 μL.

2.5.3. Analysis with gas chromatography–mass spectrometry (GC/MS)

GC/MS analyses were carried out with a quadrupol Trace MS mass spectrometer (Thermoquest, Germany) linked to a Mega Series HRGC 5160 gas chromatograph (Carlo Erba, Italy), equipped with a ZB-5 fused silica capillary column (Phenomenex, Aschaffenburg, Germany, 30 m × 0.25 mm ID × 0.25 μm film thickness). The GC was programmed from 60 to 310 °C at a rate of 5 °C min^{-1} after 3 min at initial temperature, and was kept at 310 °C for 20 min. Helium carrier gas velocity was 30 cm s^{-1}. The injection was carried out on a split/splitless injector at 270 °C, splitless time was 60 s. The mass spectrometer was operated in full-scan mode with a source temperature of 200 °C in EI + mode (70 eV), scanning from 35 to 700 amu with a rate of 0.5 s $decade^{-1}$ and an inter-scan time of 0.1 s.

Identification of the individual compounds was based on comparison of EI+ mass spectra with those of databases (NIST'02, Wiley), and was verified with mass spectra of purchased reference compounds considering also gas chromatographic retention times and elution orders. Identified compounds were screened in all samples. Quantitative data were obtained by integration of selected ion chromatograms extracted from the total ion current. The ions used for quantification are given in Table 3. GC/MS response factors for the quantified compounds were determined from four-point linear regression functions based on calibration measurements with different compound concentrations. The concentrations ranged within the expected concentrations of the compounds in the samples and within the linear detection range. For correction of injection volume and sample volume inaccuracies the surrogate standard was used.

2.6. Macrobenthic invertebrates

Samples were stained with Bengal rose (4 g L^{-1}) for at least one day. Organisms were sorted visually from sorting trays and then stored in

Table 2
Wavelengths used for ICP–OES, lower limit of determination and recovery rates of each element as obtained from two replicate extractions of certified reference material given with relative standard deviation (RSD) of the analyses.

Element	Wavelengths (nm)	Lower limit of determination in solid matter [mg kg^{-1}]	Recovery rate [%]	Precision [%RSD]
As	189.042	6	77	2
Bi	223.061	4	Not determined	
Co	228.616, 230.786	2	87	8
Cr	267.716, 283.563	2	64	8
Cu	324.754, 327.396	2	98	5
Mn	257.611, 259.373, 260.569, 294.921	2	67	9
Mo	203.884, 202.030	2	84	2
Ni	231.604, 341.476	10	79	7
Pb	220.353	5	85	6
V	242.402, 292.464, 311.071	2	71	10
W	207.911	7	Not determined	
Zn	213.856, 206.191	2	80	5

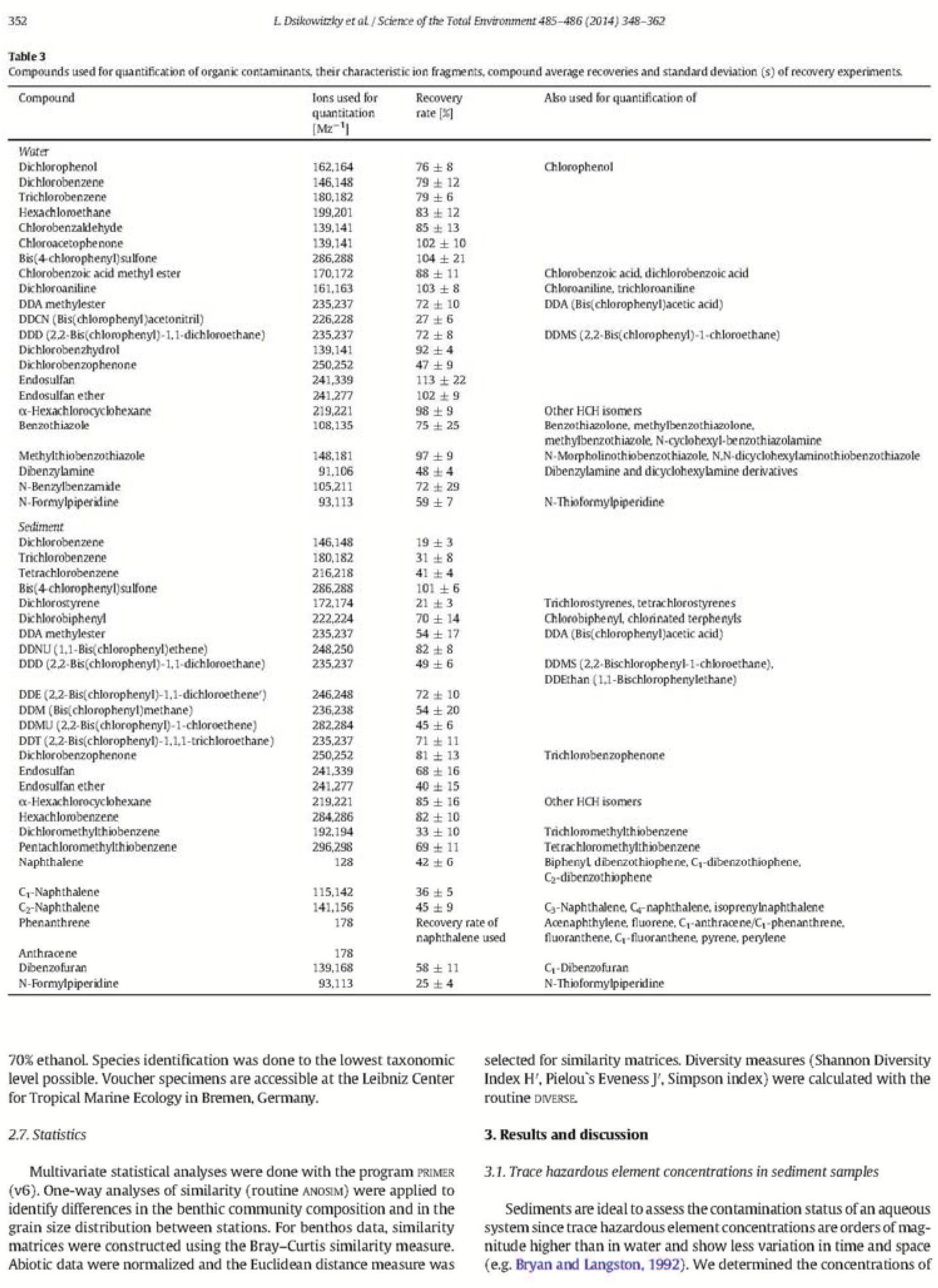

Table 3

Compounds used for quantification of organic contaminants, their characteristic ion fragments, compound average recoveries and standard deviation (s) of recovery experiments.

Compound	Ions used for quantitation [Mz^{-1}]	Recovery rate [%]	Also used for quantification of
Water			
Dichlorophenol	162,164	76 ± 8	Chlorophenol
Dichlorobenzene	146,148	79 ± 12	
Trichlorobenzene	180,182	79 ± 6	
Hexachloroethane	199,201	83 ± 12	
Chlorobenzaldehyde	139,141	85 ± 13	
Chloroacetophenone	139,141	102 ± 10	
Bis(4-chlorophenyl)sulfone	286,288	104 ± 21	
Chlorobenzoic acid methyl ester	170,172	88 ± 11	Chlorobenzoic acid, dichlorobenzoic acid
Dichloroaniline	161,163	103 ± 8	Chloroaniline, trichloroaniline
DDA methylester	235,237	72 ± 10	DDA (Bis(chlorophenyl)acetic acid)
DDCN (Bis(chlorophenyl)acetonitril)	226,228	27 ± 6	
DDD (2,2-Bis(chlorophenyl)-1,1-dichloroethane)	235,237	72 ± 8	DDMS (2,2-Bis(chlorophenyl)-1-chloroethane)
Dichlorobenzhydrol	139,141	92 ± 4	
Dichlorobenzophenone	250,252	47 ± 9	
Endosulfan	241,339	113 ± 22	
Endosulfan ether	241,277	102 ± 9	
α-Hexachlorocyclohexane	219,221	98 ± 9	Other HCH isomers
Benzothiazole	108,135	75 ± 25	Benzothiazolone, methylbenzothiazolone, methylbenzothiazole, N-cyclohexyl-benzothiazolamine
Methylthiobenzothiazole	148,181	97 ± 9	N-Morpholinothiobenzothiazole, N,N-dicyclohexylaminothiobenzothiazole
Dibenzylamine	91,106	48 ± 4	Dibenzylamine and dicyclohexylamine derivatives
N-Benzylbenzamide	105,211	72 ± 29	
N-Formylpiperidine	93,113	59 ± 7	N-Thioformylpiperidine
Sediment			
Dichlorobenzene	146,148	19 ± 3	
Trichlorobenzene	180,182	31 ± 8	
Tetrachlorobenzene	216,218	41 ± 4	
Bis(4-chlorophenyl)sulfone	286,288	101 ± 6	
Dichlorostyrene	172,174	21 ± 3	Trichlorostyrenes, tetrachlorostyrenes
Dichlorobiphenyl	222,224	70 ± 14	Chlorobiphenyl, chlorinated terphenyls
DDA methylester	235,237	54 ± 17	DDA (Bis(chlorophenyl)acetic acid)
DDNU (1,1-Bis(chlorophenyl)ethene)	248,250	82 ± 8	
DDD (2,2-Bis(chlorophenyl)-1,1-dichloroethane)	235,237	49 ± 6	DDMS (2,2-Bischlorophenyl-1-chloroethane), DDEthan (1,1-Bischlorophenylethane)
DDE (2,2-Bis(chlorophenyl)-1,1-dichloroethene′)	246,248	72 ± 10	
DDM (Bis(chlorophenyl)methane)	236,238	54 ± 20	
DDMU (2,2-Bis(chlorophenyl)-1-chloroethene)	282,284	45 ± 6	
DDT (2,2-Bis(chlorophenyl)-1,1,1-trichloroethane)	235,237	71 ± 11	
Dichlorobenzophenone	250,252	81 ± 13	Trichlorobenzophenone
Endosulfan	241,339	68 ± 16	
Endosulfan ether	241,277	40 ± 15	
α-Hexachlorocyclohexane	219,221	85 ± 16	Other HCH isomers
Hexachlorobenzene	284,286	82 ± 10	
Dichloromethylthiobenzene	192,194	33 ± 10	Trichloromethylthiobenzene
Pentachloromethylthiobenzene	296,298	69 ± 11	Tetrachloromethylthiobenzene
Naphthalene	128	42 ± 6	Biphenyl, dibenzothiophene, C_1-dibenzothiophene, C_2-dibenzothiophene
C_1-Naphthalene	115,142	36 ± 5	
C_2-Naphthalene	141,156	45 ± 9	C_3-Naphthalene, C_4-naphthalene, isoprenylnaphthalene
Phenanthrene	178	Recovery rate of naphthalene used	Acenaphthylene, fluorene, C_1-anthracene/C_1-phenanthrene, fluoranthene, C_1-fluoranthene, pyrene, perylene
Anthracene	178		
Dibenzofuran	139,168	58 ± 11	C_1-Dibenzofuran
N-Formylpiperidine	93,113	25 ± 4	N-Thioformylpiperidine

70% ethanol. Species identification was done to the lowest taxonomic level possible. Voucher specimens are accessible at the Leibniz Center for Tropical Marine Ecology in Bremen, Germany.

2.7. Statistics

Multivariate statistical analyses were done with the program PRIMER (v6). One-way analyses of similarity (routine ANOSIM) were applied to identify differences in the benthic community composition and in the grain size distribution between stations. For benthos data, similarity matrices were constructed using the Bray–Curtis similarity measure. Abiotic data were normalized and the Euclidean distance measure was selected for similarity matrices. Diversity measures (Shannon Diversity Index H′, Pielou`s Eveness J′, Simpson index) were calculated with the routine DIVERSE.

3. Results and discussion

3.1. Trace hazardous element concentrations in sediment samples

Sediments are ideal to assess the contamination status of an aqueous system since trace hazardous element concentrations are orders of magnitude higher than in water and show less variation in time and space (e.g. Bryan and Langston, 1992). We determined the concentrations of

12 trace hazardous elements in the surface sediment samples and calculated the contamination factor (CF) (Håkanson, 1980) as well as the geoaccumulation index (GAI) (Müller, 1969). The data are presented in Table 4. For calculation of the CF, the world crustal average trace element concentrations (Wedepohl, 1995) were used as background values. The CF was developed as potential ecological risk index whereas the GAI helps to understand the current contamination level as compared to natural element concentrations in aquatic systems.

A very high level of trace hazardous element contamination considering the CF was observed at station CB4 in the immediate industrial vicinity with respect to the elements Pb, V, W and Zn (Table 4). The companies Binani Zinc Ltd. discharges 550 m^3 d^{-1} wastewaters enriched with Zn and Pb and United Catalysts India Ltd. discharges 537 m^3 d^{-1} wastewaters containing Cr into Periyar River (KSPCB, 2000; Nasir, 2010). The high trace hazardous element concentrations at station CB4 can therefore be explained by the industrial inputs into this part of the estuary, which is located upstream the drainage channel and in immediate vicinity of the industrial area (Fig. 1). A severe pollution with respect to the CF of tungsten and zinc at station CB1 and to the CF of Mo and Zn at station CB3 was also observed. Pb, Zn and Ni concentrations were in the same range, whereas Mn and Cu concentrations were lower as in an earlier study from the industrial area (Harikumar and Nasir, 2010). If trace hazardous element concentrations in sediments could relate to adverse biological impacts is discussed in Section 3.3.

3.2. Organic contaminants

By applying a GC–MS non-target screening approach, 40 organic contaminants were identified and quantified in the water samples and 56 contaminants in the sediment samples. The compounds are indicated in Tables 5 and 6, respectively, and were listed according to principal substance classes. The class PACs (Table 6) includes polycyclic aromatic hydrocarbons (PAHs), alkylated PAHs, PAHs with heteroatoms and aromatic compounds exhibiting physico-chemical properties similar to PAHs (e.g. biphenyl).

In 2008 water from the drainage channel at Eloor was sampled (CB5) (Fig. 1, Section 2.2). Thus the identified contaminants represent at least a part of the organic compounds which entered (or still enter) the Periyar River due to industrial inputs (Table 5). Water and sediment samples which were taken in 2011 (Tables 5, 6) give first insights into the occurrence and spatial distribution of organic contaminants in the vicinity of the industrial area. The sediment data are in particular useful as they mirror the longer-term input of lipophilic organic contaminants into the aquatic system.

3.2.1. Sources and concentrations of organic contaminants in water samples

Several *chlorinated compounds* were detectable in the drainage channel sample (CB5) in concentrations of up to 1.3 mg L^{-1} (Table 5). Among those, chlorinated phenols (Nos. 1, 2) chlorinated benzenes (Nos. 3, 4), chlorobenzaldehyde (No. 6), chloroacetophenone (No. 7) and chlorinated benzoic acids (Nos. 9, 10) are commonly used educts for a large variety of industrial synthesis for the production of pharmaceuticals, pesticides and dye stuffs. Hexachlorethane (No. 5) is a byproduct of many industrial processes. Therefore, the occurrence of these compounds in the environment cannot be attributed to a specific industrial production process. However, trichlorobenzene (No. 4), chlorobenzaldehyde (No. 6) and chlorobenzoic acid (No. 9) are known degradation products of organochlorine pesticides in aqueous media (e.g. Magara et al., 1994; Zaleska et al., 2000). Chloroacetophenone (No. 7) and chlorinated benzoic acids (Nos. 9, 10) can be formed during aerobic degradation of polychlorinated biphenyls (PCBs) by bacteria (Bedard et al., 1987). Bis(4-chlorophenyl)sulfone (No. 8) is formed as by-product during the synthesis of 4-chlorobenzenesulfonamide, which is used for the production of chlorpropamide, a pharmaceutical drug (Ventre, 1985) and it is used as starting material for the production of thermostable polymers (e.g. Kwiatkowski et al., 1974). Interestingly, it is also an impurity in technical grade DDT (Fishbein, 1974).

Only dichlorobenzene (No. 3) and bis(4-chlorophenyl)sulfone (No. 8) were also detectable in water samples from the Periyar River, in concentrations which were several magnitudes lower than in the drainage channel sample. Chlorinated anilines (Nos. 11–13) are commonly used educts for industrial synthesis, therefore have an unspecific origin, and were only found in the Periyar River samples from 2011.

Organochlorine pesticides and metabolites present in water samples were the DDT-metabolites DDA (No. 14), DDCN (No. 15), DDD (No. 16) and DDMS (No. 17) (Table 5). The metabolic pathway of

Table 4

Mean metal concentrations (mg kg^{-1} dry weight) and standard deviation(s) as determined by analyses of three replicated extractions of surface sediments from the Cochin Backwaters, India. Sampling stations are indicated in Fig. 1. CF is contamination factor and GAI geoaccumulation index (Section 3.1). CF values ≥6 and GAI values >5 indicating an extremely high contamination are highlighted. SQGs (sediment quality guidelines) are effects range-median in mg kg^{-1} dry weight (ERM) from Long et al. (1995) for marine and estuarine sediments, the contaminant concentration at or above which adverse effects on benthic species frequently occur (Section 3.3). Concentrations in sediments from Cochin Backwaters which were higher than ERM are highlighted.

	Station CB 1			Station CB 2			Station CB 3			Station CB 4			
Element	Mean	CF	GAI	Mean	CF	GAI	Mean	CF	GAI	Mean	CF	GAI	SQG
As	<6			<6			7 ± 2	4.0	1.4	<6			70
Bi	<4			<4			<4			<4			
Co	16.6 ± 0.4	0.7	-1.1	2.6 ± 0.1	0.1	-3.8	17.6 ± 0.1	0.7	-1.0	17.8 ± 0.2	0.7	-1.0	
Cr	146 ± 3	1.2	-0.4	18 ± 2	0.1	-3.4	137 ± 2	1.1	-0.5	**700** ± 6	5.6	1.9	**370**
Cu	79 ± 5	3.2	1.1	30 ± 6	1.2	-0.3	56 ± 1	2.2	0.6	95 ± 4	3.8	1.3	270
Mn	243 ± 4	0.3	-2.1	62 ± 12	0.1	-4.1	391 ± 3	0.6	-1.5	560 ± 3	0.8	-0.9	
Mo	<2			<2			9.0 ± 0.3	**6.4**	2.1	<2			
Ni	51 ± 2	0.9	-0.7	<10			45 ± 1	0.8	-0.9	40 ± 1	0.7	-1.1	51.6
Pb	78 ± 10	5.3	1.8	10.4 ± 1	0.7	-1.1	58 ± 4	3.9	1.4	133 ± 1	**9.0**	2.6	218
V	89 ± 1	1.7	0.2	17 ± 2	0.3	-2.3	90 ± 1	1.7	0.2	323 ± 2	**6.1**	2.0	
W	19 ± 2	**13.6**	3.2	<7			8 ± 2	5.5	1.9	48 ± 1	**34**	4.5	
Zn	**1120** ± 25	**17.2**	3.5	60 ± 9	0.9	-0.7	**417** ± 2	**6.4**	2.1	**2940** ± 32	**45**	4.9	**410**

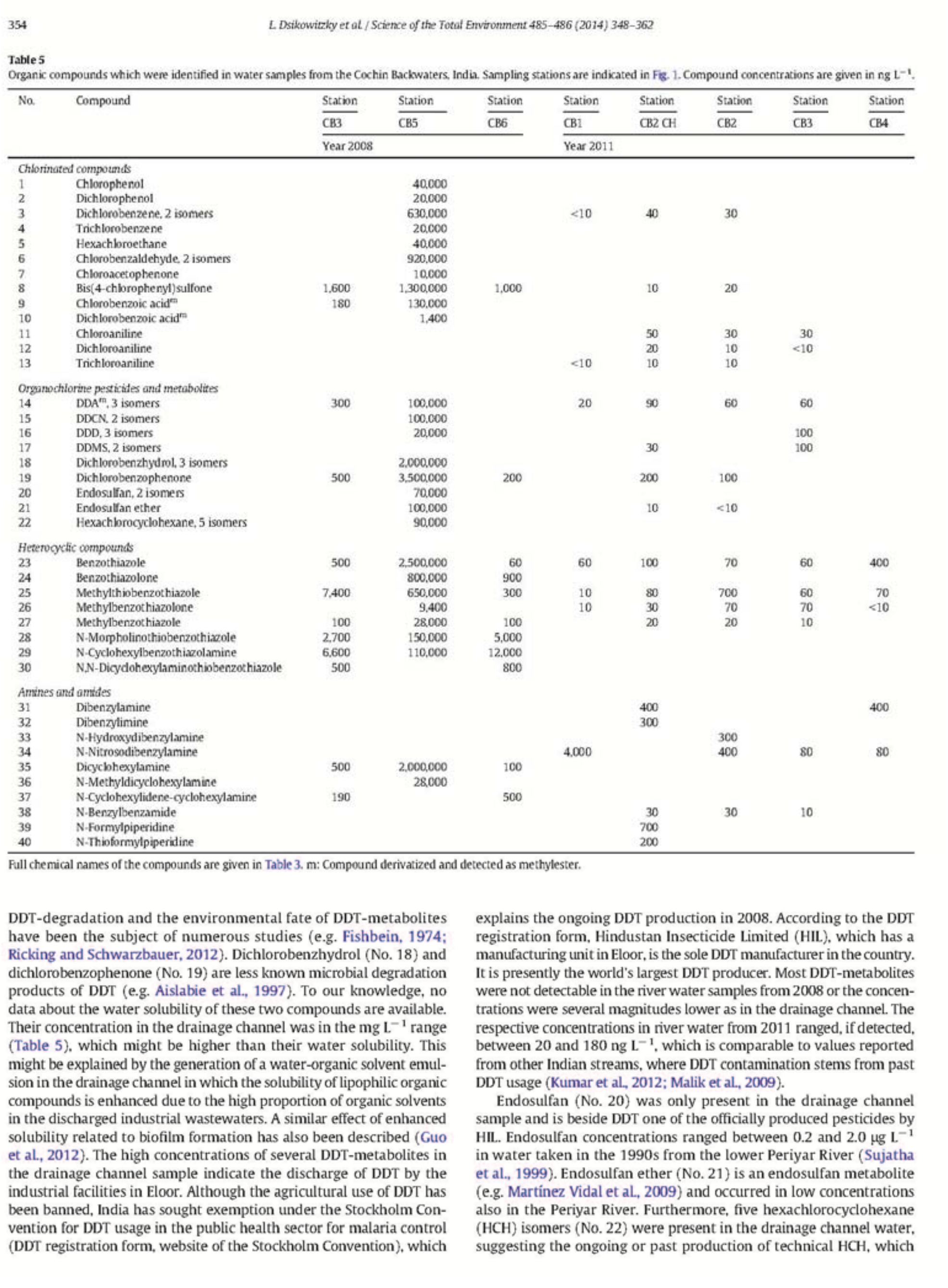

Table 5
Organic compounds which were identified in water samples from the Cochin Backwaters, India. Sampling stations are indicated in Fig. 1. Compound concentrations are given in ng L^{-1}.

No.	Compound	Station	Station	Station	Station	Station	Station	Station	Station
		CB3	CB5	CB6	CB1	CB2 CH	CB2	CB3	CB4
		Year 2008			Year 2011				
Chlorinated compounds									
1	Chlorophenol		40,000						
2	Dichlorophenol		20,000						
3	Dichlorobenzene, 2 isomers		630,000		<10	40	30		
4	Trichlorobenzene		20,000						
5	Hexachloroethane		40,000						
6	Chlorobenzaldehyde, 2 isomers		920,000						
7	Chloroacetophenone		10,000						
8	Bis(4-chlorophenyl)sulfone	1,600	1,300,000	1,000		10	20		
9	Chlorobenzoic acid^{m}	180	130,000						
10	Dichlorobenzoic acid^{m}		1,400						
11	Chloroaniline					50	30	30	
12	Dichloroaniline					20	10	<10	
13	Trichloroaniline				<10	10	10		
Organochlorine pesticides and metabolites									
14	DDA^{m}, 3 isomers	300	100,000		20	90	60	60	
15	DDCN, 2 isomers		100,000						
16	DDD, 3 isomers		20,000					100	
17	DDMS, 2 isomers					30		100	
18	Dichlorobenzhydrol, 3 isomers		2,000,000						
19	Dichlorobenzophenone	500	3,500,000	200		200	100		
20	Endosulfan, 2 isomers		70,000						
21	Endosulfan ether		100,000			10	<10		
22	Hexachlorocyclohexane, 5 isomers		90,000						
Heterocyclic compounds									
23	Benzothiazole	500	2,500,000	60	60	100	70	60	400
24	Benzothiazolone		800,000	900					
25	Methylthiobenzothiazole	7,400	650,000	300	10	80	700	60	70
26	Methylbenzothiazolone		9,400		10	30	70	70	<10
27	Methylbenzothiazole	100	28,000	100		20	20	10	
28	N-Morpholinothiobenzothiazole	2,700	150,000	5,000					
29	N-Cyclohexylbenzothiazolamine	6,600	110,000	12,000					
30	N,N-Dicyclohexylaminothiobenzothiazole	500		800					
Amines and amides									
31	Dibenzylamine					400			400
32	Dibenzylimine					300			
33	N-Hydroxydibenzylamine						300		
34	N-Nitrosodibenzylamine				4,000		400	80	80
35	Dicyclohexylamine	500	2,000,000	100					
36	N-Methyldicyclohexylamine		28,000						
37	N-Cyclohexylidene-cyclohexylamine	190		500					
38	N-Benzylbenzamide					30	30	10	
39	N-Formylpiperidine					700			
40	N-Thioformylpiperidine					200			

Full chemical names of the compounds are given in Table 3. m: Compound derivatized and detected as methylester.

DDT-degradation and the environmental fate of DDT-metabolites have been the subject of numerous studies (e.g. Fishbein, 1974; Ricking and Schwarzbauer, 2012). Dichlorobenzhydrol (No. 18) and dichlorobenzophenone (No. 19) are less known microbial degradation products of DDT (e.g. Aislabie et al., 1997). To our knowledge, no data about the water solubility of these two compounds are available. Their concentration in the drainage channel was in the mg L^{-1} range (Table 5), which might be higher than their water solubility. This might be explained by the generation of a water-organic solvent emulsion in the drainage channel in which the solubility of lipophilic organic compounds is enhanced due to the high proportion of organic solvents in the discharged industrial wastewaters. A similar effect of enhanced solubility related to biofilm formation has also been described (Guo et al., 2012). The high concentrations of several DDT-metabolites in the drainage channel sample indicate the discharge of DDT by the industrial facilities in Eloor. Although the agricultural use of DDT has been banned, India has sought exemption under the Stockholm Convention for DDT usage in the public health sector for malaria control (DDT registration form, website of the Stockholm Convention), which explains the ongoing DDT production in 2008. According to the DDT registration form, Hindustan Insecticide Limited (HIL), which has a manufacturing unit in Eloor, is the sole DDT manufacturer in the country. It is presently the world's largest DDT producer. Most DDT-metabolites were not detectable in the river water samples from 2008 or the concentrations were several magnitudes lower as in the drainage channel. The respective concentrations in river water from 2011 ranged, if detected, between 20 and 180 ng L^{-1}, which is comparable to values reported from other Indian streams, where DDT contamination stems from past DDT usage (Kumar et al., 2012; Malik et al., 2009).

Endosulfan (No. 20) was only present in the drainage channel sample and is beside DDT one of the officially produced pesticides by HIL. Endosulfan concentrations ranged between 0.2 and 2.0 μg L^{-1} in water taken in the 1990s from the lower Periyar River (Sujatha et al., 1999). Endosulfan ether (No. 21) is an endosulfan metabolite (e.g. Martínez Vidal et al., 2009) and occurred in low concentrations also in the Periyar River. Furthermore, five hexachlorocyclohexane (HCH) isomers (No. 22) were present in the drainage channel water, suggesting the ongoing or past production of technical HCH, which

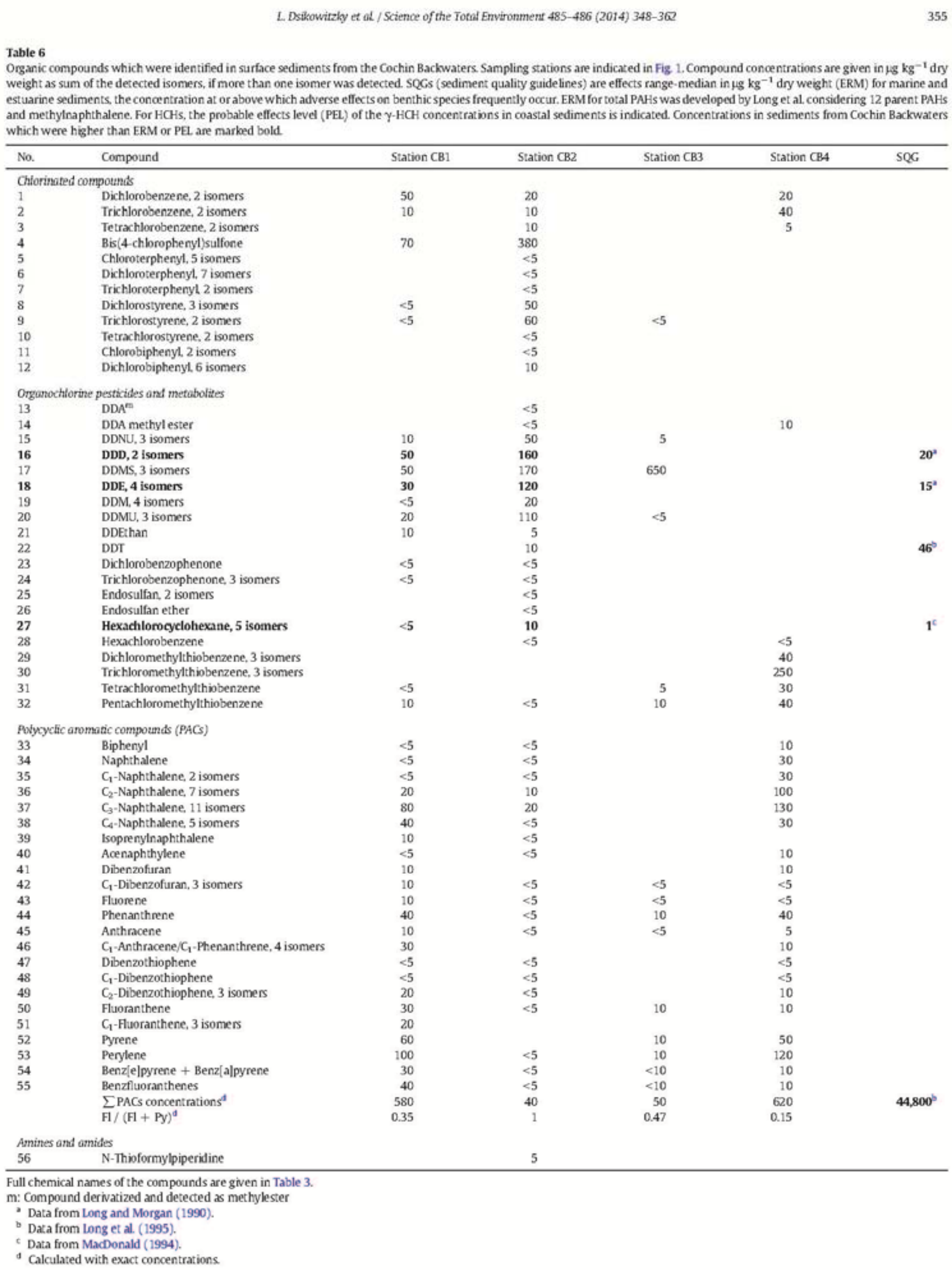

Table 6

Organic compounds which were identified in surface sediments from the Cochin Backwaters. Sampling stations are indicated in Fig. 1. Compound concentrations are given in µg kg^{-1} dry weight as sum of the detected isomers, if more than one isomer was detected. SQGs (sediment quality guidelines) are effects range-median in µg kg^{-1} dry weight (ERM) for marine and estuarine sediments, the concentration at or above which adverse effects on benthic species frequently occur. ERM for total PAHs was developed by Long et al. considering 12 parent PAHs and methylnaphthalene. For HCHs, the probable effects level (PEL) of the γ-HCH concentrations in coastal sediments is indicated. Concentrations in sediments from Cochin Backwaters which were higher than ERM or PEL are marked bold.

No.	Compound	Station CB1	Station CB2	Station CB3	Station CB4	SQG
Chlorinated compounds						
1	Dichlorobenzene, 2 isomers	50	20		20	
2	Trichlorobenzene, 2 isomers	10	10		40	
3	Tetrachlorobenzene, 2 isomers		10		5	
4	Bis(4-chlorophenyl)sulfone	70	380			
5	Chloroterphenyl, 5 isomers		<5			
6	Dichloroterphenyl, 7 isomers		<5			
7	Trichloroterphenyl, 2 isomers		<5			
8	Dichlorostyrene, 3 isomers	<5	50			
9	Trichlorostyrene, 2 isomers	<5	60	<5		
10	Tetrachlorostyrene, 2 isomers		<5			
11	Chlorobiphenyl, 2 isomers		<5			
12	Dichlorobiphenyl, 6 isomers		10			
Organochlorine pesticides and metabolites						
13	DDA^{m}		<5			
14	DDA methyl ester		<5		10	
15	DDNU, 3 isomers	10	50	5		
16	**DDD, 2 isomers**	**50**	**160**			**20**[a]
17	DDMS, 3 isomers	50	170	650		
18	**DDE, 4 isomers**	**30**	**120**			**15**[a]
19	DDM, 4 isomers	<5	20			
20	DDMU, 3 isomers	20	110	<5		
21	DDEthan	10	5			
22	DDT		10			**46**[b]
23	Dichlorobenzophenone	<5	<5			
24	Trichlorobenzophenone, 3 isomers	<5	<5			
25	Endosulfan, 2 isomers		<5			
26	Endosulfan ether		<5			
27	**Hexachlorocyclohexane, 5 isomers**	<5	**10**			**1**[c]
28	Hexachlorobenzene		<5		<5	
29	Dichloromethylthiobenzene, 3 isomers				40	
30	Trichloromethylthiobenzene, 3 isomers				250	
31	Tetrachloromethylthiobenzene	<5		5	30	
32	Pentachloromethylthiobenzene	10	<5	10	40	
Polycyclic aromatic compounds (PACs)						
33	Biphenyl	<5	<5		10	
34	Naphthalene	<5	<5		30	
35	C_1-Naphthalene, 2 isomers	<5	<5		30	
36	C_2-Naphthalene, 7 isomers	20	10		100	
37	C_3-Naphthalene, 11 isomers	80	20		130	
38	C_4-Naphthalene, 5 isomers	40	<5		30	
39	Isoprenylnaphthalene	10	<5			
40	Acenaphthylene	<5	<5		10	
41	Dibenzofuran	10			10	
42	C_1-Dibenzofuran, 3 isomers	10	<5	<5	<5	
43	Fluorene	10	<5	<5	<5	
44	Phenanthrene	40	<5	10	40	
45	Anthracene	10	<5	<5	5	
46	C_1-Anthracene/C_1-Phenanthrene, 4 isomers	30			10	
47	Dibenzothiophene	<5	<5		<5	
48	C_1-Dibenzothiophene	<5	<5		<5	
49	C_2-Dibenzothiophene, 3 isomers	20	<5		10	
50	Fluoranthene	30	<5	10	10	
51	C_1-Fluoranthene, 3 isomers	20				
52	Pyrene	60		10	50	
53	Perylene	100	<5	10	120	
54	Benz[e]pyrene + Benz[a]pyrene	30	<5	<10	10	
55	Benzfluoranthenes	40	<5	<10	10	
	∑ PACs concentrations[d]	580	40	50	620	**44,800**[b]
	Fl / (Fl + Py)[d]	0.35	1	0.47	0.15	
Amines and amides						
56	N-Thioformylpiperidine		5			

Full chemical names of the compounds are given in Table 3.
m: Compound derivatized and detected as methylester

[a] Data from Long and Morgan (1990).

[b] Data from Long et al. (1995).

[c] Data from MacDonald (1994).

[d] Calculated with exact concentrations.

contains five stable isomers in characteristic proportions, in the industrial facilities of Eloor. The Republic of India signed the Stockholm Convention, which bans the production and agricultural usage of α-, β-, and γ-HCH, in 2006.

A so far unidentified contaminant was also found in the drainage channel water (Fig. 2). We postulate that this compound is – according to its mass spectral properties – bis(chlorophenyl)hydroxy acetic acid, a DDA analogous metabolite of the organochlorine insecticide Dicofol.

Heterocyclic compounds were present in all investigated water samples belonging dominantly to the group of benzothiazole derivatives (Table 5, chemical structures in Fig. 3). High concentrations of these compounds in the drainage channel sample indicate their discharge by the industrial facilities. Thiazol derivatives are used during rubber production as accelerators that catalyze the vulcanization process (Fishbein, 1991). Benzothiazole (No. 23), benzothiazolone (No. 24), methylthiobenzothiazole (No. 25) and methylbenzothiazole (No. 27) were also found in effluents of rubber and tire production facilities in the US and in Spain (Jungclaus et al., 1976; Puig et al., 1996). Accordingly we conclude that the presence of these compounds in the study area is an indicator for inputs of effluents from tire and rubber production facilities in Eloor. Methylthiobenzothiazole (No. 25) and N-morpholinothiobenzothiazole (No. 28) were previously detected in municipal sewage and street runoff and originate from tire abrasion (e.g. Spies et al., 1987; Takada and Eganhouse, 1998; Dsikowitzky et al., 2004). However, the combination of Nos. 23, 25 and 27, which were present in the drainage channel and in the river water samples from 2011 and 2008 in concentrations of up to 7400 ng L^{-1} could be useful to trace emissions from rubber and tire manufacturing facilities in aquatic systems. The high concentrations of heterocyclic compounds at station CB6 which was sampled in 2008 as compared to the other river water samples suggests a second input pathway of industrial contaminants located upstream the drainage channel (Section 3.1). To our knowledge, methylbenzothiazolone (No. 26), N-cyclohexylbenzothiazolamine (No. 29) and N,N-dicyclohexylaminothiobenzothiazole (No. 30) have as yet not been described as constituents of industrial effluents or as environmental contaminants. The structural relation to the other benzothiazol derivatives suggests a similar origin — wastewaters from rubber and tire production facilities.

Among the identified *amines and amides*, dibenzylamine derivatives were only found in the river water samples from 2011 in concentrations of up to 4000 ng L^{-1} (Table 5, chemical structures in Fig. 3). Dibenzylamine (No. 31) and its alkylated derivatives are used as antidegradants during rubber processing (Fishbein, 1991) and dibenzylamine was present in effluents from of a tire manufacturing plant (Jungclaus et al., 1976). However, dibenzylamine is probably also formed during the environmental degradation of explosives (Schwarzbauer et al., 2010). N-nitrosodibenzylamine (No. 34) was one of the most commonly used retarders to prevent the premature vulcanization of rubber (Fishbein, 1991). We conclude that the occurrence of these compounds in the river originates from discharges of rubber and tire production facilities. Dicyclohexylamine (No. 35) and N-cyclohexylidenecyclohexylamine (No. 37) are formed as by-products during the synthesis of substituted hydrazines, which are well known as pesticides, drugs and synthetic building blocks for heterocyclic synthesis (Vázquez et al., 2009). N-methyldicyclohexylamine (No. 36) is an additive for the synthesis of polyurethane (Hartz, 1975), which is used as tire fillings. These facts and that Nos. 35 and 36 occurred in the drainage channel sample indicate the industrial origin of these compounds.

N-Benzylbenzamide (No. 38) was present in low concentrations in three water samples taken in 2011 from the Periyar River (Table 5). Interestingly, it is used as inhibitor of tyrosinase, which is the key enzyme for the production of melamine (e.g. Cho et al., 2006). Tyrosinase inhibitors are important for the food industry and are also ingredients in personal care products, e.g. skin whitening agents. Consequently, the origin of this compound is unclear, it could either derive from industrial sources (large-scale synthesis of the compound) or from municipal sources (ingredient of personal care or medical products). N-Formylpiperidine (No. 39) and N-thioformylpiperidine (No. 40) occurred only in one water sample from 2011. Whereas N-formylpiperidine is used as solvent and as educt for industrial syntheses, the application of the latter remains unclear.

3.2.2. Sources and concentrations of organic contaminants in sediment samples

Among the identified *chlorinated compounds* in the sediments (Table 6), chlorinated benzenes (Nos. 1–3) and polychlorinated biphenyls

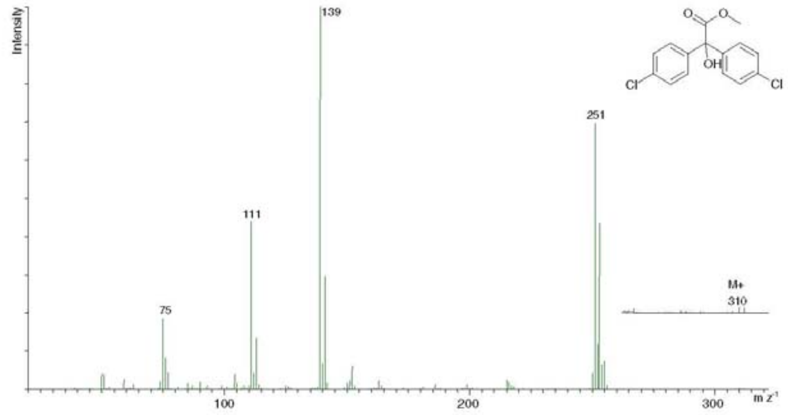

Fig. 2. Mass spectrum and chemical structure of a compound which we identified as Dicofol metabolite (Bis(chlorophenyl)hydroxy acetic acid). The compound is the structural equivalent to the DDT-metabolite DDA (Bis(chlorophenyl) acetic acid). Two isomers were present in the third fraction, in which the compounds are derivatized and detected as methyl esters (Section 2.5.2). Mz^{-1} 310 is the molecular ion (M^{+}) of the Dicofol metabolite methyl ester.

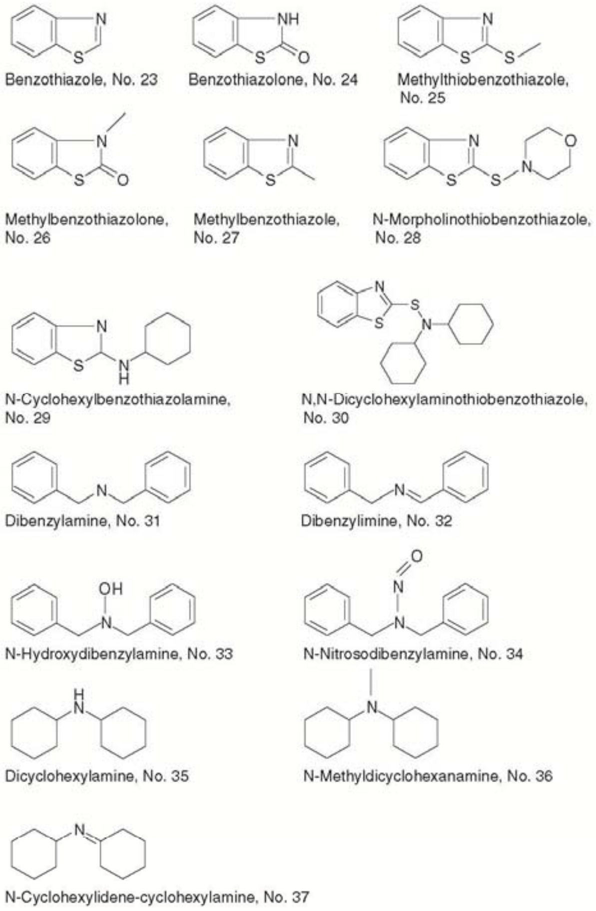

Fig. 3. Chemical structures of the heterocyclic compounds and amines which were identified in water samples from the Cochin Backwaters, India (the compound numbers are indicated according to Table 5).

(PCBs, Nos. 11, 12) have a widespread industrial application and are part of many industrial products, therefore their origin is unspecific. Only chlorobiphenyls and dichlorobiphenyls were found, PCBs with a higher number of chlorine atoms were not detected. This can be explained by differences of the PCB composition in technical formulations. For example, Aroclor 1221 and Aroclor 1232 technical PCB mixtures contain mainly congeners with one or two chlorine atoms, congeners with more chlorine atoms are only present in minor proportions (e.g. Frame et al., 1996). Therefore, the emission of technical PCB formulations with a low chlorine content in the study area is obvious.

Bis(4-chlorophenyl)sulfone (No. 4) was also found in Periyar River water (Section 3.2.1). Polychlorinated terphenyls (PCTs, Nos. 5–7) were present in one sample. They exhibit similar physicochemical properties as PCBs and are used as flame retardants, plasticizers, coatings and lubricants. Technical PCT was formerly produced in the US, the formulations contained predominantly terphenyls substituted with three to five or more chlorine atoms (Hale et al., 1990). We found solely terphenyls substituted with one to three chlorine atoms, suggesting that technical PCT formulations manufactured in India exhibit a different composition. The possible ortho- or ortho-para-configurations of the terphenyl structure explain the high number of possible isomers and lead to different mass spectra. Chlorinated styrenes (Nos. 8–10) were found in three sediment samples. Hexa-, hepta- and octachlorostyrenes are performed as byproducts during electrolytical processes and are well known environmental contaminants (e.g. Bestert et al., 1998). However, mixtures of mono- to tetrachlorinated styrenes are used for the copolymerization with butadiene to synthesize polymers with rubber-like properties (Marvel et al., 1947). Their occurrence in Periyar River sediments could therefore be related to the inputs from the rubber and tire production facilities (Section 3.2.1). PCTs (Nos. 5–7) and chlorinated styrenes (Nos. 8–10) were detectable in highest concentrations in sediment from station CB2, which is located at the outlet of the industrial drainage channel (Fig. 1), denoting this channel as input pathway.

Organochlorine pesticides and metabolites present in the sediment samples (Table 6) were mainly DDT and related degradation products (Nos. 13–24). This includes trichlorobenzophenone (No. 24), which is a less known photodegradation product of DDT in water (Ho et al., 1997). DDA was interestingly present as acid (No. 13) and as methyl ester derivative (No. 14). The DDA methyl ester is probably formed as microbial transformation product of DDA in the sediments. The concentrations of DDT and the DDT-metabolites as well as of endosulfan (No. 25) and HCHs (No. 27) were highest at station CB2 (Fig. 1), reflecting the origin of these compounds, the industrial drainage channel (Section 3.2.1). This also explains the absence of most organochlorine pesticides and metabolites at station CB4.

In contrast, highest hexachlorobenzene (No. 28) and chlorinated methylthiobenzenes (Nos. 29–32) concentrations were found at station CB4, which is located upstream the drainage channel (Fig. 1). Hexachlorobenzene is a fungicide of which the production and usage have been banned by the Stockholm Convention. Chlorinated methylthiobenzenes are formed during the biotransformation of hexachlorobenzene (Renner and Nguyen, 1984). The hexachlorobenzene contamination at CB4 could stem from agricultural runoff. A further possibility is the existence of a second input pathway of Eloor wastewater discharges near CB4 (Section 3.1). Overall, concentrations of HCHs (No. 27) and hexachlorobenzene (No. 28) were in the same range as in a previously investigated sediment sample from an agricultural area in Cochin (Senthilkumar et al., 2001), whereas we found higher concentration of DDTs.

More than twenty *polycyclic aromatic compounds (PACs)* were present in the sediment samples, with highest concentrations at station CB4 (Table 6). The dominance of alkylated PACs as compared to the respective parent compounds indicates input of crude oil or petroleum products (e.g. Schwarzbauer et al., 2000). The fluoranthene/pyrene ratio is a further source indicator of PACs (Yunker et al., 2002). It was <0.5 at stations CB1, CB3 and CB4 (Table 6), which also points to a petrogenic source of the contamination, which could be e.g. shipping traffic or oil refinery effluents.

Overall, the occurrence of organic contaminants at the different stations is somewhat erratic as the lowest number of contaminants was found at station CB3, although it is situated closer to the drainage channel as station CB1 (Fig. 1). This could be related to grain size distribution, as the sediment at station CB3 contains more medium and coarse sand and less clay and fine silt than sediment at station CB1 (Table 1). It is generally accepted that contaminants are enriched in the clay/fine silt fraction, which is due to the large specific surface area of this fraction and the strong adsorptive properties of clay minerals (e.g. Horowitz and Elrick, 1987). The higher contaminant concentrations at CB2 despite the high coarse sand content and low clay/fine silt content can be explained by the proximity to the industrial drainage channel (Fig. 1). A discussion whether the organic contaminant concentrations in sediments could relate to adverse biological impacts is presented in Section 3.3.

3.3. Bioaccumulation potential and toxicity of the detected compounds

It is known that lipophilic and persistent organochlorine contaminants such as DDT, endosulfan, HCHs and PCBs are accumulated in aquatic organisms (e.g. Chopra et al., 2011) and for hexachlorobenzene, DDT, PCBs and HCHs also the biomagnification in aquatic food chains was documented (e.g. Kelly et al., 2007). Further organic contaminants which were found in the Periyar River, and which also tend to bioaccumulate are for example chlorinated styrenes (Bestert et al., 1998). Bis(4-chlorophenyl)sulfone was observed to bioaccumulate in fish and mammals from freshwater and marine environments in Sweden (Norström et al., 2004). Hexachlorobenzene and pentachlorothioanisole were detected in freshwater fish from China (Ren et al., 2013). Chlorinated terphenyls exhibit similar properties as PCBs and accumulate in shellfish, fish and seals (e.g. Jensen and Jørgensen, 1983). Bioaccumulation of Cr, Pb and Zn – which occurred in high concentrations at station CB4 (Table 4) – in bivalves and fish has also been reported (e.g. Bryan and Langston, 1992; Canli and Atli, 2003; Fukunaga and Anderson, 2011). Fish and benthic invertebrates from the study area are therefore probably severely contaminated calling for studies which focus on the food safety of fishery resources from Cochin Backwaters.

Since India presently has no established sediment quality guidelines, the US National Oceanic and Atmospheric Administration (NOAA) guidelines were used as interim measures to assess whether the concentrations of contaminants in sediments could relate to adverse biological impacts. The guidelines were developed based on the analyses of benthic invertebrate communities combined with chemical data from numerous modeling, laboratory and field studies, including several hazardous elements and well known organochlorine contaminants (Long et al., 1995). The comparison of our data with these guidelines shows that the thresholds are exceeded for several trace hazardous elements and organic contaminants (Tables 4 and 6). At station CB1 Zn, DDD and DDE concentrations exceeded the thresholds, at CB2 DDD, DDE and HCHs, at CB3 Zn and at CB4 Cr and Zn. Therefore, adverse effects on benthic species can be expected at all stations.

Data on the acute toxicity of some of the detected organic contaminants on aquatic crustacean and fish species are compiled in Table 7. Accordingly, the water sample from the drainage channel was acutely toxic to aquatic organisms due to the high DDD, endosulfan, benzothiazole and dicyclohexylamine concentrations therein. In all other water samples, organic contaminant concentrations were lower than reported toxicity thresholds. Further detected compounds such as the dicyclohexylamine derivatives Nos. 36 and 37 (Table 5) might exhibit a toxic potential, but have not been subject to toxicity evaluations so far.

3.4. Macrobenthic invertebrates

Overall 15 macrobenthic and one planktonic taxa were recorded in the sediments (Table 8). The highest number of species and individuals were found at station CB1 (13 species), at the largest distance to the industrial facilities (Fig. 1). The Shannon diversity was also highest at CB1, followed by CB2. At station CB4 no animals were recorded. The benthic community was composed of Crustacea (44.5% of all individuals), Polychaeta (39.1%), Gastropoda (14.2%), and Bivalvia (2.2%). The benthic community composition differed significantly between the four stations (ANOSIM, global $R = 0.81$, $p = 0.02$; Fig. 4).

The species recorded at the four stations are only a small subset of the 92 macrobenthic species which were found in the whole Cochin Backwaters 30 years ago (Batcha, 1984) and of the 47 species found in 2005 (Martin et al., 2011). Most of them have been previously reported for the Cochin Backwaters, e.g. the abundant amphipods *Cheiriphotis megacheles* and *Corophium triaenonyx* (Nair et al., 1983; Sarala Devi et al., 1991; Martin et al., 2011). *C. triaenonyx* is described as brackish water or estuarine species, which tolerates a wide range of salinities and is widely distributed in the Cochin Backwaters (Nair et al., 1983; Martin et al., 2011). A study at the industrial area from 1981 revealed an overall much higher number of amphipod and polychaete species than in 2011. However, close to the industrial complex near station CB4 species richness was already low in 1981 and the opportunistic polychaetes *Capitella capitata* and *Dendronereis aestuarina* were recorded in high densities (Sarala Devi et al., 1991). In 2011, polychaetes of the families Capitellidae and Nereididae were abundant at stations CB1 and CB2, where several organochloride pesticides exceeded toxicity thresholds. Several species from the families Capitellidae, Nereididae and Spionidae have been described as pollution indicators in other estuaries (e.g. Pocklington and Wells, 1992; Reish and Gerlinger, 1997 and references therein, Dix et al., 2005).

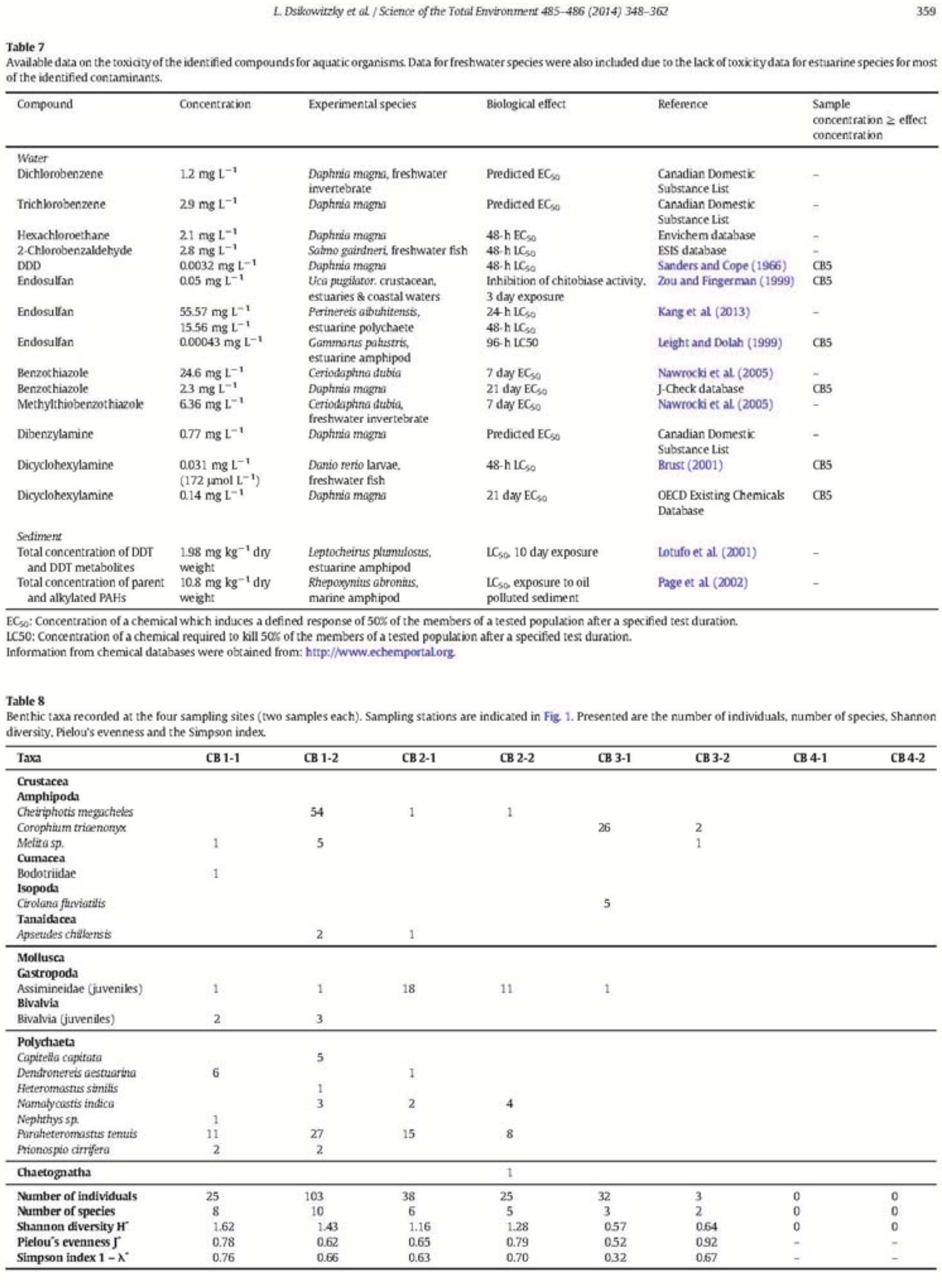

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Table 7
Available data on the toxicity of the identified compounds for aquatic organisms. Data for freshwater species were also included due to the lack of toxicity data for estuarine species for most of the identified contaminants.

Compound	Concentration	Experimental species	Biological effect	Reference	Sample concentration ≥ effect concentration
Water					
Dichlorobenzene	1.2 mg L^{-1}	*Daphnia magna*, freshwater invertebrate	Predicted EC_{50}	Canadian Domestic Substance List	–
Trichlorobenzene	2.9 mg L^{-1}	*Daphnia magna*	Predicted EC_{50}	Canadian Domestic Substance List	–
Hexachloroethane	2.1 mg L^{-1}	*Daphnia magna*	48-h EC_{50}	Envichem database	–
2-Chlorobenzaldehyde	2.8 mg L^{-1}	*Salmo gairdneri*, freshwater fish	48-h LC_{50}	ESIS database	–
DDD	0.0032 mg L^{-1}	*Daphnia magna*	48-h LC_{50}	Sanders and Cope (1966)	CB5
Endosulfan	0.05 mg L^{-1}	*Uca pugilator*. crustacean, estuaries & coastal waters	Inhibition of chitobiase activity, 3 day exposure	Zou and Fingerman (1999)	CB5
Endosulfan	55.57 mg L^{-1} 15.56 mg L^{-1}	*Perinereis aibuhitensis*, estuarine polychaete	24-h LC_{50} 48-h LC_{50}	Kang et al. (2013)	–
Endosulfan	0.00043 mg L^{-1}	*Gammarus palustris*, estuarine amphipod	96-h LC50	Leight and Dolah (1999)	CB5
Benzothiazole	24.6 mg L^{-1}	*Ceriodaphna dubia*	7 day EC_{50}	Nawrocki et al. (2005)	–
Benzothiazole	2.3 mg L^{-1}	*Daphnia magna*	21 day EC_{50}	J-Check database	CB5
Methylthiobenzothiazole	6.36 mg L^{-1}	*Ceriodaphna dubia*, freshwater invertebrate	7 day EC_{50}	Nawrocki et al. (2005)	–
Dibenzylamine	0.77 mg L^{-1}	*Daphnia magna*	Predicted EC_{50}	Canadian Domestic Substance List	–
Dicyclohexylamine	0.031 mg L^{-1} (172 μmol L^{-1})	*Danio rerio* larvae, freshwater fish	48-h LC_{50}	Brust (2001)	CB5
Dicyclohexylamine	0.14 mg L^{-1}	*Daphnia magna*	21 day EC_{50}	OECD Existing Chemicals Database	CB5
Sediment					
Total concentration of DDT and DDT metabolites	1.98 mg kg^{-1} dry weight	*Leptocheirus plumulosus*, estuarine amphipod	LC_{50}, 10 day exposure	Lotufo et al. (2001)	–
Total concentration of parent and alkylated PAHs	10.8 mg kg^{-1} dry weight	*Rhepoxynius abronius*, marine amphipod	LC_{50}, exposure to oil polluted sediment	Page et al. (2002)	–

EC_{50}: Concentration of a chemical which induces a defined response of 50% of the members of a tested population after a specified test duration.
LC50: Concentration of a chemical required to kill 50% of the members of a tested population after a specified test duration.
Information from chemical databases were obtained from: http://www.echemportal.org.

Table 8
Benthic taxa recorded at the four sampling sites (two samples each). Sampling stations are indicated in Fig. 1. Presented are the number of individuals, number of species, Shannon diversity, Pielou's evenness and the Simpson index.

Taxa	CB 1-1	CB 1-2	CB 2-1	CB 2-2	CB 3-1	CB 3-2	CB 4-1	CB 4-2
Crustacea								
Amphipoda								
Cheiriphotis megacheles		54	1	1				
Corophium triaenonyx					26	2		
Melita sp.	1	5				1		
Cumacea								
Bodotriidae	1							
Isopoda								
Cirolana fluviatilis					5			
Tanaidacea								
Apseudes chilkensis		2	1					
Mollusca								
Gastropoda								
Assimineidae (juveniles)	1	1	18	11	1			
Bivalvia								
Bivalvia (juveniles)	2	3						
Polychaeta								
Capitella capitata		5						
Dendronereis aestuarina	6		1					
Heteromastus similis		1						
Namalycastis indica		3	2	4				
Nephthys sp.	1							
Paraheteromastus tenuis	11	27	15	8				
Prionospio cirrifera	2	2						
Chaetognatha				1				
Number of individuals	25	103	38	25	32	3	0	0
Number of species	8	10	6	5	3	2	0	0
Shannon diversity H´	1.62	1.43	1.16	1.28	0.57	0.64	0	0
Pielou´s evenness J´	0.78	0.62	0.65	0.79	0.52	0.92	–	–
Simpson index 1 – λ´	0.76	0.66	0.63	0.70	0.32	0.67	–	–

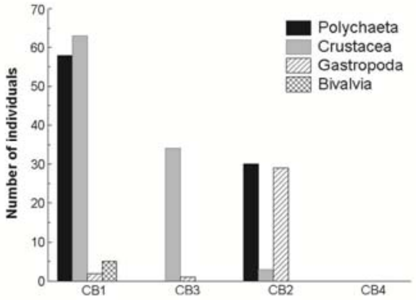

Fig. 4. Benthic community composition at three stations in the industrial vicinity CB2–CB4 and at one station further away (CB1). The location of the stations is indicated in Fig. 1.

Also the bivalves *Villorita cypreinoides* and *Pandora flexuosa* were encountered in high densities at the discharge site in 1981 (Sarala Devi et al., 1991) which is in contrast to our study. Only five juvenile bivalves were found in 2011. However, *V. cypreinoides* is still distributed in other parts of the Cochin Backwaters and the Vembanad Lake and is a major fishery resource, accounting for nearly 70% of the total clam fishery in the Vembanad Lake (Laxmilatha and Appukuttan, 2002; Raveendran and Sujatha, 2011).

Dominant bivalve and gastropod species in the early 1970s have disappeared from the central and northern part of the estuary already in 2005 (Martin et al., 2011). Overall low species numbers and particularly the lack of species at CB4 are likely to be a result of the high concentration of pollutants. This station is located upstream of the drainage channel in close vicinity of the industrial area. At CB4 concentrations of Cr and Zn exceeded by far the SQGs and were higher than the respective concentrations at the other stations (Table 4). Here also the highest PAC concentrations were recorded, and it was the only station where hexachlorobenzene was found (Table 6). However, PAC concentrations were much lower than the reported toxicity thresholds, and for hexachlorobenzene no threshold was developed. At this station, a high number of sulfur pellets were found in the sediment which probably indicates anoxic conditions. Such conditions could in addition to the chemical contamination severely affect the benthic community.

Most species and individuals were found at CB1, although concentrations of two organochlorine pesticides and Zn exceeded the thresholds (Tables 4, 6). The low portion of coarse sand and high portion of silt and fine sand (Table 1) could have contributed to the higher number of species and individuals as small and fragile organisms such as amphipods can be crashed during movement of big sand grains. Also, organic matter content of the sediment usually negatively correlates with the median grain size, thus sediments composed of silt and fine sand may sustain a higher density and biomass of benthic organisms than sand alone. However, also the species inventory at CB1 can be assessed as depleted when compared to earlier studies in the Cochin Backwaters (Sarala Devi et al., 1991).

4. Summary and conclusions

The aim of this study was a first comprehensive survey of relevant organic and inorganic contaminants in water and sediments from the industrial area Eloor and a source apportionment of the identified contaminants. Macrobenthic invertebrates in the sediments were investigated to get an impression on the related biological response to the industrial contamination.

The chemical characterization of water and sediments beyond the measurement of a set of well-known priority pollutants revealed the presence of structural diverse organic contaminant groups which could be attributed to inputs from different industrial facilities such as rubber and tire producing facilities and a manufacturer of organochlorine pesticides. The very high sediment contamination in the immediate industrial vicinity with respect to several trace hazardous elements is related to inputs from the metal industry. However, post-depositional remobilization of these elements can make it difficult to determine the proportions of element concentrations attributable to anthropogenic contributions.

To our knowledge, several of the identified benzothiazole, dibenzylamine and dicyclohexylamine derivatives which are intensively used by the rubber and tire industry are here described for the first time as environmental contaminants. Many contaminants from industrial sources entering the environment obviously escape our view if conventional analytical methods searching for a predefined contaminant spectrum are applied. Our findings highlight the complex chemical composition of industrial effluents.

Sediment quality guidelines were considered to assess whether the chemical contamination could relate to adverse biological impacts. The thresholds were exceeded for several trace hazardous elements and organic contaminants at all stations, so that adverse effects of the contamination on benthic organisms can be expected.

The benthic species inventory around the industrial area can be assessed as depleted when compared to earlier studies. Polychaetes and amphipods dominated the benthic community. Benthic organisms were completely lacking at the site with the highest trace hazardous element concentrations. As concentrations of several trace hazardous element and organic priority pollutants in sediments exceeded reported quality thresholds also at the other sites, adverse effects on the benthic community can be expected in the whole area around the industrial facilities. A reduced number of species and individuals belonging to a specific functional group may result in the impairment of the respective function. For instance, the nearly complete lack of filter feeders in the investigated area probably leads to an impairment of the filter function of the system. However, due to the unknown toxicity of many of the detected compounds, the synergistic or antagonistic effects of such complex compound mixtures and the role of natural stressors, it remains unclear, which set of compounds and stressors negatively affected the aquatic organisms.

A limitation of this study is the small sample set, therefore a better spatial resolution and higher replication of samples are necessary in future studies. Many of the organochlorine contaminants as well as some trace hazardous elements were present in high concentrations and tend to accumulate in fish and benthic invertebrates. Therefore, fishery resources from the study area are probably highly contaminated pointing out a potential health risk to humans and calling for studies on food safety.

As shown in this study, a combination of chemical and biological methods is an innovative approach to achieve a comprehensive characterization of industrial contamination, to evaluate ecological risks regarding sediment quality guidelines, and to observe associated adverse effects on the benthic diversity and community directly in the field.

Acknowledgments

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Core sediment biogeochemistry in specific zones of Cochin Estuarine System (CES)

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Geochemical composition is a set of data for predicting the climatic condition existing in an ecosystem. Both the surficial and core sediment geochemistry are helpful in monitoring, assessing and evaluating the marine environment. The aim of the research work is to assess the relationship between the biogeochemical constituents in the Cochin Estuarine System (CES), their modifications after a long period of anoxia and also to identify the various processes which control the sediment composition in this region, through a multivariate statistical approach. Therefore the study of present core sediment geochemistry has a critical role in unraveling the benchmark of their characterization. Sediment cores from four prominent zones of CES were examined for various biogeochemical aspects. The results have served as rejuvenating records for the prediction of core sediment status prevailing in the CES.

1. Introduction

Estuaries are commonly described as semi-enclosed bodies of water, situated at the interface between land and ocean, where seawater is measurably diluted by the inflow of freshwater (Hobbie 2000). These dynamic ecosystems have the highest biotic diversity and production in the world. Recent estimates indicate that 61% of the world population lives along the coastal margin (Alongi 1998). Impacts of demographic changes in human populations have clearly had detrimental effects on the overall biogeochemical cycling in estuaries. Nutrient enrichment is perhaps the most widespread problem in estuaries around the world (Howarth *et al.* 2000, 2002). Understanding the biogeochemical and physical processes that play an important role in regulating the chemistry and biology of estuaries is fundamental to evaluate the complex management issues (Hedges and Kiel 1995; Middelburg *et al.* 1996; Bianchi *et al.* 1999a; Hobbie 2000). Biogeochemical cycles involve the interaction of biological, chemical as well as geological processes that determine sources, sinks, and fluxes of elements through different reservoirs within the ecosystems.

Cochin Estuary, one of the largest tropical estuaries of India is facing gross pollution problems following the release of untreated effluents from industries and domestic sectors. The major polluting industries in the region include fertilizer plant, oil refinery, rare earth processing plant, minerals and rutiles plant, zinc smelter plant, insecticide manufacturing unit and organic chemical plant. Reclamations over the past several decades have resulted in considerable shrinkage (40%) of the Cochin Estuary (Gopalan *et al.* 1983). Further, construction of hydraulic barriers on the northern and southern limbs of the estuary to prevent saline intrusion into the upstream agricultural fields has imposed severe flow restrictions and increased sedimentation in the estuary (Menon *et al.* 2000). The developmental activities in and around Cochin Backwater System have added to the

Keywords. Cochin Estuarine System; core sediment; biogeochemical constituents.

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complexities and environmental dilemmas in this coastal niche. The rapid growth in the region accompanied by very high population growth, housing shortages, haphazard industrial and commercial improvement along transportation corridors have greatly increased the problems of urban development. The hydrologic changes in these water bodies were mainly on account of port extension, large scale land reclamation, construction of dams on the rivers that discharge into the backwaters and diversion of water flows by the construction of spillways, etc. For a long period there were no pollution control regulations and the untreated effluents including those from heavily polluting industries were being discharged into the backwaters. Geochemical studies of sediment core profiles describe the degree of contamination by encapsulating various amounts of biogenic compounds (including biogenic alkanes, sterols, carbohydrates, protein, hydrocarbons, etc.) and provide furthermore useful information on the changes in the quality of the sediments from past period (Faganelli *et al.* 1987; Holm 1988; Karbassi and Shankar 2005; Al-Juboury 2009; Ahmad *et al.* 2010; Chibunda *et al.* 2010). The present investigation also infers the quality of the biogeochemical constituents in the core sediments of the Cochin estuary which would strengthen the environmental dynamics of the studied site.

2. Study area

The study area was divided into three zones, *viz.*, south, middle, and north (figure 1).

2.1 *South zone*

The zone originated from the southern bough of the fresh water river Moovattupuzha. One sediment core (SS_1) was taken from this zone which is far from industrial effluents.

2.2 *Middle zone*

This zone was considered as two segments and the first site (MS_1) is well regulated by a bund (namely Thannirmukham) which was constructed in order to prevent the intrusion of salt water into the paddy fields. The bund remains open during the monsoon season.

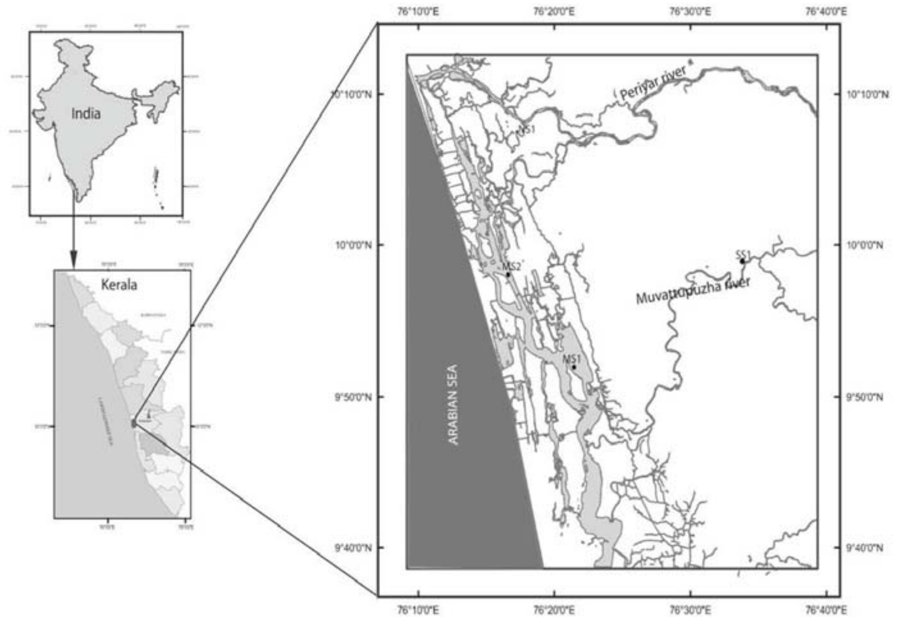

Figure 1. Location map of the study area.

The second site (MS_2) was at Vallarpadam. With the advent of ICTT project, this area has become the backbone of the economy of Kerala State. It focuses on the enhancement of containerization in India, resulting in the improvement of trade and economic growth. Widespread activities like dredging and piling, along with anthropogenic inputs are carried out frequently. This zone has a perennial connection with the Arabian Sea and experiences an irregular encroachment of saline water intrusion thereby making cradle grounds for diverse types of flora and fauna.

2.3 *North zone*

This zone instigate from the industrial locale of Periyar – the life line of Kerala. One sediment core (NS_1) sample was collected from this zone. Large scale industries on the river bank discharge effluents directly into these waterways resulting in the accumulation of varying amounts of nutrients in the Periyar River.

3. Sampling and methods

The cores were collected at low tide by pushing a hand-held PVC core (150 cm long with a diameter of 6.3 cm) in November 2009 by a diver at the above-mentioned three zones of the CES, in varying depths (1–3.50 m) of the water body. The different length of the core obtained were 45 cm (SS_1), 55 cm (MS_1), 63 cm (MS_2) and 23 cm (NS_1). The sediment cores were sliced into 3 cm segments, transferred to plastic vessels and each subsample constitutes 15, 19, 21 and 10 for SS_1, MS_1, MS_2 and NS_1 cores, respectively. The pH (Thermo Orion 420A+ model) of the subsamples was immediately measured and then they were frozen at 4°C for further analysis. These subsamples were air dried, finely powdered and used for further chemical analysis.

The sediment samples were mixed and subjected for the analysis of tannin and lignin, lipid, carbohydrate and protein. Textural characteristics (sand, silt, and clay) and quantification of OM (protein, lipid and carbohydrate) were carried out by standard procedure. Texture was determined using pipette analysis (Lewis 1984). Total Organic Carbon (TOC) was processed by treating the samples with 1 M HCl to remove the carbonates and repeated two/three times in order to ensure the complete exclusion of carbonates. Samples were washed with Milli-Q water to remove salts and finally freeze dried. Organic carbon was determined using TOC analyzer (Elementar Vario Select, Germany). Samples were run with blank cups in order to correct the carbon associated with the tin cups. Standard sediments supplied by Elementar Vario Select, Germany, were used for calibration in the TOC analyzer. The detection limit for OC is 0.06%. Total proteins were determined using the method of Lowry *et al.* (1951). Carbohydrate estimation was done by Phenol-Sulphuric acid method (Dubois *et al.* 1956). Tannin and lignin were batch-extracted from the sediments with 0.05 M NaOH solution for 90 minutes and filtered. To 5 ml aliquots of filtrates, 1 ml of citrate solution was added followed by 1 ml folin reagent and 10 ml carbonate tartarate reagent and kept it for 30 minutes. The optical density was measured at 765 nm (APHA 1995; Jose *et al.* 2008). Total lipid was estimated by the Sulphophosphovanillin method (Barnes and Blackstock 1973). All the analyses were carried out in triplicate and the average was reported. Protein, carbohydrate and lipid concentrations were converted to carbon equivalents by using the following conversion factors: 0.49, 0.40 and 0.75 g of C/g respectively (Fabiano and Danovaro 1994). The sum total of protein, carbohydrate and lipid carbon were referred to as biopolymeric carbon (BPC) (Fichez 1991; Fabiano *et al.* 1995) and the study accounted accordingly. Sediment samples for the pigment analysis were immediately collected in 15 cm plastic vials for preservation by direct freeze drying. For the analysis of sedimentary chlorophyll and their degradation products, 0.5 g of freeze-dried sample was added to the glass centrifuge tube with 90% acetone and the mixture was sonicated at 5 atm for 30 sec to disrupt the cells and kept in dark at 4°C for nearly 5 hrs in order to ensure the complete extraction of the pigment. The mixture was then centrifuged at 3000 rpm to separate the pigment solvent complex from the remaining sediment. This process was repeated until the colour of the extract was clear. The supernatant liquid was then transferred to UV spectrometer (GENESYS 10 UV Thermo spectra) for further analysis. The concentrations of chlorophyll, pheophytin and carotenoid pigments were measured by the spectrophotometric method (Parsons *et al.* 1984; APHA 1995; Aneeshkumar and Sujatha 2012). All the four core sediment standard deviation varied for lipid, tannin and lignin, carbohydrate, pigment and texture as 2.1–5.6; 0.1–0.6; 0.4–10.4; 0.2–1.9; 0.1–30.4 and 5.7–31.3, respectively. Elemental compositions, CHNS of the samples were determined using Vario EL 111 CHNS Analyzer. The Principal Component Analysis (PCA) method, which enables a reduction in data and description of a given multidimensional system by means of small number of new variables, has been applied to the data. The data processing was carried out using the software Statistica 6.0.

4. Results

4.1 *Sediment characteristics*

Colour, pH and texture for each core sediment are discussed.

4.1.1 *Core SS_1*

Varying colour combination in core sediment was observed. Up to 10 cm it showed blackish brown, brownish black till 40 cm and then blackish brown. Values of pH ranged from 5.4 at 3 cm depth to 7.2 at 42 cm depth and it was found to exhibit an increasing trend with minor fluctuations from surface to bottom. Clay content dominated in this core and showed a variation ranging from 3.2% to 97.8%. Along the core, as depth increased clay fraction also increased.

4.1.2 *Core MS_1*

The whole core appeared blackish brown in colour. Values of pH ranged from 7 to 8. Sand content dominated in this core. Relative textural distribution was in the order; sand > clay > slit.

4.1.3 *Core MS_2*

Mixed black and grey colour at 0–36 cm and uniform black colour up to 63 cm were noted. Values of pH ranged from 7.9 at 63 cm depth to 8.7 at 9 cm depth and it exhibited a decreasing trend with minor fluctuations from surface to bottom. Sand content was intensified in this core. The textural variation was in the order; sand > clay > slit.

4.1.4 *Core NS_1*

The entire core were blackish brown in colour. Values of pH ranged from 6.1 to 6.6. The highest pH at 6 cm depth and lowest at 21 cm depth. Clay content varied between 1.9% and 85.4%. Along the core as depth increased sand content also intensified.

5. Organic matter (OM)

The distribution and variation of OM in different core sediments are illustrated as follows.

5.1 *Core SS_1*

Percentage of TOC ranged from 2.7 to 3.8, showing the lowest and the highest at a depth of 27 cm and 12 cm, respectively. Total carbohydrate concentration ranged from 4.7 to 11.7 mg/g. Maximum and minimum concentrations were observed at 6, 18 cm depths, respectively. Towards the lower end of the core, concentration of carbohydrate was found increased. Concentration of total protein ranged from 0.9 to 7.1 mg/g and concentration of protein was fairly high at middle portions. The maximum was observed at a depth of 6 cm and minimum was at 39 cm. Concentration of lipid was prime at the top portions and lowest towards bottom. At 39 cm depth the concentration reached maximum (34.1 mg/g) and again decreased to 15.1 mg/g at 45 cm. Concentration of tannin and lignin ranged from 1.0 to 1.6 mg/g. The highest was noted at 39 cm depth and the lowest at 18 cm depth. Relative OM distribution was in the order: lipid>carbohydrate>protein>tannin and lignin (figure 2).

5.2 *Core MS_1*

TOC decreased from top (0.7%) to bottom (0.6%) of the core. Total carbohydrate concentration ranged from 0.7 to 9.1 mg/g. The lowest concentration was observed at the depth, 24 cm and the highest at 39 cm. Concentration of carbohydrate was enriched at the bottom of the core. Concentration of total protein ranged from 0.2 to 1.6 mg/g at 3 and 24 cm depth, respectively. Concentration of protein was the maximum at the middle portion and almost constant towards the bottom. Total lipid concentration ranged from 1.3 to 9.1 mg/g and lowest at 45 cm depth and the highest at 39 cm depth. Concentration of lipid was enriched from the surface to the middle portions of the core. The tannin and lignin concentration ranged from 0.09 to 0.46 mg/g. The lowest concentration was observed at 3 cm depth and the highest at 54 cm depth. Concentration of tannin and lignin augmented towards the bottom of the core. Relative OM distribution was in the order; lipid>carbohydrate>protein>tannin and lignin (figure 2).

5.3 *Core MS_2*

Percentage of TOC ranged from 0.7 to 1.2. The maximum was noted at 24 cm depth and minimum at 6 cm of the core. TOC values increased towards the bottom of the core. Concentration of total carbohydrate ranged from 0.9 to 1.6 mg/g. The lowest concentration was observed at 54 cm depth and the highest at 36 cm depth. Concentration of carbohydrate was enriched in the surface and middle portions of the core. Total protein concentration ranged from 0.2 to 0.8 mg/g. The lowest concentration was observed at 6 cm depth and the highest at 29 cm depth of the core. Concentration of protein increased from the middle to the bottom

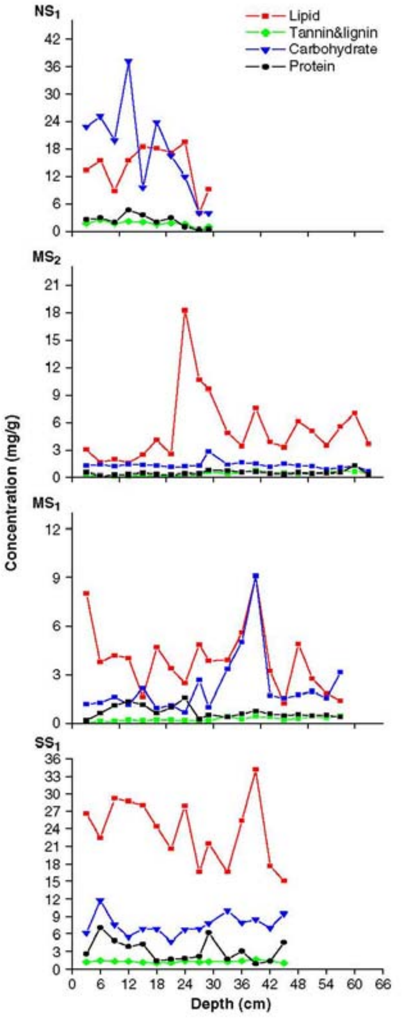

Figure 2. Distribution profile of organic matters (mg/g) in different cores.

portions of the core. Total lipid concentration ranged from 1.6 to 18.3 mg/g. The lower concentration was observed at the depth of 12 cm and the higher at 21 cm depth. Lipid concentration was the highest in the middle portions of the core. Concentration of tannin and lignin ranged from 0.1 to 0.8 mg/g. The lowest concentration was observed at 9 cm depth and the highest concentration was at 39 cm depth of the core. Concentrations of tannin and lignin were found increasing towards the bottom portions of the core. Relative OM distribution was in the order: lipid>carbohydrate>protein>tannin and lignin (figure 2).

5.4 *Core NS$_1$*

Percentage of TOC ranged from 0.6 to 2.9. The maximum was noted at 12 cm depth and the minimum at 27 cm of the core. In this core the amount of all the OM were drove upon same manner. Concentration was the highest in middle portions and the lowest in bottom portions of the core. Concentration of the total carbohydrate ranged from 3.9 to 37.1 mg/g. Concentration of total protein ranged from 0.3 to 4.6 mg/g. Total lipid concentration ranged from 4.0 to 19.5 mg/g and finally the tannin and lignin content ranged from 0.3 to 2.4 mg/g. The relative OM distribution was in the order: carbohydrate>lipid>protein>tannin and lignin (figure 2).

6. Discussion

Estuaries are highly dynamic and influenced by strong tidal action, entangled with fresh water and coastal discharges. A number of investigations in recent years have shed light on the varied nature and character of estuarine and mangrove sediments in and around Cochin estuary (Geetha *et al.* 2008; Manju *et al.* 2008; Niffy Benny 2009; Deepulal *et al.* 2011; Aneeshkumar and Sujatha 2012). The present study deals with the first detailed research work on core sediment biogeochemistry in the specific zones of Cochin estuarine system. In sediments, a wide variety of organic carbon forms are present and they range from freshly deposited litter to highly decomposed forms such as humus. The quality of organic matter in sediments is critical to the partitioning and bioavailability of sediment associated contaminants. Influence of total organic matter (TOM) in sediments is important to assess the fate, transport, deposition and retention of various inorganic and organic constituents. The high organic carbon associations which coincided with the high clay contents in the southern and northern parts of the estuary is attributed to the enhanced adsorption of organic carbon onto the clay minerals in the low salinity regimes (figure 2a). Lipid is one of the major biochemical compound produced by living organisms and constitute an important fraction of dissolved and particulate OM (Skoog and Benner 1997; Borsheim *et al.* 1999; Burdige *et al.* 2000). Besides, they are consumed by microheterotops in both fresh water and marine ecosystems and contribute essentially to the bacterial production (Rich et al. 1996). Its concentrations have been associated with the most labile fraction of sedimentary organics and it is considered the best descriptor of meiofauna abundance and biomass, over enzymatically hydrolysable aminoacids or protein contents (Gremare et al. 1997; Fabiano et al. 1995; Gremare et al. 2002). Elevated levels of lipid concentration found at three cores (SS_1, MS_1 and MS_2) indicates the biological activity associated with the productive nature of the environment (figure 2). Prevalence of carbohydrate concentration in the northern zone (NS_1) could be attributed to the anthropogenic input and the death and decay of aquatic organisms and floating plants. In the present study, the carbon normalized value was suggestive of its terrestrial origin. Proteins are the most important nitrogen-bearing compound in most of the organisms. The study revealed that concentration of protein accounted was fairly high at SS_1 core and maximum at 6 cm depth (7.1 mg/g). Both carbohydrates and protein serve as structural and storage components and comprise of up to 40% of the OM in the marine niche and 75% of the OM in terrestrial organisms (Aspinall 1983; Parsons et al. 1984; Biersmith and Benner 1998). Tannins and lignins are high molecular weight polycyclic aromatic compounds which are widely distributed throughout the plant kingdom (Schnitzer and Khan 1972; Finar 1976; Field and Lettinga 1987). These compounds are highly resistant to biological degradation and have a great potential to damage the aquatic environment. The identification and quantification of these compounds in these marine environment infers the importance of land-derived organic detritus. Concentration of tannins and lignins was found higher at cores collected from the northern and southern regions, and it establishes the character of allochthonous origin. The weak flow and the huge input of industrial/agricultural waste in the northern and southern parts of the estuary result in high organic input in the study area. Decreasing trends of organic carbon detected in the middle zone may be due to strong rectilinear current, which maintains an effective flushing. Organic matter has significant relation with fine fraction of the sediment. In the top sections of the core concentration of protein, lipid and carbohydrate were found intensified in the northern (NS_1) and southern (SS_1) regions, and diminished in the core samples obtained from the middle zone (MS_1 and MS_2). Mid-portions of the cores NS_1, MS_1 and MS_2 were enriched with organic matters. In the southern zone (SS_1), concentration of these OM was deficient. Bottom sections of the cores showed decrease in the concentration of OM in the cores NS_1, MS_1 and MS_2, whereas SS_1 revealed a heavier input of these organic matters. These observations confirmed the dependence of texture on the modification of sediment OM.

For the past several years sedimentary plant pigments have been studied and proved to be a valuable indicator of paleoecology and so the pigment parameter was also included in the study. The concentration of pheophytin pigment subjugated in three cores (MS_1, MS_2 and NS_1) were highlighted (figure 3). The highest concentration (96.3 mg/kg) of pheophytin was observed in NS_1 core at a depth of 6 cm and towards the bottom, concentration was below detectable level due to low adsorbing nature of the sandy sediment. In rest of the two cores, pheophytin content dominated in the bottom portions of the sediment core. According to Dell'Anno's et al. (2002), the predominance of pheopigments might be attributed to high turbidity, chemical contamination or other factors affecting photosynthetic potential of the primary producers. Generally carotenoids hold the largest potential for identifying the phototropic community contributing to the sediment record due to their taxonomical specificity and high stability in relation to other pigments. The higher concentration of carotenoid (40.7 mg/kg) detected (figure 3) in the fresh water augmented core, SS_1 (at 36 cm depth) also confirmed the above concept (figure 2a).

Protein–carbohydrate ratio (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 was generally higher in estuarine sediments which point to the presence of low dead organic matter accumulation, probably due to the vibrant condition of estuaries. In the present study this ratio showed an average value of 0.42, 0.50, 0.4 and 0.1 in SS_1, MS_1, MS_2 and NS_1 cores, respectively. Even though the middle zone is subjected to strong hydrodynamic conditions, sediments from this region also showed less PRT:CHO value. This may be due to the influence of anthropogenic inputs and rapid development activities in and around the study area. Low protein–carbohydrate ratios suggest the presence of aged OM and the role of protein as a potentially limiting factor for benthic consumers. Less dynamic nature of waters in northern and southern parts of the study area also caused low protein–carbohydrate ratio. Earlier report suggests the dominance of carbohydrate and lower PRT:CHO ratio is a typical feature of detrital heterotrophic environments (Danovaro 1996). Lipid–carbohydrate ratio (LPD:CHO) showed an average value of 3.3, 2.4, 4.2 and 1.1 in SS_1, MS_1, MS_2 and NS_1 cores, respectively, which in turn reflects energetic (food) quality of the organic

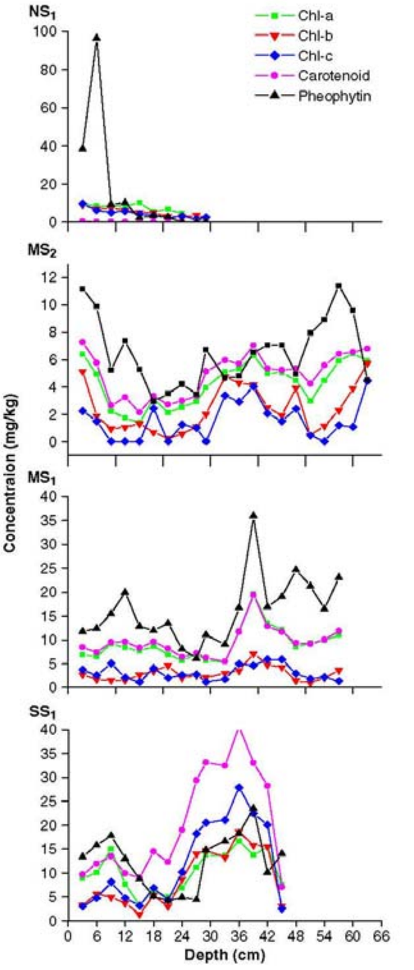

Figure 3. Variation pattern of pigments (mg/kg) in cores.

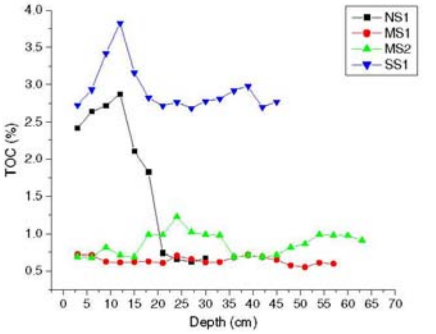

Figure 4. Distribution pattern of TOC (%) in different cores.

contents in the study area and well supports the earlier literatures (Gremare *et al.* 1997, 2002; Fabiano and Pusceddu 1998). Elevated value (15.758) was found in MS_2 core at a depth of 21 cm. Percent average of BPC was in the order 2.23, 0.42, 0.47 and 1.9 in SS_1, MS_1, MS_2 and NS_1 cores, respectively. The correlation analysis of various biogeochemical parameters of sediment cores was shown in tables 1–4. In core SS_1, biopolymeric carbon (BPC) showed a high significant correlation with lipid followed by tannin and lignin, and establishes them as the major contributors to BPC. A well momentous correlation of clay with chl-*a* and pheo pigments was also noticed. In core MS_1, BPC had high significant correlation with lipid followed by carbohydrate. These observations suggest that lipid and carbohydrate also become a major contributor of BPC. A significant correlation of clay with carbohydrate, chl-*a*, chl-*b*, carotenoid and pheophytin was also observed. Generally carbohydrate has high affinity for the fine grained sediments, which constitute clay particles with increased surface area per unit weight for the absorption of OM. OM present in the sediments is found in the form of aggregates that are surrounded by clay particles. In core MS_2, BPC exhibited a significant correlation with lipid. In core NS_1, BPC had significant positive correlations with lipid, tannin and lignin, carbohydrate, protein and clay, indicating an equal contribution of all organic matter to BPC. A significant correlation was observed between BPC and clay. It was found that there is a positive correlation between the proportions of clay and OM in the aggregates and degradation of OM.

The ratio of TOC percentages to total sulfur (TS) percentages (TOC:TS) in sediments was determined. It ranges from 1.2–3.0 for core SS_1, 0.7–3.0 for MS_1, 0.465–1.226 for MS_2 and 1.2–3.0 for NS_1. Generally, under anoxic conditions dissolved sulfate is reduced to hydrogen sulfide gas, which reacts with iron minerals to form iron sulfides causing a qualitative redox status of the environment under deposition. Marine sediments undergoing sulfate reduction under euxinic/inhospitable bottom conditions typically have TOC:TS ratios lower than 1.5 (Niffy Benny 2009) and similar observation was found at core from

Table 1. *Correlation between sedimentary parameters in SS_1 core.*

		Lipid (mg/g)	Tannin and lignin (mg/g)	Carbohydrate (mg/g)	Protein (mg/g)	Chl-*a* (mg/kg)	Chl-*b* (mg/kg)	Chl-*c* (mg/kg)	Carotenoid (mg/kg)	Pheophytin (mg/kg)	Sand%	Clay%	Silt%	BPC%
Correlation	Lipid (mg/g)	1.000												
	Tannin and lignin (mg/g)	0.503	1.000											
	Carbohydrate (mg/g)	−0.241	0.276	1.000										
	Protein (mg/g)	−0.036	−0.026	0.446	1.000									
	Chl-*a* (mg/kg)	−0.058	0.529	0.359	0.011	1.000								
	Chl-*b* (mg/kg)	−0.131	0.509	0.233	−0.276	0.805	1.000							
	Chl-*c* (mg/kg)	−0.085	0.474	0.200	−0.292	0.808	0.984	1.000						
	Carotenoid (mg/kg)	−0.101	0.440	0.194	−0.284	0.769	0.979	0.993	1.000					
	Pheophytin (mg/kg)	0.325	0.571	0.556	0.281	0.637	0.338	0.378	0.335	1.000				
	Sand%	0.101	−0.372	−0.521	−0.188	−0.674	−0.370	−0.357	−0.304	−0.773	1.000			
	Clay%	−0.119	0.290	0.366	−0.040	0.732	0.489	0.483	0.428	0.708	−0.922	1.000		
	Silt%	0.092	0.031	0.142	0.478	−0.457	−0.467	−0.479	−0.449	−0.198	0.270	−0.622	1.000	
	BPC%	0.944	0.539	0.028	0.262	0.006	−0.151	−0.114	−0.130	0.478	−0.030	−0.065	0.222	1.000

Table 2. *Correlation between sedimentary parameters in MS_1 core.*

		Lipid (mg/g)	Tannin and lignin (mg/g)	Carbohydrate (mg/g)	Protein (mg/g)	Chl-*a* (mg/kg)	Chl-*b* (mg/kg)	Chl-*c* (mg/kg)	Carotenoid (mg/kg)	Pheophytin (mg/kg)	Sand%	Clay%	Silt%	BPC%
Correlation	Lipid (mg/g)	1.000												
	Tannin and lignin (mg/g)	−0.130	1.000											
	Carbohydrate (mg/g)	0.544	0.509	1.000										
	Protein (mg/g)	−0.187	−0.302	−0.146	1.000									
	Chl-*a* (mg/kg)	0.311	0.524	0.740	−0.096	1.000								
	Chl-*b* (mg/kg)	0.333	0.328	0.646	−0.119	0.710	1.000							
	Chl-*c* (mg/kg)	0.323	−0.074	0.238	−0.082	0.590	0.448	1.000						
	Carotenoid (mg/kg)	0.367	0.479	0.734	−0.058	0.988	0.715	0.548	1.000					
	Pheophytin (mg/kg)	0.276	0.584	0.633	−0.025	0.823	0.423	0.238	0.852	1.000				
	Sand%	−0.209	−0.504	−0.700	−0.049	−0.834	−0.607	−0.175	−0.861	−0.826	1.000			
	Clay%	0.395	0.332	0.719	0.204	0.733	0.628	0.153	0.774	0.656	−0.907	1.000		
	Silt%	−0.416	0.418	−0.015	−0.352	0.268	−0.023	0.059	0.237	0.426	−0.257	−0.174	1.000	
	BPC%	0.944	0.068	0.779	−0.105	0.509	0.488	0.328	0.552	0.448	−0.430	0.591	−0.352	1.000

Table 3. *Correlation between sedimentary parameters in* MS_2 *core.*

		Lipid (mg/g)	Tannin and lignin (mg/g)	Carbohydrate (mg/g)	Protein (mg/g)	Chl-*a* (mg/kg)	Chl-*b* (mg/kg)	Chl-*c* (mg/kg)	Carotenoid (mg/kg)	Pheophytin (mg/kg)	Sand%	Clay%	Silt%	BPC%
Correlation	Lipid (mg/g)	1.000												
	Tannin and lignin (mg/g)	0.203	1.000											
	Carbohydrate (mg/g)	0.199	0.150	1.000										
	Protein (mg/g)	0.306	0.592	0.343	1.000									
	Chl-*a* (mg/kg)	−0.048	0.702	−0.056	0.431	1.000								
	Chl-*b* (mg/kg)	−0.111	0.484	−0.028	0.391	0.798	1.000							
	Chl-*c* (mg/kg)	0.029	0.378	−0.198	0.049	0.660	0.785	1.000						
	Carotenoid (mg/kg)	−0.085	0.702	−0.015	0.397	0.973	0.810	0.624	1.000					
	Pheophytin (mg/kg)	−0.230	0.303	−0.013	0.259	0.503	0.172	−0.174	0.566	1.000				
	Sand%	−0.249	−0.743	−0.116	−0.569	−0.549	−0.392	−0.196	−0.591	−0.378	1.000			
	Clay%	0.528	0.506	0.309	0.368	−0.012	−0.166	−0.293	0.076	0.132	−0.568	1.000		
	Silt%	−0.033	0.580	−0.055	0.456	0.674	0.582	0.424	0.668	0.374	−0.852	0.053	1.000	
	BPC%	0.997	0.228	0.263	0.353	−0.035	−0.095	0.020	−0.069	−0.216	−0.270	0.546	−0.020	1.000

Table 4. *Correlation between sedimentary parameters in* NS_1 *core.*

		Lipid (mg/g)	Tannin and lignin (mg/g)	Carbohydrate (mg/g)	Protein (mg/g)	Chl-*a* (mg/kg)	Chl-*b* (mg/kg)	Chl-*c* (mg/kg)	Carotenoid (mg/kg)	Pheophytin (mg/kg)	Sand%	Clay%	Silt%	BPC%
Correlation	Lipid (mg/g)	1.000												
	Tannin and lignin (mg/g)	0.668	1.000											
	Carbohydrate (mg/g)	0.381	0.716	1.000										
	Protein (mg/g)	0.526	0.826	0.750	1.000									
	Chl-*a* (mg/kg)	0.483	0.852	0.618	0.817	1.000								
	Chl-*b* (mg/kg)	−0.001	0.519	0.647	0.498	0.750	1.000							
	Chl-*c* (mg/kg)	0.124	0.548	0.612	0.475	0.728	0.920	1.000						
	Carotenoid (mg/kg)	0.240	0.604	0.634	0.613	0.847	0.907	0.912	1.000					
	Pheophytin (mg/kg)	0.084	0.566	0.410	0.282	0.406	0.563	0.605	0.478	1.000				
	Sand%	−0.638	−0.913	−0.766	−0.880	−0.948	−0.705	−0.697	−0.820	−0.469	1.000			
	Clay%	0.668	0.854	0.714	0.843	0.926	0.695	0.714	0.837	0.444	−0.985	1.000		
	Silt%	0.096	0.664	0.573	0.541	0.487	0.330	0.189	0.235	0.318	−0.471	0.314	1.000	
	BPC%	0.803	0.850	0.855	0.811	0.694	0.423	0.467	0.555	0.310	−0.868	0.850	0.436	1.000

Table 5. *Factor analysis matrix for core* SS_1.

	Component			
	1	2	3	4
Component matrix[a]				
Lipid (mg/g)	−0.018	0.708	0.670	−0.187
Tannin and lignin (mg/g)	0.595	0.505	0.369	0.232
Carbohydrate (mg/g)	0.433	0.318	−0.611	0.335
Protein (mg/g)	−0.104	0.557	−0.583	0.292
Chl-*a* (mg/kg)	0.932	−0.007	−0.040	0.048
Chl-*b* (mg/kg)	0.869	−0.303	0.225	0.297
Chl-*c* (mg/kg)	0.869	−0.290	0.260	0.268
Carotenoid (mg/kg)	0.835	−0.312	0.266	0.316
Pheophytin (mg/kg)	0.716	0.588	−0.168	−0.182
Sand%	−0.734	−0.248	0.465	0.304
Clay%	0.809	0.022	−0.310	−0.484
Silt%	−0.527	0.447	−0.168	0.587
BPC%	0.033	0.879	0.433	−0.064

Extraction method: Principal Component Analysis.
[a] Four components extracted.

Table 6. *Factor analysis matrix for core* MS_1.

	Component			
	1	2	3	4
Component matrix[a]				
Lipid (mg/g)	0.507	0.726	0.316	−0.182
Tannin and lignin (mg/g)	0.518	−0.598	0.044	−0.394
Carbohydrate (mg/g)	0.870	0.135	0.045	−0.284
Protein (mg/g)	−0.103	0.218	−0.857	0.321
Chl-*a* (mg/kg)	0.944	−0.172	0.035	0.232
Chl-*b* (mg/kg)	0.758	0.086	0.062	0.165
Chl-*c* (mg/kg)	0.446	0.169	0.392	0.754
Carotenoid (mg/kg)	0.958	−0.123	−0.011	0.207
Pheophytin (mg/kg)	0.837	−0.317	−0.096	−0.047
Sand%	−0.881	0.225	0.307	0.049
Clay%	0.842	0.145	−0.433	−0.096
Silt%	0.127	−0.858	0.275	0.105
BPC%	0.706	0.619	0.177	−0.215

Extraction method: Principal Component Analysis.
[a] Four components extracted.

middle zone (MS_2). These sites were under the threat of anthropogenic inputs and were associated with dredging and piling activities. These sediments also undergo sulfate reduction below an oxygenated water column exhibiting TOC:TS ratios in the range 1.5 to 5 and well corroborated earlier by Berner and Raiswell (1983). Sediments in the stations (SS_1, MS_1 and NS_1) were characterized under predominantly anoxic stipulation. Increased anoxia in the study area not only increases preservation of the pigments but also excludes the benthic animal community, thereby reducing ingestion and bioturbation, which has significant effect on the degradation of sedimentary pigments.

C/N ratios are often used to differentiate marine from terrestrial organic matter (Redfield *et al.* 1963; Atkinson and Smith 1983; Perdue and Koprivnjak 2007), although selective degradation of different minerals in sediments can affect the C/N ratios of organic matter (Muller 1997). Organic matter should have a C/N ratio lower than 17 in order to be of nutritional use to invertebrates (Russel Hunter 1970). In this research findings, C/N ratio varied from 18.5 to 25.23, averaging 22.75 for core SS_1; from 11.9 to 14.2, averaging 12.9 for core MS_1; from 20 to 22, averaging 21 for core MS_2 and from 14.4 to 32.8, averaging 20.7 for core NS_1. Among the four cores, C/N ratio

Table 7. *Factor analysis matrix for core MS_2.*

	Component		
	1	2	3
Component matrix[a]			
Lipid (mg/g)	0.126	0.835	0.432
Tannin and lignin (mg/g)	0.843	0.230	−0.062
Carbohydrate (mg/g)	0.077	0.466	−0.173
Protein (mg/g)	0.633	0.404	−0.138
Chl-*a* (mg/kg)	0.909	−0.280	0.065
Chl-*b* (mg/kg)	0.773	−0.374	0.325
Chl-*c* (mg/kg)	0.566	−0.382	0.695
Carotenoid (mg/kg)	0.917	−0.271	−0.017
Pheophytin (mg/kg)	0.463	−0.157	−0.702
Sand%	−0.814	−0.311	0.218
Clay%	0.267	0.789	−0.268
Silt%	0.818	−0.124	−0.094
BPC%	0.150	0.855	0.407

Extraction method: Principal Component Analysis.
[a]Three components extracted.

Table 8. *Factor analysis matrix for core NS_1.*

	Component		
	1	2	3
Component matrix[a]			
Lipid (mg/g)	0.554	−0.694	−0.357
Tannin and lignin (mg/g)	0.915	−0.250	0.184
Carbohydrate (mg/g)	0.833	−0.050	0.222
Protein (mg/g)	0.862	−0.268	0.086
Chl-*a* (mg/kg)	0.929	0.042	−0.075
Chl-*b* (mg/kg)	0.771	0.596	−0.015
Chl-*c* (mg/kg)	0.774	0.558	−0.172
Carotenoid (mg/kg)	0.848	0.413	0.236
Pheophytin (mg/kg)	0.550	0.399	0.246
Sand%	−0.984	0.101	0.089
Clay%	0.958	−0.081	−0.250
Silt%	0.525	−0.139	0.801
BPC%	0.860	−0.423	−0.052

Extraction method: Principal Component Analysis.
[a]Three components extracted.

was greater than 20 in three cores (SS_1, MS_2, and NS_1) ascertaining the input of terrestrial material into the area, justifying that the source of organic matter is allochthonous. From middle zone (core MS_1), the ratio points out autochthonous character of the sediment. However, the succession of post-depositional changes may also modify the environment niche drastically. Percentage of elemental distributions (CHNS) in all the four sediment cores were in the order: C>S>H>N.

To confirm different variable associations, and identification of parameters controlling the organic matter distribution, factor analysis was carried out (tables 5–8). 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). In core SS_1, four factors account for 71.3% of the total variance. The first factor accounted for high positive loadings on all the sedimentary parameters except sand, slit and lipid. Factor-2 exibit significant positive loadings for all OM and BPC. This clearly shows that high negative loading has occurred for all pigments and sand. Factor-3 showed significant positive loading for lipid and high negative loadings for carbohydrate, protein, pigments, clay and slit. Thus it is well established that the third component has undergone geochemical processes rather than diagenesis, which includes siltation and sorption/desorption. Factor-4 shows no such significant positive loadings. In MS$_1$ core, four factors account for 84.5% of the total variance. The first factor shows positive loadings of all sedimentary parameters except for sand and protein, evidence to high significant loadings of pigments. Hence, this can be called the 'pigment controlled factor'. High positive loadings of lipid and BPC are the features of factor-2. No such high positive loadings to the sedimentary parameters were found in factor-3, but factor-4 shows significant positive loadings to chl-*c*. In MS$_2$ core, three factors account for 71.1% of the total variance. The first factor shows positive loadings of all sedimentary parameters except sand and resulting in significant loadings of pigments, and profoundly it could be called the 'pigment controlled factor'. Factor-2 shows high positive loadings on lipid, clay and BPC. But factor-3 shows no such high positive loadings. In core NS$_1$, three factors account for 69.1% of the total variance. The same trend as in the core MS$_2$ was observed in the first factor. Though factor-2 shows no such high positive loadings, the factor-3 showed high positive loading to slit. Thus from factor analysis it is inferred that 'organic matter controlled factor', has a maximum amount of total variance in all the four core sediments, indicating good correlation of OM in most of the variables studied. However, combining the sedimentary record with other biological and geochemical indicators in multi-proxy studies still constitutes the most robust method for interpreting long term changes in ecosystem structure.

7. Conclusion

The present study has been the first comprehensive attempt ever made to characterize the core sediment biogeoorganics in the CES. It has served to emphasis the prominent role of biogeoorganics in regulating the complex interactive forces that operate within the estuarine system and also provides a baseline data for future research on anthropogenic impacts in the region. Characterization of organic matter has made it possible to trace the source and predict the fate of allochthonous and autochthonous inputs that find their way into this transition zone. Among the four sediment cores, percentage of TOC was higher at SS$_1$ and NS$_1$ coinciding with high clay contents in the southern and northern parts of the estuary. This is attributed to the enhanced adsorption of organic carbon onto the clay minerals in the low salinity regimes. Their relative organic matter distributions in the three cores except NS$_1$ core were in the order: lipid>carbohydrate>protein>tannin and lignin. Dominance of carbohydrates over lipids and proteins in the northern zone indicated lower nutritive aspect of the organic matter, and their aged and refractory nature. TOC/TS ratio indicates the anoxic behaviour of all the core sediments. C/N ratio supports the allochthonous character of the three sediment cores (SS$_1$, NS$_1$, MS$_2$). Concentration of pheophytin pigment was found subjugated in three cores (MS$_1$, MS$_2$ and NS$_1$) indicating the long term diagenesis. Increased anoxia in the study area not only increases preservation of pigments, but also excludes the benthic animal community, thereby reducing ingestion and bioturbation, which have a significant effect on the degradation of sedimentary pigments.

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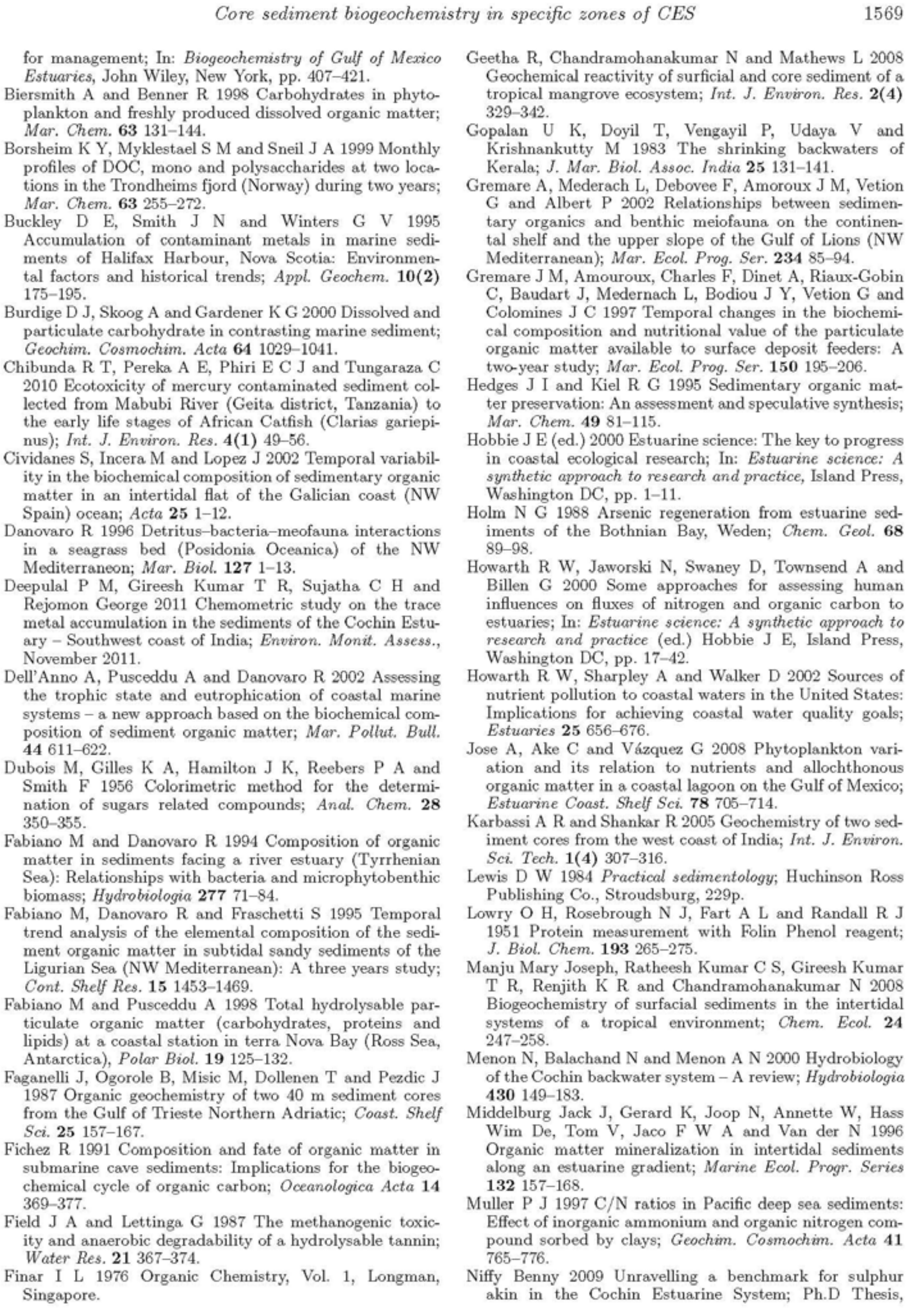

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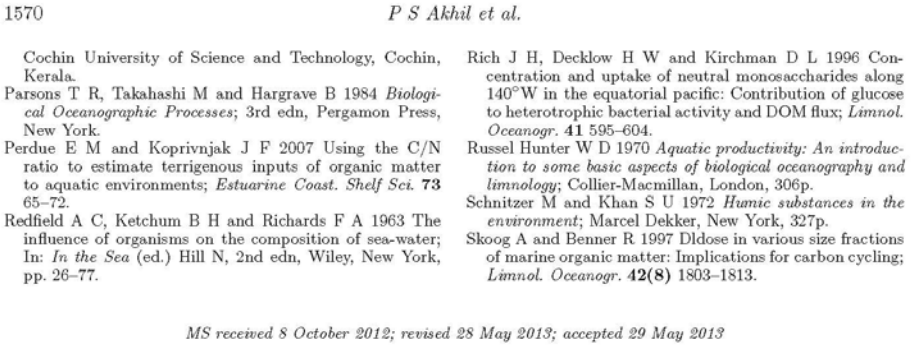

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Geochemistry of Core Sediment from Antarctic Region

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Abstract

Southern Ocean (SO) is the fourth largest Ocean comprising the southern portions of the Atlantic Ocean, Indian Ocean and Pacific Ocean. Sediment core sample (66^0 34'S and 58^0 40'E)was collected onboard O.R.V Sagar Nidhi from January to March 2010 in the Fourth Southern Ocean expedition cruise launched by the National Centre for Antarctic and Ocean Research, Goa . Sedimentary records from this area reveal the sensitivity and climatic variability's of the region over a large time scale. Organic matter (OM) and textural behaviour of the samples were analyzed and processed concurrently. Distribution of OM, Total Organic Carbon (TOC), Protein, Lipid and Carbohydrate along with the trace metal was highlighted. Textural variation was in the array of Sand >Clay >Silt. Sand content ranges from 30.29% to 80.11%. The order of relative distribution of OM was Lipid >Protein > TOC > Carbohydrate.

The average concentrations of TOC, Protein, Lipid and Carbohydrate were 2.2 mg/g, 1.2 mg/g, 3.3 mg/g and 1.1mg/g respectively. Protein to carbohydrate ratio and lipid to carbohydrate ratio were also encountered to understand the respective freshness and nutritional quality of the sediments. Trace metal distribution showed the average concentration was maximum for Mn and minimum for Co.

Keywords: Organic matter, Core sediment, Texture, Trace metal, Antarctica, Southern Ocean.

Introduction

SO is the most significant part of the world oceans and comprises several physically and biologically distinct regimes with latitudinally separated by fronts. The SO is important in the global biogeochemical cycling and climate change because it contains sites of deep water convection and its surface waters contain a large pool of unutilized nutrients. The dynamic ocean processes encountered in SO have played a key role in the long-term global palaeo-environmental evolution[17]. The Antarctic continent with its surrounding SO regimes contribute as the major climate engines of the earth[20,26].

Sediment cores are the store houses of fundamental raw data source for providing new research finding information on sea bed character, depositional history and environmental changes. Sea-floor sediment cores act as sinks and sources of contaminants in the aquatic systems because of their variable physical and chemical properties. [5,24, 27-30, 34, 35] The sediment found on the deep sea floor is unique and closely linked with the geochemical history of the earth. The investigations of sediments have recently become a major subject of interest in research since they reflect the current quality of the system and provide insight on the impact of human. They behave both as a carrier and possible source of biochemical constituents. Geochemical studies of surficial sediment as well as sediment cores are helpful in the assessment of environmental composition.[1, 2, 6,7, 13,15]

The OM and trace metal in marine sediments are important and play a major role in the chemistry of oceans not only providing a significant reservoir in the global carbon cycle, but also driving in the early digenesis. Analysis of sediment OM gives the changes in the environmental chemical pattern which exerts a strong control on the diagenic alterations in the sediment. This paper presents the distributional pattern of Core Sediment Organic matter (CSOM) and trace metal in the coastal region of Antarctica.

Material and Methods

Sediment core sample was collected using piston corer, onboard O.R.V Sagar Nidhi in the Fourth Southern Ocean expedition cruise (January to March 2010) launched by the National Centre for Antarctic and Ocean Research, Goa. One 31 cm core (66^0 34'S and 58^0 40'E) was taken from coastal region of Antarctica at depth of 707.33 m.

The core sediment was sliced in to approximately 1cm depth intervals and then sub samples were tightly packed and stored in a deep freezer at 4^{0}C until analysis. These sub samples were air dried, finely powdered and used for chemical analysis. Textural characteristics (sand, silt, and clay), quantification of OM (TOC, Protein, Lipid and Carbohydrate) were estimated based on standard procedure. Texture was determined using pipette analysis by Lewis[19]. TOC was done by the Chromic acid oxidation method[10]. Protein was measured using Copper and Folin–Ciocalteu phenol reagent[22]. Carbohydrate estimation was carried out by Phenol- Sulphuric acid method[9]. Total lipid was found by the Sulpho-phospho-vanillin method[3]. The bulk 0.5g samples were treated with 5:1 mixture of concentrated HNO_3 and $HClO_4$ [21]and metal concentration was analyzed by AAS (Perkin Elmer 3110). Pearson correlation was carried out to test the correlation pattern of *OM* with Textural characteristics.

Results and Discussion

The grain size distribution in the core sediments was measured to understand the depositional environment history. In general the textural variation of the core was found to be sand >clay >silt. The entire core was mostly dominated by sand and was high both at the top and bottom layer of the core. The average sand, clay and silt content of these samples were around 58.17%, 31.39% and 10.44% respectively.

The sandy textural nature of the sediment resulted in low OM content. TOC is an essential part of any site characterization because it behaves as a tool to understand the biogeochemistry of sediments. In this study TOC content of the core ranges from 3.87% to 0.36% (Figure 1a) and faintly elevated at the bottom of the core indicating an ancient sedimentary phase. The peak value was at a depth of 21cm (3.89%). The top section of the core was enriched with lipid and was depleted towards the bottom portion. Lipid was greater at 2cm (10.85 mg/g) and low at 23cm depth (0.43 mg/g) (Figure 1c). Protein and Carbohydrate were highly concentrated at the middle portion and decreased at the top and bottom of the core. Protein was depleted at the top, then enriched and again depleted. Protein was high at 20 cm (5.35mg/g) and low (0.24mg/g) at 31cm (Figure 1b). Carbohydrate was low at the top with minimum concentration at 2cm (0.43mg/g) and high at 14cm with 2.068 mg/g. Finally the concentration diminished (Figure 1d).

The order of relative distribution of OM was Lipid >Protein > TOC > Carbohydrate. The average of the OM constituents: TOC, Protein, Lipid, Carbohydrate was 2.2 mg/g, 1.2 mg/g, 3.3 mg/g and 1.1mg/g respectively. Relative high concentration of lipid may be due to the low hydrophilic nature. They are responsible for their higher survival rates during sedimentation when compared to other biogenic compound classes like amino acids or sugars. Digenetic processes that affect lipid distribution in marine sediments include particle reworking due to digestion of organic matter by benthic fauna, microbial decomposition and abiotic reactions[33]. Decreased rate of these processes may also account for the greater lipid concentration. Similar trend was found in the coastal sediment of NW Adriatic Sea[8].

Protein to carbohydrate ratio and lipid to carbohydrate ratio were also encountered to understand the respective freshness and nutritional value of the sediments [12], [14] .Mean protein to carbohydrate ratio in the present study (Figure 2) was found to be 1.2. As reported by these results, protein to carbohydrate ratio was greater than one indicating the freshness of the sample. Likewise proteins tend to be mineralized faster than carbohydrate and causing higher amounts of fresh particles.[18-25] The nutritional value of the analyzed samples was high because the lipid to carbohydrate ratio (Figure 3) was greater than one. Therefore the visibility of freshness and high nutritional quality of the core sediment in these regions were viewed.

The dynamics of trace metals is more complicated in oceans since they are coupled with strong physical movement with the varying chemistries of water. In most aquatic systems, concentrations of trace metals in suspended sediment and the top few centimetres of bottom sediment are far greater than concentrations of trace metals dissolved in the water column. Bottom sediments serve as a source for suspended sediment and can provide a historical record of chemical conditions. Metal concentration averages are given in table 1.Trace metal distribution showed the average concentration was maximum for Mn and Fe and minimum for Cd and Co. Enrichment factor was interpreted as suggested by Birth [4] for metal studied with respect to natural background concentration. EF< 1 indicates no enrichment, EF< 3 is minor enrichment, EF = 3-5 is moderate enrichment, EF=5-10 moderately severe enrichment, EF=10-25 severe enrichment, EF= 25-50 is very severe enrichment and EF >50 is extremely severe enrichment. The study attributes extremely severe enrichment to Mn and next to Cd. Pb had moderate enrichment and for others observed minor enrichment. The greater enrichment of these metals may be due to the allothonus input.

Correlation analysis of OM with textural behaviour was carried out to check any significant correlation between OM with textural characteristics (Table 2).Generally textural characteristics and OM content are interrelated but the present work highlights insignificant correlation of OM with texture. The average concentration of OM in this core sediment was very low. Several studies agree on the limited role of deep-sea burial because OM produced in the euphotic zone decomposes before it reaches the seafloor [11, 32]. The sandy nature of the sediment also contributes to the same result. Previous studies by Josia Jacob et al[16] and Manju P.Nair[23] also support the result.

Conclusion

Analysis of sediment core sample from the coastal regions of Antarctica reveals the distribution pattern of sediment OM with textural behaviour. The relative allotment of OM was found to be Lipid >Protein > TOC > Carbohydrate. Textural variation was in the order of sand >clay >silt. The sandy nature of the sediment results in the diminished average concentration of OM. Protein to carbohydrate ratio and lipid to carbohydrate ratio were greater than one showing the freshness and high nutritional value of the sediment in these regions. Trace metal distribution showed the average concentration was maximum for Mn and minimum for Co.

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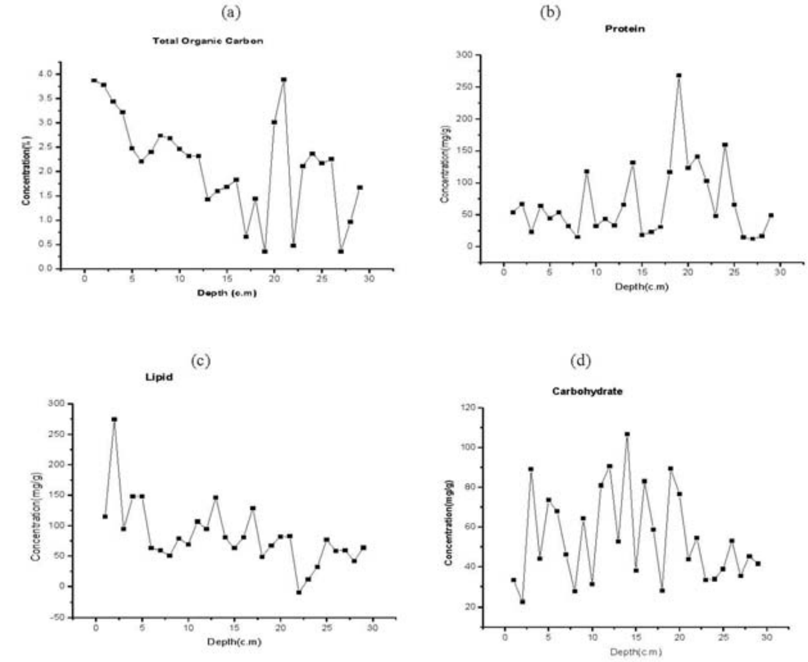
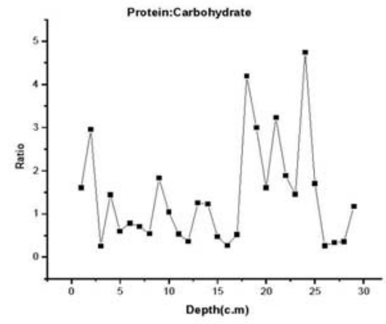


Figure 1(a-d): Organic matter Distribution



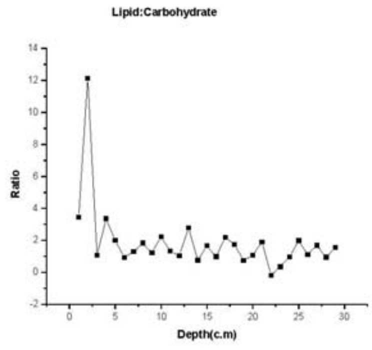


Figure 2: Protein to Carbohydrate Ratio

Figure 3: Lipid to Carbohydrate Ratio

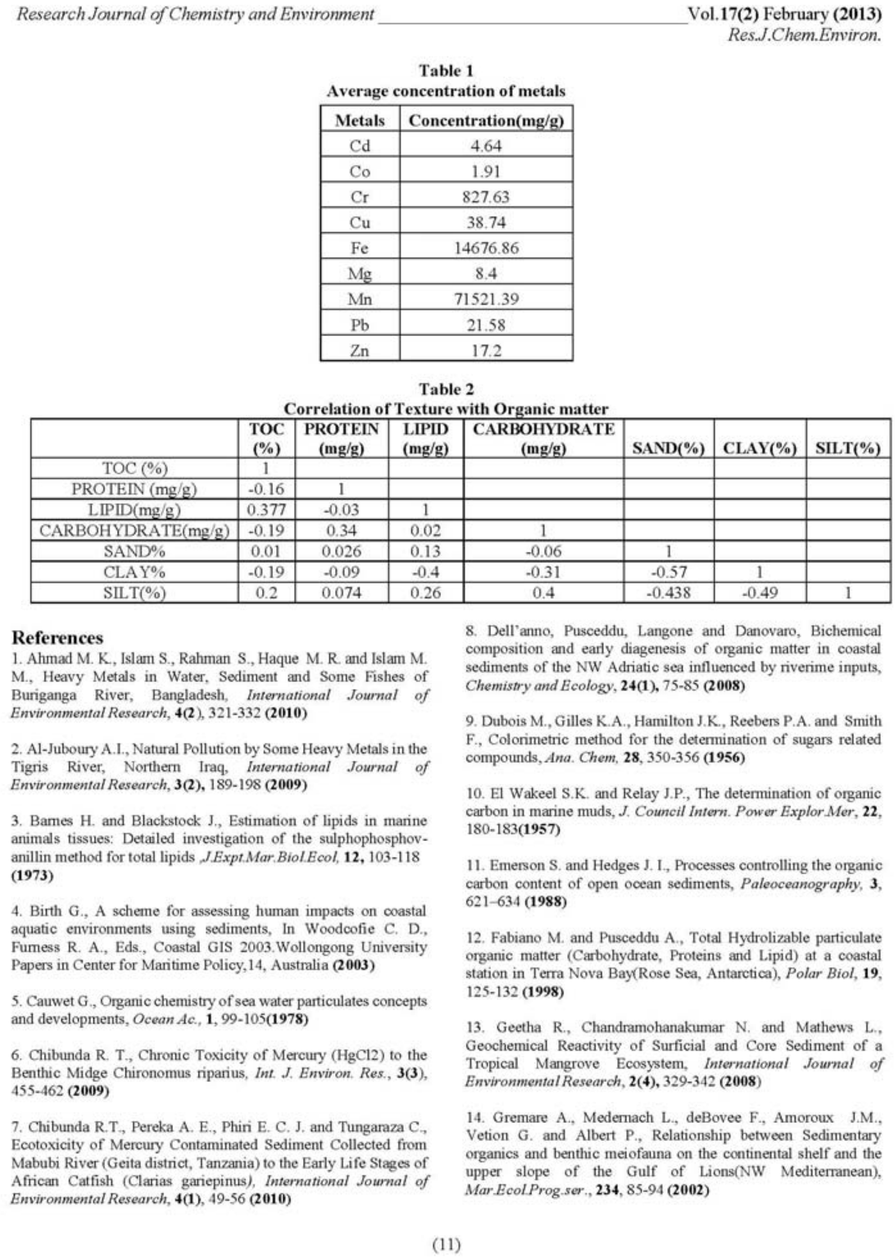


Table 1
Average concentration of metals

Metals	Concentration(mg/g)
Cd	4.64
Co	1.91
Cr	827.63
Cu	38.74
Fe	14676.86
Mg	8.4
Mn	71521.39
Pb	21.58
Zn	17.2

Table 2
Correlation of Texture with Organic matter

	TOC (%)	PROTEIN (mg/g)	LIPID (mg/g)	CARBOHYDRATE (mg/g)	SAND(%)	CLAY(%)	SILT(%)
TOC (%)	1						
PROTEIN (mg/g)	-0.16	1					
LIPID(mg/g)	0.377	-0.03	1				
CARBOHYDRATE(mg/g)	-0.19	0.34	0.02	1			
SAND%	0.01	0.026	0.13	-0.06	1		
CLAY%	-0.19	-0.09	-0.4	-0.31	-0.57	1	
SILT(%)	0.2	0.074	0.26	0.4	-0.438	-0.49	1

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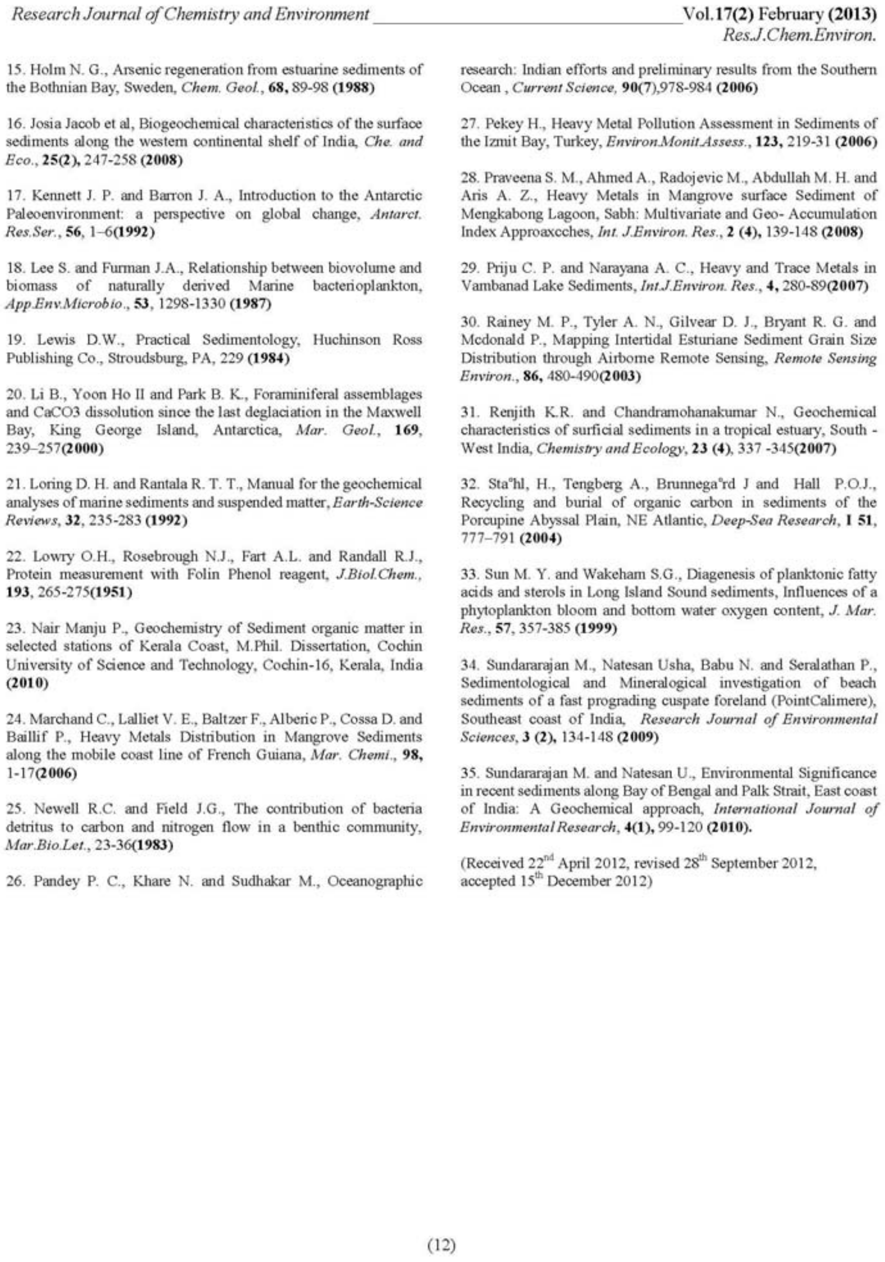

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Groundwater hydrochemistry in the crystalline laterites/ forest loams of Kasargod district, Kerala, India

P. S. Akhil, K. N. Sumangala and C. H. Sujatha

ABSTRACT

Groundwater quality assessment for drinking and irrigation purposes in the specific hot spot areas of Kasargod District, Kerala, India, was conducted during July 2009 to January 2011. Groundwater samples were examined and quantified for the major cations and anions, microbiological parameters, irrigation quality parameters such as sodium adsorption ratio (SAR), residual Mg/Ca ratio and %Na. Most of the ground samples were acidic in nature and the fluoride concentrations exhibited below the desirable limit. Concentration of iron exceeds the desirable limit of 0.3 mg/l during monsoon 2009 and pre-monsoon 2010. The competitive and non-competitive ion relationship between the major ions was authenticated by the correlation study.

Key words | groundwater, Kasargod district, quality assessment, sodium adsorption ratio

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INTRODUCTION

Groundwater resources are overexploited due to urbanization, agricultural, industrial and domestic activities and the resulting contamination of these geogenic and anthropogenic causes has become a serious problem. The World Health Organization (WHO) has repeatedly insisted that the single major factor adversely influencing the general health and life expectancy of a population in many developing countries is lack of ready access to clean drinking water (Nash & McCall 1995). It is projected that by 2020, the number of people living in water-scarce countries will increase from about 131 million to more than 800 million (Gardner-Outlaw & Engelman 1997). In the view of international perspective of '$< 1,700\ m^3$/person per year' as water stressed and '$< 1,000\ m^3$/person per year' as water scarce, India is water stressed today and is likely to be water scarce by 2050 (Gupta & Deshpande 2004). In recent years, many parts of India, especially in the arid- and semi-arid regions, owing to the vagaries of monsoon and deficiency of surface water, dependence on groundwater has increased tremendously. However, groundwater contamination due to agricultural activities and the illegal use of agrochemicals have been extensively reported earlier (Singh 1983; Hem 1985; Palaniswami & Ramulu 1994; Datta *et al.* 1997, 2000; Prasad 1998; Patel *et al.* 2004; Mondal *et al.* 2005; Marechal *et al.* 2006; Kumar *et al.* 2006a, b; Salve *et al.* 2008; Sivasankar & Gomathi 2009; Ravikumar *et al.* 2010; Subba Rao *et al.* 2011).

In recent decades, attention has been given to studying the natural concentration of the many ions in groundwater in order to establish the anthropogenic and geogenic sources affecting groundwater quality as well as the reactions that take place within the aquifer. Although no systematic and scientifically documented research on the groundwater quality assessment in Kasargod district was performed until 2009, later a detailed investigation on the prevalence of organochlorine pesticide residues was conducted (Akhil & Sujatha 2012) along with the present attempt on spatial and temporal variations in the groundwater quality. The derived inferences observed from the study delineate regions where groundwater is suitable or unsuitable for drinking and irrigation purposes.

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SITE DESCRIPTION

Physiography

Kerala state is blessed with 44 rivers and with an average annual replenishable groundwater resource of 6841.33 MCM usable groundwater storage. The state is divided into 14 districts, of which Kasargod District is the northern most and lies between north latitudes 12°02′27″ and 12°47′35″ and east longitudes 74°51′54″ and 75°25′25″. It covers an area of 1,992 km^2. Most of the area is based on crystalline rock of the Archean age; at the coastal belt, sedimentary rocks of tertiary and more recent age. Besides this, the major geological formations are alluvial, laterites, and crystallines. The aquifer in the district offers very good potential in the deeper fractured rock zone. Groundwater arises under water table conditions in alluvium, laterites and the weathered mantle of the crystallines, whereas in the deeper fractured crystallines it occurs under semi-confined to confined conditions. Alluvium occurs as narrow strips parallel to the coast and the width increases from the northern to southern part of the district.

MATERIALS AND METHODS

Groundwater samples were collected from 13 open wells representing different geological formations as well as land use pattern and different depths of the aquifer represented in Figure 1 and Table 1. The sampling period covered the three prominent seasons, viz; pre-monsoon, monsoon and post-monsoon from July 2009 to January 2011. The pH, electrical conductivity and total dissolved solids (TDS) were measured immediately from the sampling site. Water samples were collected in polyethylene bottles and stored at 4 °C, major anions and cations were analysed using the standard methods as suggested by the American Public Health Association (1995) (Table 2). Triplicate analyses of each sample were performed and average values were reported in Table 3.

The raw data generated were validated by using the ion-balance error (Mathhess 1982) and the error was well within ±10%. The results were evaluated in accordance with the Bureau of Indian standards specifications for drinking water (BIS 1998). The groundwater samples were classified based on percentage sodium (Na%), sodium adsorpti ratio (SAR), residual Mg/Ca ratio, electrical conductiv (EC), total hardness (TH) and total dissolved solids (TD Statistical analysis was also performed with t

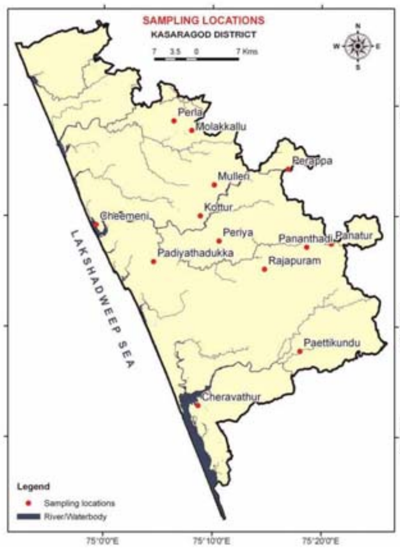


Figure 1 | Location map of the study area, Kasargod District.

Table 1 | Sampling locations

Sl. No.	Name
1	Mullria
2	Padiyathaduk
3	Parappa
4	Perla
5	Kottur
6	Paettikundu
7	Cheemeni
8	Panathady
9	Panathur
10	Rajapuram
11	Periya
12	Malakkallu
13	Cheravathur

Table 2 | Materials and methods

Sl No	Parameters	Analytical methods followed Characteristics	Analytical Method	Unit	BIS limits (1998)	Reference
1	General	pH	Electrode		6.5–8.5	APHA (1995)
2		Electrical conductivity (EC)	Conductivity meter	µS/cm	3,000	APHA (1995)
3		Total alkalinity (as $CaCO_3$)	Titrimetric	mg/L	600	APHA (1995)
4		Dissolved oxygen	Winkler method	mg/L	–	APHA (1995)
5		Calcium hardness (as CaCO3)	EDTA titrimetric	mg/L	200	APHA (1995)
6	Major cations	Sodium (as Na+)	Flame photometric	mg/L	200	APHA (1995)
7		Potassium (as K+)	Flame photometric	mg/L	10	APHA (1995)
8	Major anions	Chlorides	Argentometric titration	mg/L	1,000	APHA (1995)
9		Nitrates (as NO_3^-)	UV–VISIBLE spectrophotometry or ion selective electrode	mg/L	45	APHA (1995)
10		Fluoride (as F^-)	Ion selective electrode	mg/L	1.5	APHA (1995)
11		Phosphates (as $PO_4^{3-}P$)	Ascorbic acid method	mg/L	0.3	APHA (1995)
12		Sulfates (as SO_4^{2-})	Turbidity method	mg/L	400	APHA (1995)
13	Irrigation water quality	Hardness (as $CaCO_3$)	EDTA titrimetric	mg/L	<75	APHA (1995)

hydrochemical data by using the platform SPSS ¥ 11.4 and created Pearson correlation matrix.

RESULTS AND DISCUSSION

Groundwater chemistry

All water samples collected were colourless, which shows the absence of humic acid, fulvic acid and suspended matter. Most of the samples were acidic in nature and depicted in Figure 2. The acidic nature observed in this terrain is related to the major distribution of lateritic and forest loamy soils in the eastern hilly areas of the district and are characterized by a surface layer which is very rich in organic matter. The use of acid producing fertilizer such as ammonium sulfate and super phosphate of lime for agricultural purposes also contributes to the decline in pH (Dinesh Kumar 1997; Rajesh *et al.* 2001). EC values in the study area ranged between 75 and 590 µmhos/cm. The minimum value was observed in sample No-5 (Kottur) during post-monsoon 2010 and the maximum value observed was in sample No-10 (Cheravatur) during monsoon 2009. All the EC values were within the prescribed limits of 3,000 µmhos/cm (BIS 1998).

Generally, water having high TDS values if used for drinking purposes causes an unfavorable physiological reaction in the transient consumer and gastrointestinal irritation (Shankar *et al.* 2008). Of the 13 open well water samples analyzed the TDS values range between 48 and 377.6 mg/l. The lowest value noted was for sample No-5 (Kottur) during post-monsoon 2010. The steep hike was found for sample No-10 (Cheravatur), during monsoon 2009. All the TDS values were within the permissible limit 2,000 mg/l (BIS 1998). Dissolved oxygen (DO) is one of the most important parameters in water quality assessment and it reflects the physical and biological processes prevailing in the water. The DO values were in the range of 2.4 and 11.2 mg/l. Minimum DO value was shown for samples No-9 and 10 (Figure 3). Total hardness was found to be in the range of 20 to 160 mg/l in sample No-13 (Cheravatur) during monsoon 2009. Alkalinity values ranged between 5 and 250 mg/l. In all the samples the total hardness and alkalinity were within the BIS permissible limit. The concentration of iron in the study area varied from 0.051 to 5.64 mg/l and the majority of these samples exceeded the desirable limit of 0.3 mg/l in monsoon 2009 and pre-monsoon 2010. The maximum value of iron was present in sample No-9 (Panathur) during monsoon 2009 (Table 3). The interaction of oxidized iron-bearing minerals and

Table 3 | Average concentration of iron, fluoride and MPN count in the groundwaters of Kasargod District

	Iron (mg/l)				Fluoride (mg/l)				MPN Count/100 ml			
Sampling stations	**Monsoon 2009**	**Pre-monsoon 2010**	**Post-monsoon 2010**	**Pre-monsoon 2011**	**Monsoon 2009**	**Pre-monsoon 2010**	**Post-monsoon 2010**	**Pre-monsoon 2011**	**Monsoon 2009**	**Pre-monsoon 2010**	**Post-monsoon 2010**	**Pre-monsoon 2011**
Mullria	1.695	1.438	0.103	0.205	0.125	0.115	0.028	0.012	3	6	2	2
Padiyathadukka	1.9	1.438	0	0.308	0.236	0.594	0	0.011	6	3	6	4
Parappa	1.458	0.462	0.205	0.565	0	0	0	0	2	10	6	6
Perla	1.027	1.13	0.103	0	0	0	0	0	7	18	4	8
Kottur	1.027	1.027	0.154	0.359	0	0.275	0	0	1	9	2	12
Paettikundu	1.849	0.205	0	0	0	0	0	0	1	8	4	9
Cheemeni	2.054	1.078	0	0.051	0	0	0	0	5	16	2	10
Panathady	2.773	0	0.205	0	0.11	0	0	0	3	2	2	1
Panathur	5.649	4.879	0.103	0	0.421	0.806	0.462	0	8	2	4	3
Rajapuram	1.232	0	0	0	0.321	0.594	0.361	0.023	4	2	17	10
Periya	0.205	0.873	0.154	0.051	0	0	0	0.011	2	9	8	5
Malakkallu	2.824	0.873	0.154	0.462	0	0	0	0	5	4	7	4
Cheravathur	0.308	0.524	0.308	0.051	0	0	0	0	4	5	4	3

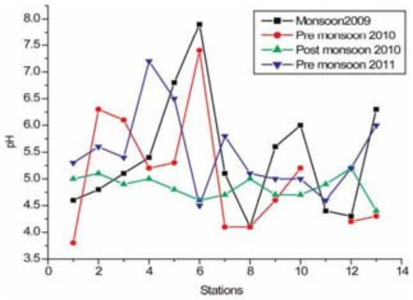


Figure 2 | Distribution of pH during the study period.

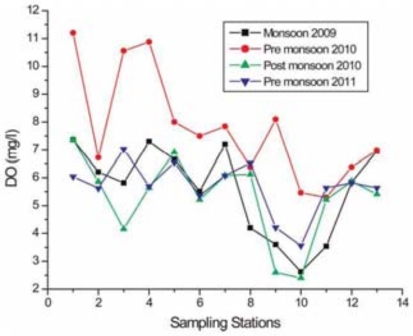


Figure 3 | Distribution of DO during the study period.

organic matter and subsequent dissolution of Fe_2CO_3 at low pH may contribute to the elevation in iron content.

Coliforms which are natural intestinal flora are n harmful by themselves, but their presence is an indicat of fecal pollution from an external source. In the prese study, MPN (most probable number) values were betwe 1 and 18/100 ml (Table 3) and the permissible MPN cou is 10 per 100 ml of total coliforms. According to Woo (1990), effluents from point-like sources such as sep tanks and general farmyard wastes were considered as t main sources of contamination of groundwater and su incidents were not identified in the present studied sampli locations. Beside this, the lack of protecting walls will le to the entry of contaminated runoff water into the w from the upstream, also increasing the bacteriologi

contamination. As a precautionary measure, the water should be boiled prior to consumption. For groundwater sources, appropriate well maintenance may help to minimize problems with coliform bacteria.

Na values ranged from 0.4 to 10.3 mg/l, while K values ranged from 0.1 to 8.7 mg/l. The natural source of potassium in water is usually from the chemical weathering and subsequent dissolution of minerals in local igneous rocks such as feldspars (orthoclase and microcline), mica and sedimentary rocks, as well as silicate and clay minerals (Howari & Banat 2002). Low concentration of K may be due to greater resistance of K mineral to weathering and its fixation in the formation of clay minerals (Sarin *et al.* 1989). All the samples showed Na and K concentration within the permissible limit of 100 and 10 mg/l (BIS 1998) respectively.

Owing to its impact on human health, fluoride concentration is an important criterion in hydrogeochemical quality. Low fluoride content (0.6 mg/l) causes dental caries, whereas high (>1.50 mg/l) levels results in fluorosis and hence the prescribed safe limit of fluoride concentration is between 0.60 and 1.50 mg/l in drinking water. The majority of the water samples were below the permissible limit (Table 3) and may have caused dental caries. The nitrate values ranged from 0.085 and 1.466 mg/l; the lowest value in sample No-11 (Periya) during pre-monsoon 2011. The intermediate monsoon effect may contribute to the hike in sample No-8 (Panathady) during post-monsoon 2010. The fertilizer applied to soils (mostly Aridisols) remained dry throughout the year without constituting a major nitrate pollution threat to the ground-water, except for the possibility when the soils were irrigated. However the heavy rainfall in the monsoon season, leached out and released a substantial quantity of nitrogen into the groundwater. All the samples showed nitrate values within the permissible limit of 45 mg/l. The sulfate in groundwater was generally present with calcium, magnesium and sodium soluble salts. It ranged between 0.021 to 30.36 mg/l and lay within the permissible limit 400 mg/l (BIS 1998) in the study area. The lowest sulfate concentration of 0.021 mg/l was found in sample No-5 (Kottur) during pre- and post-monsoon 2010 and the highest (30.36 mg/l) was observed in sample No-8(Panathady) in monsoon 2009. The source of sulfate ions to the hydrosphere may be from acid mine drainage. Moreover, significant change in the sulfate concentration also took place with time during rainfall infiltration and groundwater recharge (Jain *et al.* 2010). Phosphate values varied from 0.0015 to 0.88 mg/l and most of the samples in post-monsoon 2010 exceeded the permissible limit of 0.3 mg/l. Chloride concentration varied from 7.8 to 56 mg/l and was within the permissible limit of 1,000 mg/l.

Groundwater quality assessment for irrigation

Based on physicochemical analyses, irrigation quality parameters such as %Na, SAR and residual Mg/Ca ratio were calculated and are represented in (Tables 4–6). The

Table 4 | Sodium percentage

Stations	Monsoon'09	Pre-monsoon'10	Post-monsoon'10	Pre-monsoon'11
1. Mullria	24.57	14.63	20.4	40.37
2. Padiyathadukka	32.25	21.57	21.91	18.23
3. Parappa	30.73	42.9	31.26	14.89
4. Perla	10.53	13.56	38.38	17.61
5. Kottur	26.94	43.21	35.97	33.09
6. Paettikundu	14.61	10.26	29.52	20.06
7. Cheemeni	10.62	37.36	17.51	26.66
8. Panathady	26.19	14.57	33.87	33.83
9. Panathur	10.24	42.17	15.43	16.66
10. Rajapuram	25.57	25.59	37.56	21.83
11. Periya	17.34	21.3	52.05	32.43
12. Malakkallu	28.81	32	25.02	24.92
13. Cheravathur	1.14	25.58	20.63	22.15

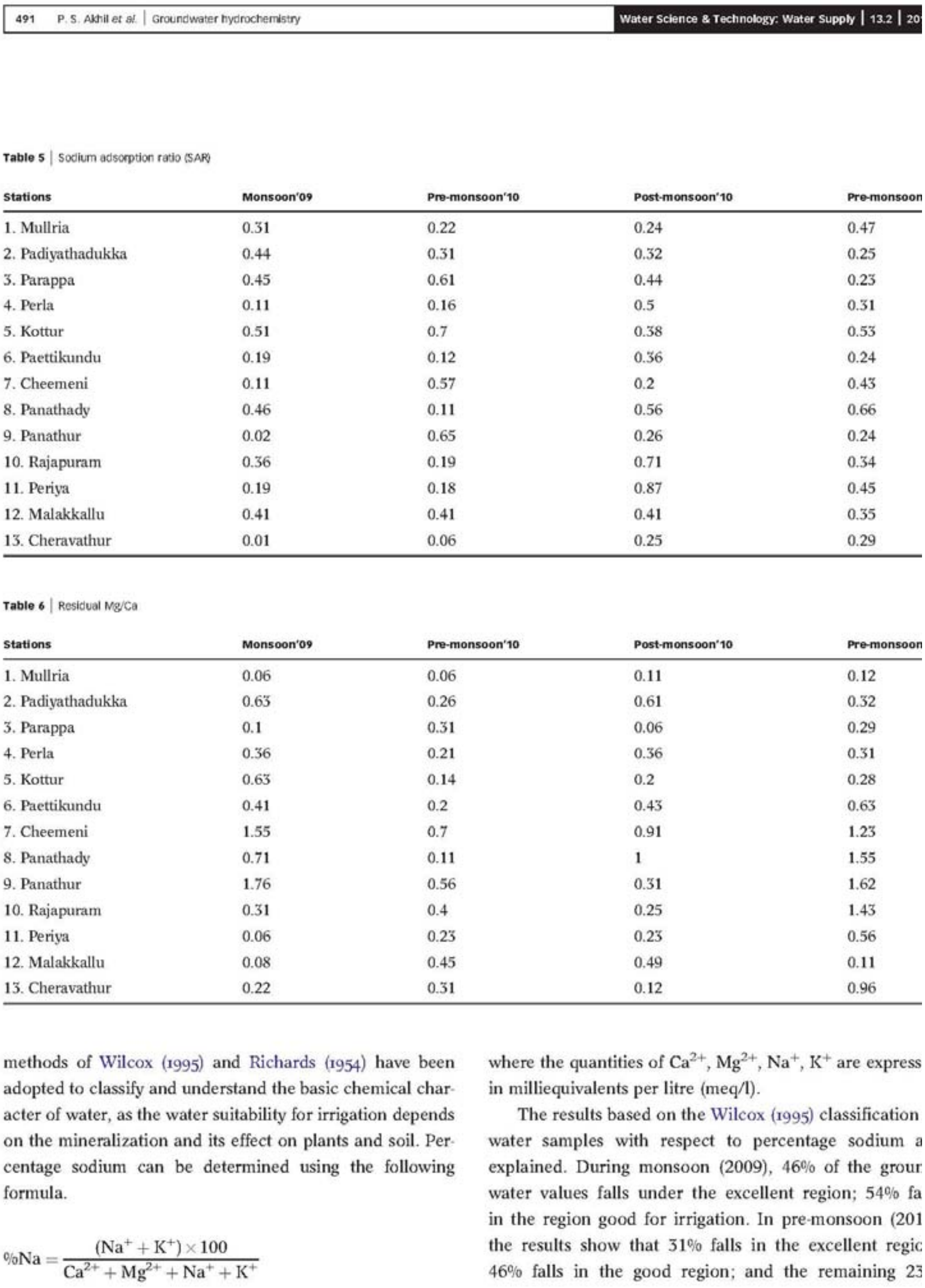


Table 5 | Sodium adsorption ratio (SAR)

Stations	Monsoon'09	Pre-monsoon'10	Post-monsoon'10	Pre-monsoon
1. Mullria	0.31	0.22	0.24	0.47
2. Padiyathadukka	0.44	0.31	0.32	0.25
3. Parappa	0.45	0.61	0.44	0.23
4. Perla	0.11	0.16	0.5	0.31
5. Kottur	0.51	0.7	0.38	0.53
6. Paettikundu	0.19	0.12	0.36	0.24
7. Cheemeni	0.11	0.57	0.2	0.43
8. Panathady	0.46	0.11	0.56	0.66
9. Panathur	0.02	0.65	0.26	0.24
10. Rajapuram	0.36	0.19	0.71	0.34
11. Periya	0.19	0.18	0.87	0.45
12. Malakkallu	0.41	0.41	0.41	0.35
13. Cheravathur	0.01	0.06	0.25	0.29

Table 6 | Residual Mg/Ca

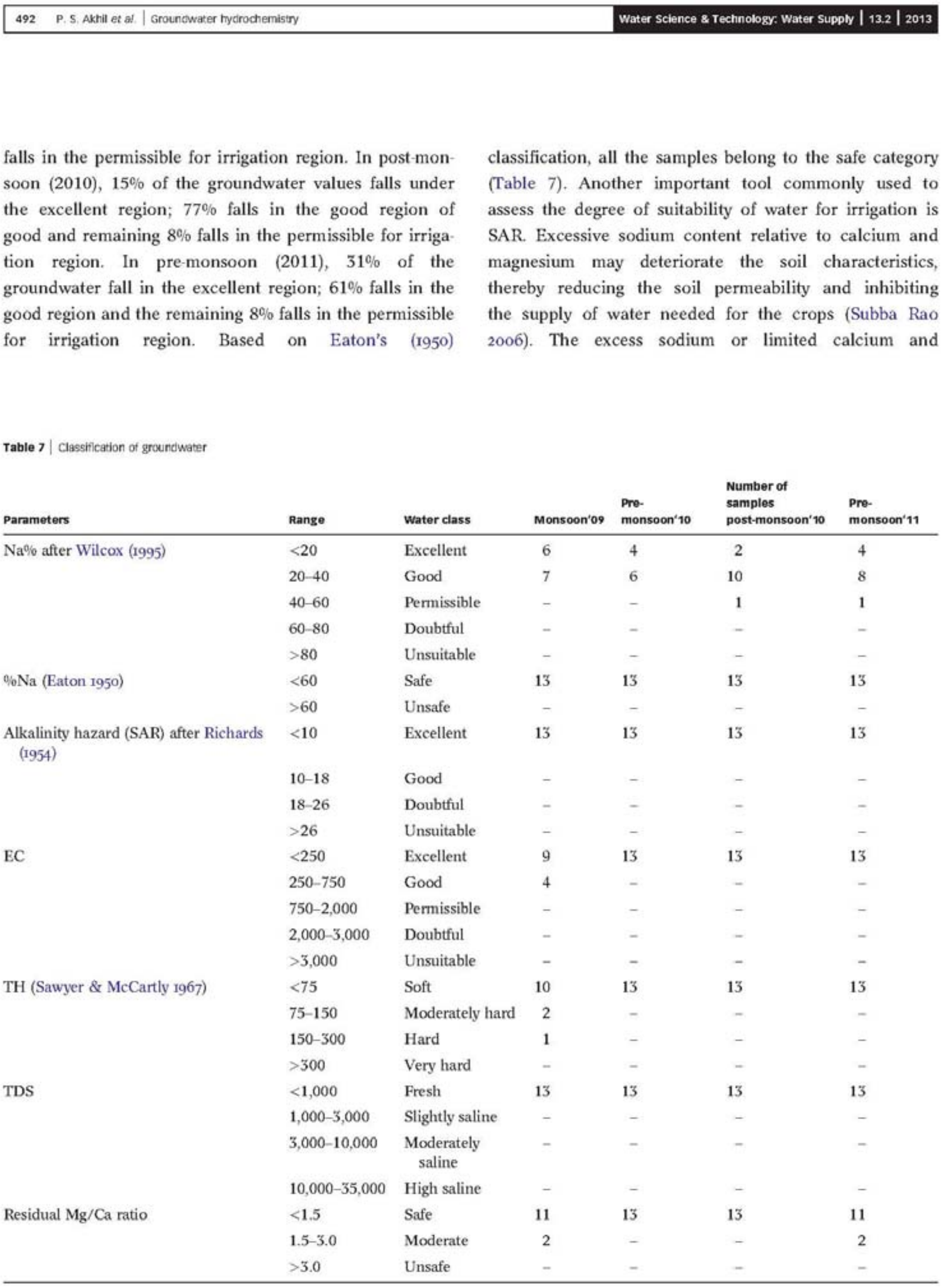
Stations	Monsoon'09	Pre-monsoon'10	Post-monsoon'10	Pre-monsoon
1. Mullria	0.06	0.06	0.11	0.12
2. Padiyathadukka	0.63	0.26	0.61	0.32
3. Parappa	0.1	0.31	0.06	0.29
4. Perla	0.36	0.21	0.36	0.31
5. Kottur	0.63	0.14	0.2	0.28
6. Paettikundu	0.41	0.2	0.43	0.63
7. Cheemeni	1.55	0.7	0.91	1.23
8. Panathady	0.71	0.11	1	1.55
9. Panathur	1.76	0.56	0.31	1.62
10. Rajapuram	0.31	0.4	0.25	1.43
11. Periya	0.06	0.23	0.23	0.56
12. Malakkallu	0.08	0.45	0.49	0.11
13. Cheravathur	0.22	0.31	0.12	0.96

methods of Wilcox (1995) and Richards (1954) have been adopted to classify and understand the basic chemical character of water, as the water suitability for irrigation depends on the mineralization and its effect on plants and soil. Percentage sodium can be determined using the following formula.

$$\%\mathrm{Na} = \frac{(\mathrm{Na}^{+} + \mathrm{K}^{+}) \times 100}{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+} + \mathrm{Na}^{+} + \mathrm{K}^{+}}$$

where the quantities of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} are express in milliequivalents per litre (meq/l).

The results based on the Wilcox (1995) classification water samples with respect to percentage sodium a explained. During monsoon (2009), 46% of the grour water values falls under the excellent region; 54% fa in the region good for irrigation. In pre-monsoon (201 the results show that 31% falls in the excellent regic 46% falls in the good region; and the remaining 23



falls in the permissible for irrigation region. In post-monsoon (2010), 15% of the groundwater values falls under the excellent region; 77% falls in the good region of good and remaining 8% falls in the permissible for irrigation region. In pre-monsoon (2011), 31% of the groundwater fall in the excellent region; 61% falls in the good region and the remaining 8% falls in the permissible for irrigation region. Based on Eaton's (1950) classification, all the samples belong to the safe category (Table 7). Another important tool commonly used to assess the degree of suitability of water for irrigation is SAR. Excessive sodium content relative to calcium and magnesium may deteriorate the soil characteristics, thereby reducing the soil permeability and inhibiting the supply of water needed for the crops (Subba Rao 2006). The excess sodium or limited calcium and

Table 7 | Classification of groundwater

Parameters	Range	Water class	Monsoon'09	Pre-monsoon'10	Number of samples post-monsoon'10	Pre-monsoon'11
Na% after Wilcox (1995)	<20	Excellent	6	4	2	4
	20–40	Good	7	6	10	8
	40–60	Permissible	–	–	1	1
	60–80	Doubtful	–	–	–	–
	>80	Unsuitable	–	–	–	–
%Na (Eaton 1950)	<60	Safe	13	13	13	13
	>60	Unsafe	–	–	–	–
Alkalinity hazard (SAR) after Richards (1954)	<10	Excellent	13	13	13	13
	10–18	Good	–	–	–	–
	18–26	Doubtful	–	–	–	–
	>26	Unsuitable	–	–	–	–
EC	<250	Excellent	9	13	13	13
	250–750	Good	4	–	–	–
	750–2,000	Permissible	–	–	–	–
	2,000–3,000	Doubtful	–	–	–	–
	>3,000	Unsuitable	–	–	–	–
TH (Sawyer & McCartly 1967)	<75	Soft	10	13	13	13
	75–150	Moderately hard	2	–	–	–
	150–300	Hard	1	–	–	–
	>300	Very hard	–	–	–	–
TDS	<1,000	Fresh	13	13	13	13
	1,000–3,000	Slightly saline	–	–	–	–
	3,000–10,000	Moderately saline	–	–	–	–
	10,000–35,000	High saline	–	–	–	–
Residual Mg/Ca ratio	<1.5	Safe	11	13	13	11
	1.5–3.0	Moderate	2	–	–	2
	>3.0	Unsafe	–	–	–	–

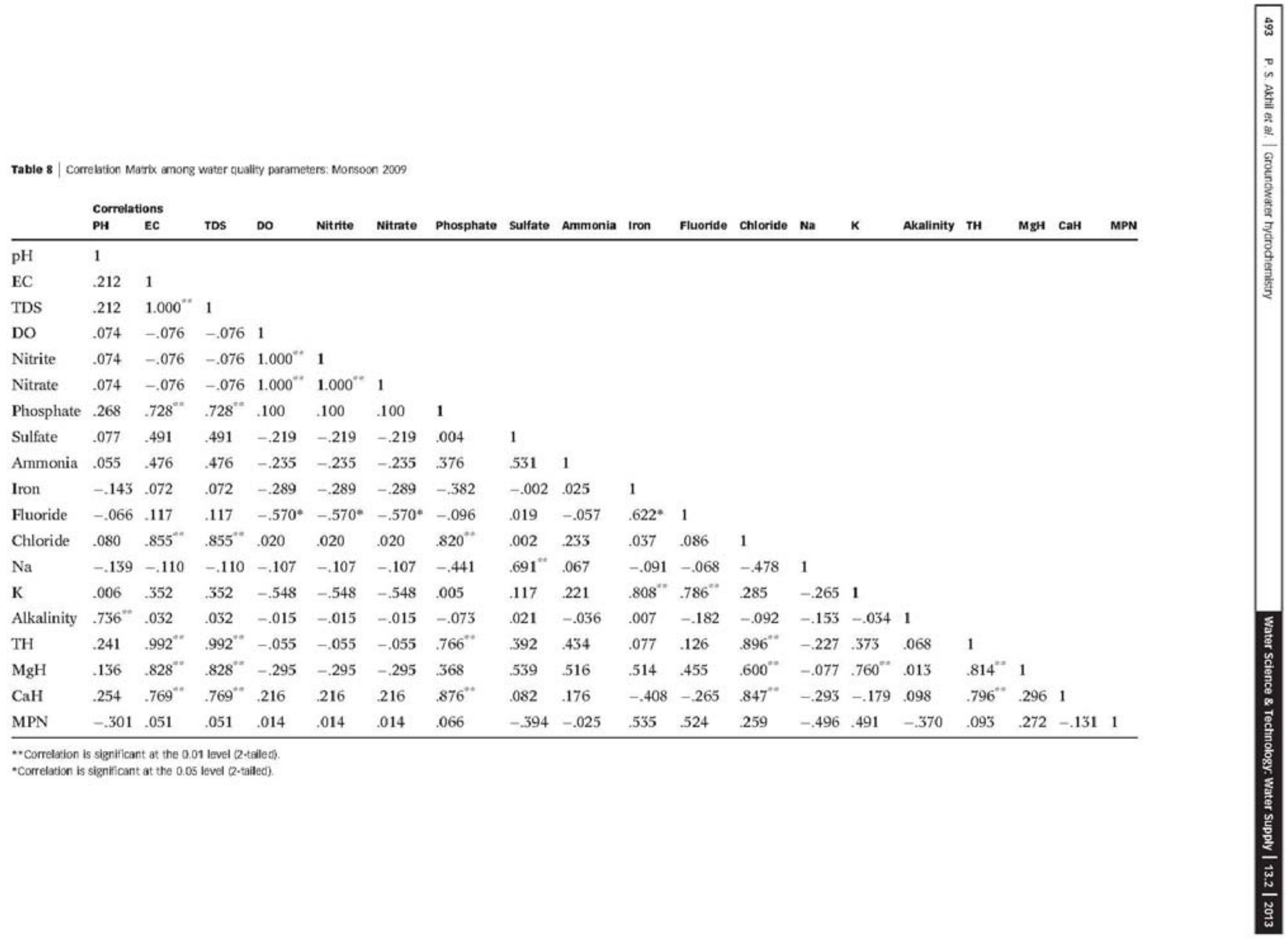


Table 8 | Correlation Matrix among water quality parameters: Monsoon 2009

	Correlations																		
	PH	**EC**	**TDS**	**DO**	**Nitrite**	**Nitrate**	**Phosphate**	**Sulfate**	**Ammonia**	**Iron**	**Fluoride**	**Chloride**	**Na**	**K**	**Akalinity**	**TH**	**MgH**	**CaH**	**MPN**
pH	1																		
EC	.212	1																	
TDS	.212	1.000**	1																
DO	.074	−.076	−.076	1															
Nitrite	.074	−.076	−.076	1.000**	1														
Nitrate	.074	−.076	−.076	1.000**	1.000**	1													
Phosphate	.268	.728**	.728**	.100	.100	.100	1												
Sulfate	.077	.491	.491	−.219	−.219	−.219	.004	1											
Ammonia	.055	.476	.476	−.235	−.235	−.235	.376	.531	1										
Iron	−.143	.072	.072	−.289	−.289	−.289	−.382	−.002	.025	1									
Fluoride	−.066	.117	.117	−.570*	−.570*	−.570*	−.096	.019	−.057	.622*	1								
Chloride	.080	.855**	.855**	.020	.020	.020	.820**	.002	.233	.037	.086	1							
Na	−.139	−.110	−.110	−.107	−.107	−.107	−.441	.691**	.067	−.091	−.068	−.478	1						
K	.006	.352	.352	−.548	−.548	−.548	.005	.117	.221	.808**	.786**	.285	−.265	1					
Alkalinity	.736**	.032	.032	−.015	−.015	−.015	−.073	.021	−.036	.007	−.182	−.092	−.153	−.034	1				
TH	.241	.992**	.992**	−.055	−.055	−.055	.766**	.392	.434	.077	.126	.896**	−.227	.373	.068	1			
MgH	.136	.828**	.828**	−.295	−.295	−.295	.368	.539	.516	.514	.455	.600**	−.077	.760**	.013	.814**	1		
CaH	.254	.769**	.769**	.216	.216	.216	.876**	.082	.176	−.408	−.265	.847**	−.293	−.179	.098	.796**	.296	1	
MPN	−.301	.051	.051	.014	.014	.014	.066	−.394	−.025	.535	.524	.259	−.496	.491	−.370	.093	.272	−.131	1

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

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

Table 9 | Correlation Matrix among water quality parameters: Pre-monsoon 2010

	Correlations																		
	PH	**EC**	**TDS**	**DO**	**Nitrite**	**Nitrate**	**Phosphate**	**Sulfate**	**Ammonia**	**Iron**	**Fluoride**	**Chloride**	**Na**	**K**	**Alkalinity**	**TH**	**MgH**	**CaH**	**MPN**
PH	1																		
EC	.268	1																	
TDS	.268	1.000**	1																
DO	−.062	.112	.112	1															
Nitrite	.284	.672*	.672*	−.195	1														
Nitrate	−.158	.074	.074	−.095	−.224	1													
Phosphate	−.422	.444	.444	.619*	.208	.038	1												
Sulfate	.085	.096	.096	−.158	.187	−.341	−.207	1											
Ammonia	.120	.193	.193	−.325	.415	−.499	−.191	.036	1										
Iron	−.194	.087	.087	.205	.075	.229	.169	−.259	−.054	1									
Fluoride	.080	.155	.155	−.191	.295	.312	−.053	.206	−.162	.620*	1								
Chloride	−.259	.669*	.669*	.176	.524	.088	.811**	−.159	.154	.246	.254	1							
Na	−.079	.177	.177	.299	.062	−.226	.303	−.257	.229	.540	.366	.433	1						
K	−.237	.035	.035	−.289	−.196	.119	−.256	.694**	−.125	−.202	.010	−.247	−.447	1					
Alkalinity	.696**	.270	.270	−.170	.094	.114	−.376	−.354	.094	−.164	−.303	−.281	−.241	−.211	1				
TH	.246	.833**	.833**	.091	.795**	.031	.388	.378	.072	−.079	.248	.537	−.081	.104	.021	1			
MgH	.270	.482	.482	−.284	.741**	−.394	−.107	.564*	.506	.081	.460	.261	.291	.079	−.116	.610*	1		
CaH	.037	.549	.549	.390	.248	.425	.581*	−.089	−.408	−.177	−.146	.403	−.385	.051	.139	.630*	−.232	1	
MPN	.100	−.125	−.125	.503	−.235	−.517	.148	−.107	−.140	−.141	−.525	−.247	.139	−.289	.220	−.203	−.168	−.085	1

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

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

Table 10 | Correlation Matrix among water quality parameters: Post-monsoon 2010

	Correlations																		
	pH	**EC**	**TDS**	**DO**	**Nitrite**	**Nitrate**	**Phosphate**	**Sulfate**	**Ammonia**	**Iron**	**Fluoride**	**Chloride**	**Na**	**K**	**Alkalinity**	**TH**	**MgH**	**CaH**	**MPN**
pH	1																		
EC	.307	1																	
TDS	.307	1.000**	1																
DO	.351	−.606*	−.606*	1															
Nitrite	.303	.423	.423	.027	1														
Nitrate	.031	.412	.412	−.459	.479	1													
Phosphate	.373	−.253	−.253	.307	.146	−.047	1												
Sulfate	.150	.811**	.811**	−.693**	.087	.238	−.179	1											
Ammonia	.443	.391	.391	.041	−.023	−.068	.060	.218	1										
Iron	−.088	−.172	−.172	.157	.219	.251	−.038	−.318	.187	1									
Fluoride	−.280	.447	.447	−.816**	−.123	.453	−.127	.636*	−.101	−.262	1								
Chloride	−.152	.330	.330	−.283	−.048	.098	−.249	.124	−.189	−.032	.289	1							
Na	.272	.632*	.632*	−.487	.568*	.577*	−.158	.496	.187	−.010	.309	−.257	1						
K	.211	−.686**	−.686**	.755**	−.295	−.559*	.292	−.571*	.171	.335	−.620*	−.431	−.540	1					
Alkalinity	.366	.249	.249	.072	−.267	−.209	−.105	.114	.894**	.075	−.223	−.185	−.003	.249	1				
TH	.139	.724**	.724**	−.440	.027	.237	−.186	.606*	.264	−.196	.483	.691**	−.022	−.464	.234	1			
MgH	.292	.557*	.557*	−.081	.171	.065	−.273	.350	.088	−.408	.028	.466	−.032	−.268	.187	.741**	1		
CaH	−.115	.463	.463	−.565*	−.148	.282	.023	.517	.296	.158	.689**	.515	.002	−.395	.143	.671*	.000	1	
MPN	−.022	.638*	.638*	−.669*	.258	.184	−.145	.700**	.194	−.270	.474	−.159	.768**		−.643*	.035	.081		
−.116	.249	1																	

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

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

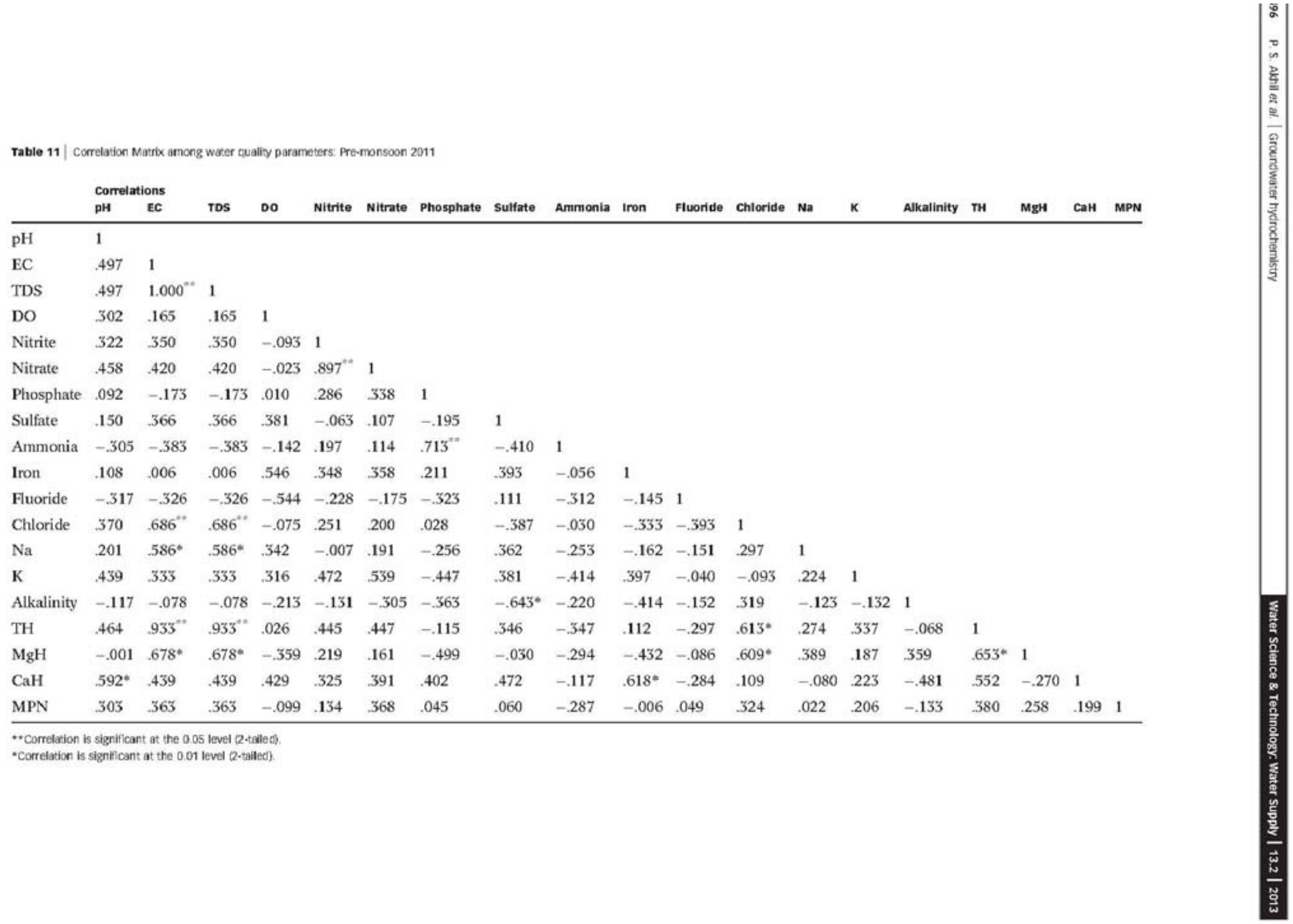
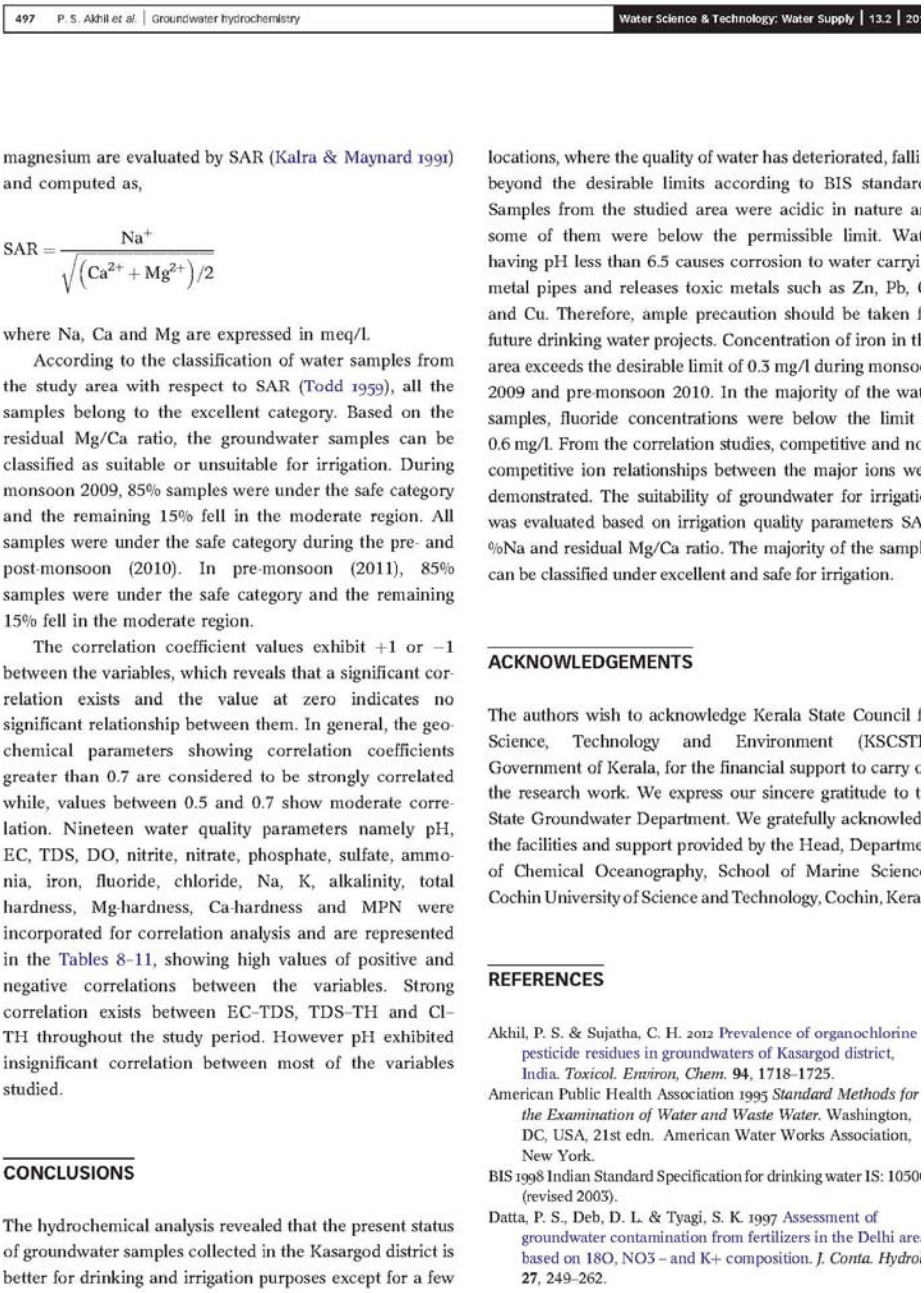


Table 11 | Correlation Matrix among water quality parameters: Pre-monsoon 2011

	Correlations																		
	pH	**EC**	**TDS**	**DO**	**Nitrite**	**Nitrate**	**Phosphate**	**Sulfate**	**Ammonia**	**Iron**	**Fluoride**	**Chloride**	**Na**	**K**	**Alkalinity**	**TH**	**MgH**	**CaH**	**MPN**
pH	1																		
EC	.497	1																	
TDS	.497	1.000**	1																
DO	.302	.165	.165	1															
Nitrite	.322	.350	.350	−.093	1														
Nitrate	.458	.420	.420	−.023	.897**	1													
Phosphate	.092	−.173	−.173	.010	.286	.338	1												
Sulfate	.150	.366	.366	.381	−.063	.107	−.195	1											
Ammonia	−.305	−.383	−.383	−.142	.197	.114	.713**	−.410	1										
Iron	.108	.006	.006	.546	.348	.358	.211	.393	−.056	1									
Fluoride	−.317	−.326	−.326	−.544	−.228	−.175	−.323	.111	−.312	−.145	1								
Chloride	.370	.686**	.686**	−.075	.251	.200	.028	−.387	−.030	−.333	−.393	1							
Na	.201	.586*	.586*	.342	−.007	.191	−.256	.362	−.253	−.162	−.151	.297	1						
K	.439	.333	.333	.316	.472	.539	−.447	.381	−.414	.397	−.040	−.093	.224	1					
Alkalinity	−.117	−.078	−.078	−.213	−.131	−.305	−.363	−.643*	−.220	−.414	−.152	.319	−.123	−.132	1				
TH	.464	.933**	.933**	.026	.445	.447	−.115	.346	−.347	.112	−.297	.613*	.274	.337	−.068	1			
MgH	−.001	.678*	.678*	−.359	.219	.161	−.499	−.030	−.294	−.432	−.086	.609*	.389	.187	.359	.653*	1		
CaH	.592*	.439	.439	.429	.325	.391	.402	.472	−.117	.618*	−.284	.109	−.080	.223	−.481	.552	−.270	1	
MPN	.303	.363	.363	−.099	.134	.368	.045	.060	−.287	−.006	.049	.324	.022	.206	−.133	.380	.258	.199	1

**Correlation is significant at the 0.05 level (2-tailed).
*Correlation is significant at the 0.01 level (2-tailed).



magnesium are evaluated by SAR (Kalra & Maynard 1991) and computed as,

$$\mathrm{SAR} = \frac{\mathrm{Na}^{+}}{\sqrt{\left(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}\right)/2}}$$

where Na, Ca and Mg are expressed in meq/l.

According to the classification of water samples from the study area with respect to SAR (Todd 1959), all the samples belong to the excellent category. Based on the residual Mg/Ca ratio, the groundwater samples can be classified as suitable or unsuitable for irrigation. During monsoon 2009, 85% samples were under the safe category and the remaining 15% fell in the moderate region. All samples were under the safe category during the pre- and post-monsoon (2010). In pre-monsoon (2011), 85% samples were under the safe category and the remaining 15% fell in the moderate region.

The correlation coefficient values exhibit +1 or −1 between the variables, which reveals that a significant correlation exists and the value at zero indicates no significant relationship between them. In general, the geochemical parameters showing correlation coefficients greater than 0.7 are considered to be strongly correlated while, values between 0.5 and 0.7 show moderate correlation. Nineteen water quality parameters namely pH, EC, TDS, DO, nitrite, nitrate, phosphate, sulfate, ammonia, iron, fluoride, chloride, Na, K, alkalinity, total hardness, Mg-hardness, Ca-hardness and MPN were incorporated for correlation analysis and are represented in the Tables 8–11, showing high values of positive and negative correlations between the variables. Strong correlation exists between EC–TDS, TDS–TH and Cl–TH throughout the study period. However pH exhibited insignificant correlation between most of the variables studied.

CONCLUSIONS

The hydrochemical analysis revealed that the present status of groundwater samples collected in the Kasargod district is better for drinking and irrigation purposes except for a few locations, where the quality of water has deteriorated, falli beyond the desirable limits according to BIS standar Samples from the studied area were acidic in nature a some of them were below the permissible limit. Wa having pH less than 6.5 causes corrosion to water carryi metal pipes and releases toxic metals such as Zn, Pb, (and Cu. Therefore, ample precaution should be taken f future drinking water projects. Concentration of iron in th area exceeds the desirable limit of 0.3 mg/l during monso 2009 and pre-monsoon 2010. In the majority of the wa samples, fluoride concentrations were below the limit 0.6 mg/l. From the correlation studies, competitive and no competitive ion relationships between the major ions we demonstrated. The suitability of groundwater for irrigati was evaluated based on irrigation quality parameters SA %Na and residual Mg/Ca ratio. The majority of the sampl can be classified under excellent and safe for irrigation.

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Environmental Science

Research Article

Hydrogeochemical Quality Assessment of Ground Waters in Ernakulam District, Kerala, India

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Abstract: The present study paves the way to provide the first baseline data on chemical characteristics of ground water with respect to the hydro geo chemical facies highlighting the distribution trend in the levels of trace metal and prominent organochlorine, organophosphorus and commercially available pesticides which are used in the Ernakulam district. The district lies between North latitudes 9^0 42' and 10^0 18' and East longitudes 76^0 09' and 77^0 02', having a geographical area of 2408 sq km. Due to the inherent industrial pollution augmented in the district, an urgent need for conducting water quality monitoring studies is essential. Fifteen groundwater samples were examined and quantified for major ions, trace metals and pesticides during the period of September 2007 to May 2008. Out of the 15 observation stations (12 Open wells and 3 Bore wells) none of them were affected by the influence of pesticides as they are well protected groundwater structures. Concentration of Lead, Zinc, Cadmium and Arsenic were below the BIS permissible limits.

Keywords: Ernakulam district. Groundwater. Pesticides. Trace metals

INTRODUCTION

Water, the universal solvent has the ability to dissolve a wide range of materials, including soluble inorganic and organic constituents. Furthermore, it could carry a large amount of insoluble materials that are held in suspension and transport to a greater distance. Both the amounts and types of impurities found in natural water vary from place to place and time to time. Their hydro geochemical characteristics assess the quality of water for various purposes. The demand for ground water resource has increased tremendously despite the inadequate supply of surface water, an important drinking water source. In Asia alone about 1 billion people are directly dependent upon this as drinking water resource[1]. However, many groundwater exploitation schemes in developing countries are designed without due attention to quality issues. In recent years, in many parts of India especially in the arid and semi-arid regions, due to the vagaries of monsoon and scarcity of surface water, dependence on groundwater has increased enormous.

The World Health Organization (WHO) has repeatedly insisted that the single major factor adversely influencing the general health and life expectancy of a population in many developing countries is lack of ready access to clean drinking water[2]. Ground water contamination due to irrigation water quality and drinking water quality has been reported exclusively[3-12]. In order to understand the pollution trends and their impacts on an aquifer, it is therefore imperative to have knowledge on the natural baseline quality for assessment of environmental changes[13] for initiating appropriate management measures for sustainable development.

The present study initiates the assessment of ground water quality by analyzing the water characteristics from specific area in Ernakulam district. It is imperative to monitor the water quality of this district in view of the faster growth of urbanization on one side and salinity problem on the other side. Salinity problems exist and associate in the coastal sedimentary area due to intrusion from the Arabian Sea. Industrial pollution has contributed to the water quality deterioration by the untreated or partially treated effluent discharges from the factories or industries situated around Eloor, Alwaye, Ambalamugal etc in the district.

Agricultural activity using fertilizers and pesticides are the next major contributors. Furthermore, the water transport facilities affect the water quality of the open wells and around the river course area. Fish processing units also provide to a great extent for contaminating the water bodies and thereby changing the phreatic aquifer quality pattern. Based on the water quality pre requisites and the typical groundwater structures have leaded to select the study area. The spatial and temporal variations in the groundwater quality including heavy metals and pesticides in fifteen selected areas in this district were encountered.

Study Area: The study area, Ernakulam district lies between north latitudes 9^0 42’ and 10^0 18’ East longitudes 76^0 09’ and 77^0 02’ **(Figure 1)** is situated in the northern side of Kerala State bound by Trichur district on the north, Idukki on the East, Kottayam and Alleppy districts on the South and Lakshadweep sea on the West. Physiographically the District is divided into 3 main divisions. The coastal plains in the west with an area of 1126 Sq km and elevation less than 7.6 m above mean sea level. The midland region in the centre over an area of 1218 Sq km, with elevation ranging from 7.6 to 76 m above mean sea level. Hill ranges in the north east over a small area of 64 Sq km. Charnockite and gneisses of the archean age; laterite of the sub recent age; unconsolidated alluvium of recent formation with sand and clays form the main geological units in the district **(Figure 2)**.

Groundwater occurs under phreatic conditions in weathered and fractured crystalline rocks, laterites and unconsolidated coastal sediments. It originates to a semi-confined to confined conditions in the deep seated fractured aquifer in the crystalline and tertiary rocks. The weathered zone in the crystalline below water table acts as a good storage for groundwater. Based on the morphological and physico-chemical properties, the soils of the district have been classified as lateritic, hydromorphic saline, brown hydromorphic, riverine alluvium, and coastal alluvium **(Figure 3)**.

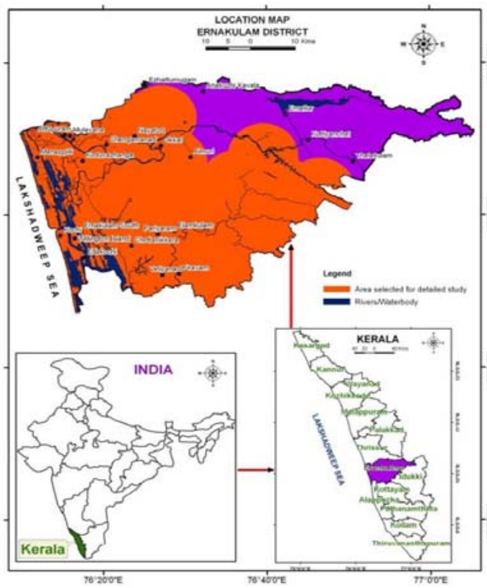
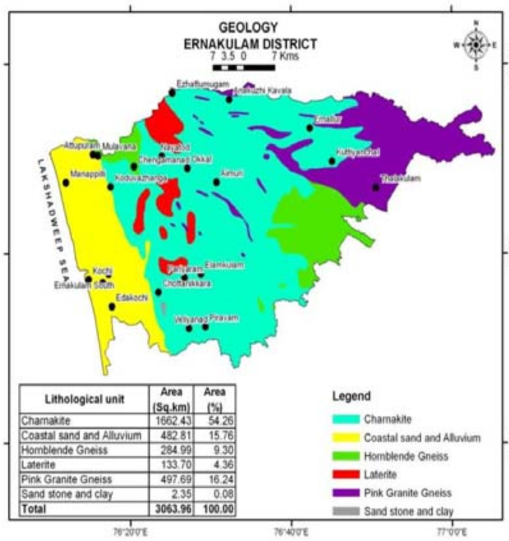
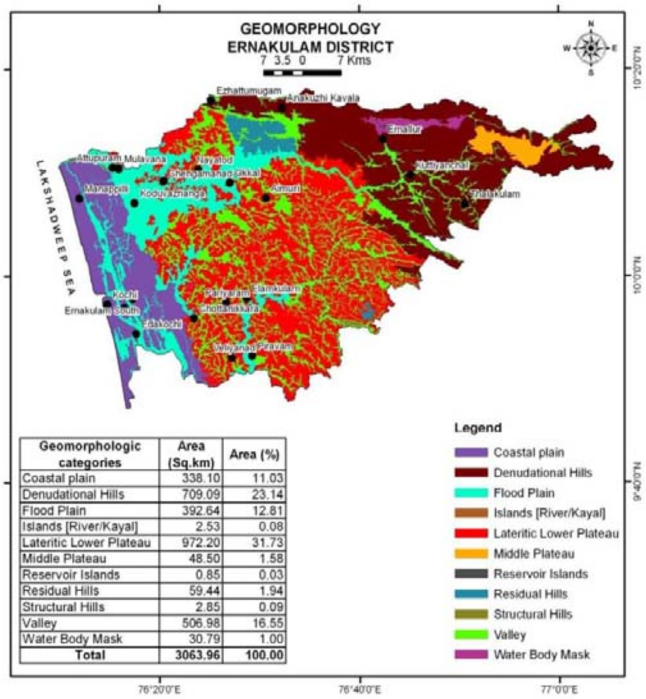


Fig.1: Study Area - Ernakulam District



Lithological unit	Area (Sq.km)	Area (%)
Charnakite	1662.43	54.26
Coastal sand and Alluvium	482.81	15.76
Hornblende Gneiss	284.99	9.30
Laterite	133.70	4.36
Pink Granite Gneiss	497.69	16.24
Sand stone and clay	2.35	0.08
Total	**3063.96**	**100.00**

Fig. 2: Geological map of Ernakulam District



Geomorphologic categories	Area (Sq.km)	Area (%)
Coastal plain	338.10	11.03
Denudational Hills	709.09	23.14
Flood Plain	392.64	12.81
Islands [River/Kayal]	2.53	0.08
Lateritic Lower Plateau	972.20	31.73
Middle Plateau	48.50	1.58
Reservoir Islands	0.85	0.03
Residual Hills	59.44	1.94
Structural Hills	2.85	0.09
Valley	506.98	16.55
Water Body Mask	30.79	1.00
Total	**3063.96**	**100.00**

Fig.3: Map showing geomorphic units of the study area.

TMPOW-01: This sampling station is situated in the District Agriculture Farm (DAF), Neryamangalam of Kothamangalam Taluk and gets the maximum rainfall in Kerala. The Farm covers an area of approximately 300 Acres. The well is located at the valley portion, about 100m towards 45°W of the farm. River Periyar flows 150 meters away from the site. The area is provided with thick vegetation mainly areca nut and the farm is using various kinds of pesticides and the area is potentially recharging one with a possibility of pesticide contamination and the effect of the flowing water canal near to the well makes it diluted.

TMPOW-02: This observation well is placed 30m south of Coconut Development Board (CDB), Neryamangalam and is located on a slope beside the valley portion in the laterite formation. It is a pumping open well which is exclusively used for drinking and domestic purpose. The water is slightly acidic. The planting material available in the farm is only coconut seedlings and is under the privilege of severe pesticide usage.

TMPOW-03: It is an open well; water yielding formation is laterite and is available only during rainy season. Hence a bore well is drilled inside the open well and throughout the year no scarcity of water was found **(Figure 4).** During rainy season water is clear but in summer season an oily layer appears on the surface.

Fig.4: Dug cum Bore well

TMPBW-04: This pumping bore well is exclusively used for drinking and domestic purpose. The water yielding formation is charnockite. The bore well is drilled, piercing the fractured zone in the charnockite and is acquiring sufficient quantity of water, but having H_2S smell during pre and post monsoon periods facing with a little water quality problem.

TMPOW-05: It is an open well in which a bore well of 45 m depth is drilled. Previously there was no sufficient water, both in the open well and in the bore well. Afterwards construction of canal at a distance of 10 m from the well at a higher elevation contributed the open well charged with sufficient good quality water.

TMPOW-06: The well is located in the laterite formation which becomes highly saturated during monsoon due to the good permeability of soil structure. Water table goes down during summer season may be due to the high slope of the location.

TMPOW-07: Topsoil is covering the laterite followed by soft clay content in this site. The water is acidic in nature and water table is in the low level.

TMPOW-08: This well is located near the industrial hub inside the Binanipuram Hospital Compound, Edayar. This open well is deep and was constructed at charnockite formation. There is a fine textured clay layer with yellow colour which occurs at 6 m thickness. With regards to the reduced permeability of the clay layer, the water level fluctuation is very less in this well.

TMPOW-09: The well is located very near to a paddy field. An irrigation canal passes through the location at a distance of 7 m. The well was chosen owing to the presence of agriculture land with frequent fertilizer application.

TMPBW-10: The bore well is having a depth of 54 m below the ground level and it is in the middle of a paddy field owned by the District Seed Farm, Okkal. The water table is only 0.6 m below ground, whereas the water level in the bore well was below 2 m. It is a typical bore well unaffected by the surface water around, hence chosen for the study.

TMPOW-11: This is a large diameter open well located in the Medicinal and Aromatic Plant Research Station at Odakkali, Assamannoor **(Figure 5).** Before the construction of subsurface dyke, the open well showed significantly low water level. The well was chosen due to the presence of a sub-surface dyke of 20 m length and 6-8 m depth provided with separate piezometers in the upstream and downstream of the dyke to assess the leakage if any, from the subsurface dyke. The sub-surface dyke is acting as a barrier to the run off of groundwater between the layers of laterite and the bed rock. This is a typical water conservation structure to have sustainable water in the well.

Fig.5: Sampling station TMPOW-11

TMPBW-12: This observation station is a bore well (5 m) situated very near to the sampling station **TMPOW-11**. The influence of the sub-surface dyke makes the bore well overflow during the rainy seasons. The water level in this well is high during all seasons.

TMPOW-13: The water yielding formation is sand which act as a good aquifer and hence the water table is at a raised level just below the parapet. Two sides of the well are surrounded by lake. The well was selected due to the presence of surface water body, and it is an ideal potential aquifer.

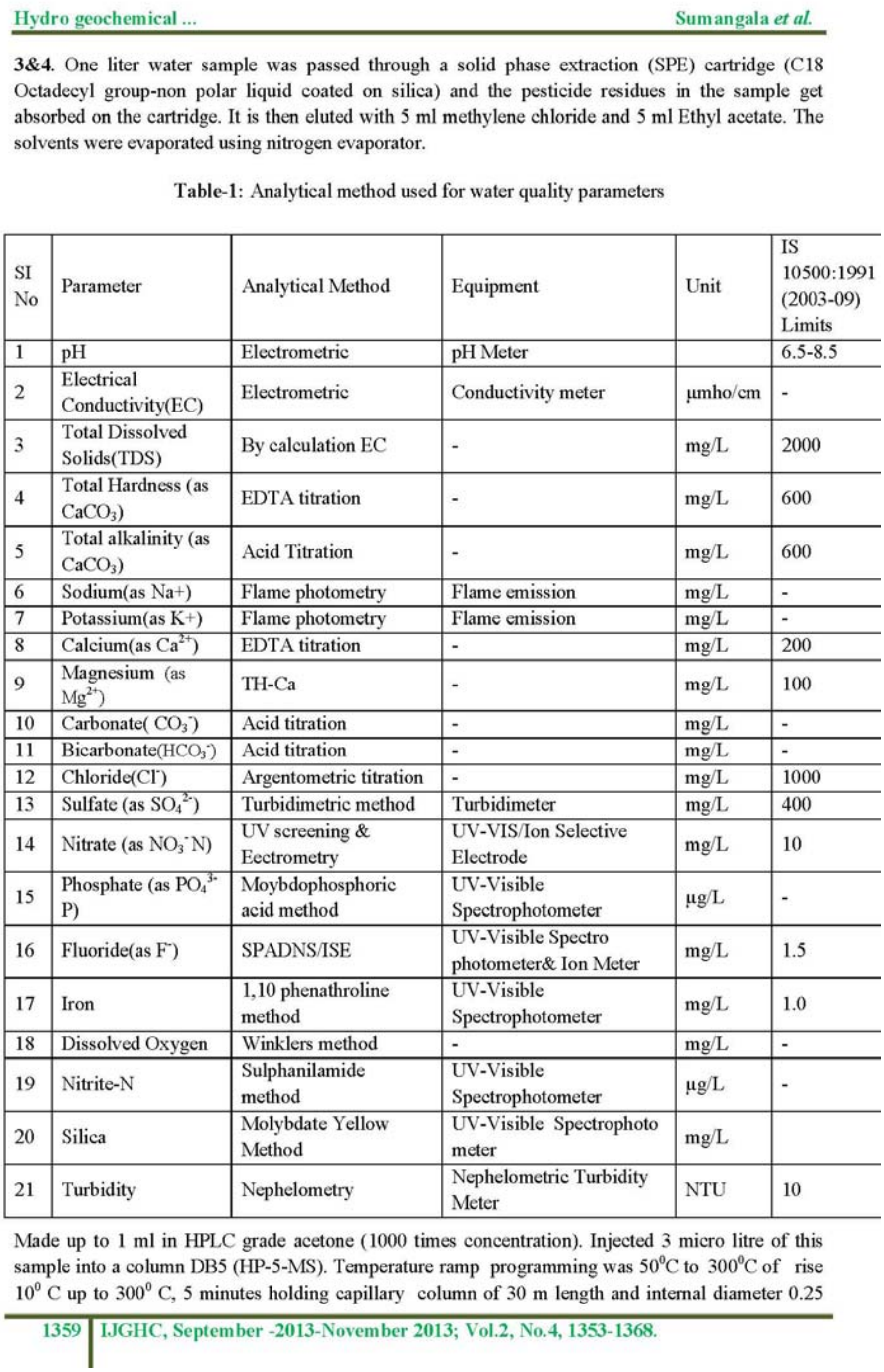
TMPOW-14: This open well is located in the sedimentary area nearer to the westerly flowing sea, the Arabian Sea. Water table is at a raised condition. The seaward coastal effects contribute the water quality problem.

TMPOW-15: This well is located in the sedimentary area. The water table is at a raised condition and water quality problem exists due to the influence of coastal inputs.

MATERIALS AND METHODS

pH, Electrical Conductivity and Total Dissolved Solids(TDS) of ground water samples were measured immediately from the sampling site. All the samples were collected in polyethylene bottles and stored at 4^0C, major anions and cations were analyzed using the standard methods as suggested by the American Public Health Association (1995) **(Table.1)** . Triplicate analyses of each sample were performed and average values were reported.

Pesticide analyses for water samples were conducted using AGILANT make GC-MS 6890-5975 and the method followed was 525.5 solid phase extraction. These analyses were classified under 3 parent groups such as: Organo chlorine pesticides (30 No's), Organo phosphorus pesticides (35 No's), and other miscellaneous pesticides which are used commercially (30 No's) are described in the **Tables 2,**

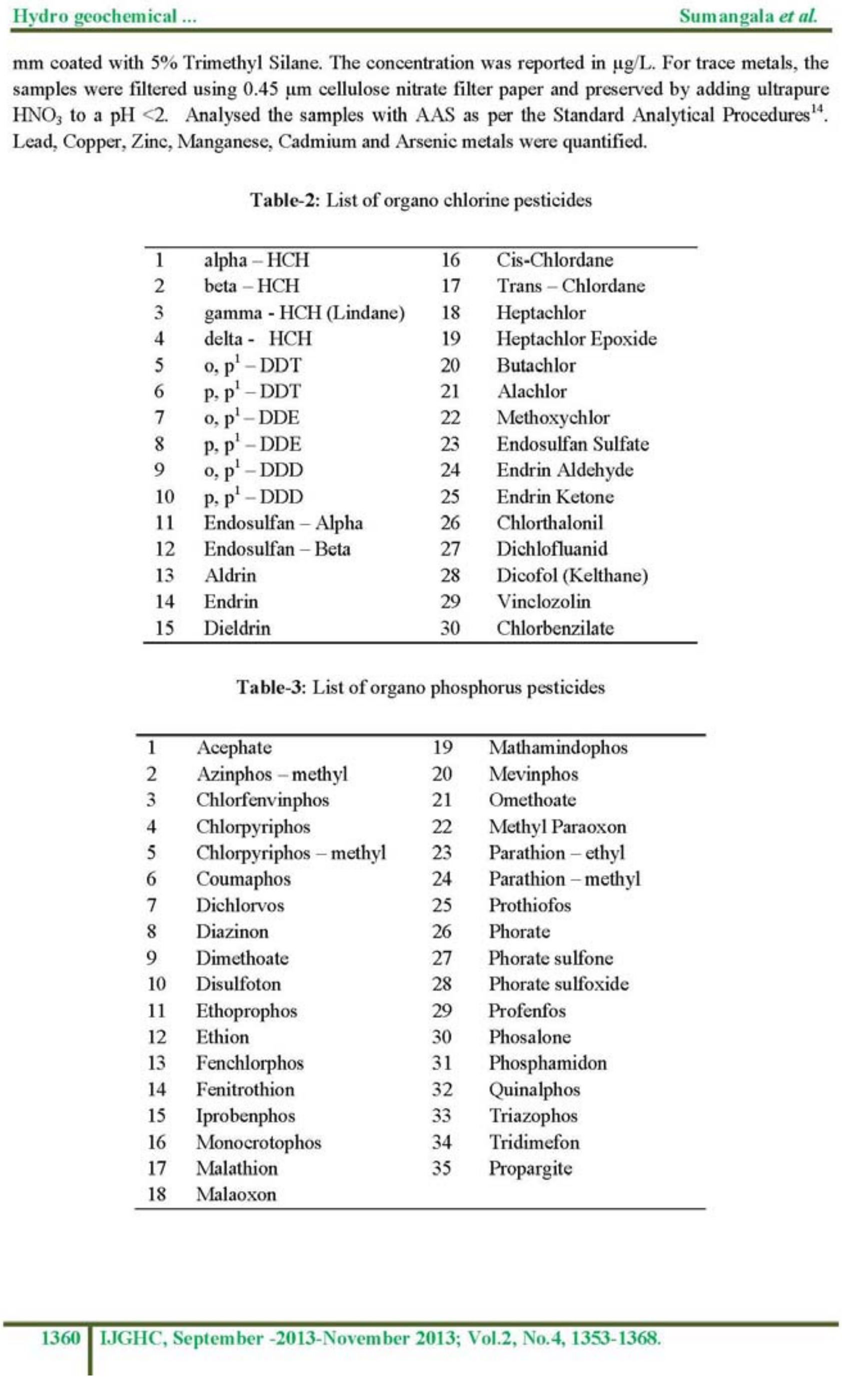


3&4. One liter water sample was passed through a solid phase extraction (SPE) cartridge (C18 Octadecyl group-non polar liquid coated on silica) and the pesticide residues in the sample get absorbed on the cartridge. It is then eluted with 5 ml methylene chloride and 5 ml Ethyl acetate. The solvents were evaporated using nitrogen evaporator.

Table-1: Analytical method used for water quality parameters

SI No	Parameter	Analytical Method	Equipment	Unit	IS 10500:1991 (2003-09) Limits
1	pH	Electrometric	pH Meter		6.5-8.5
2	Electrical Conductivity(EC)	Electrometric	Conductivity meter	µmho/cm	-
3	Total Dissolved Solids(TDS)	By calculation EC	-	mg/L	2000
4	Total Hardness (as $CaCO_3$)	EDTA titration	-	mg/L	600
5	Total alkalinity (as $CaCO_3$)	Acid Titration	-	mg/L	600
6	Sodium(as Na+)	Flame photometry	Flame emission	mg/L	-
7	Potassium(as K+)	Flame photometry	Flame emission	mg/L	-
8	Calcium(as Ca^{2+})	EDTA titration	-	mg/L	200
9	Magnesium (as Mg^{2+})	TH-Ca	-	mg/L	100
10	Carbonate(CO_3^-)	Acid titration	-	mg/L	-
11	Bicarbonate(HCO_3^-)	Acid titration	-	mg/L	-
12	Chloride(Cl^-)	Argentometric titration	-	mg/L	1000
13	Sulfate (as SO_4^{2-})	Turbidimetric method	Turbidimeter	mg/L	400
14	Nitrate (as NO_3^-N)	UV screening & Eectrometry	UV-VIS/Ion Selective Electrode	mg/L	10
15	Phosphate (as PO_4^{3-} P)	Moybdophosphoric acid method	UV-Visible Spectrophotometer	µg/L	-
16	Fluoride(as F^-)	SPADNS/ISE	UV-Visible Spectro photometer& Ion Meter	mg/L	1.5
17	Iron	1,10 phenathroline method	UV-Visible Spectrophotometer	mg/L	1.0
18	Dissolved Oxygen	Winklers method	-	mg/L	-
19	Nitrite-N	Sulphanilamide method	UV-Visible Spectrophotometer	µg/L	-
20	Silica	Molybdate Yellow Method	UV-Visible Spectrophoto meter	mg/L	
21	Turbidity	Nephelometry	Nephelometric Turbidity Meter	NTU	10

Made up to 1 ml in HPLC grade acetone (1000 times concentration). Injected 3 micro litre of this sample into a column DB5 (HP-5-MS). Temperature ramp programming was 50^0C to 300^0C of rise 10^0 C up to 300^0 C, 5 minutes holding capillary column of 30 m length and internal diameter 0.25



mm coated with 5% Trimethyl Silane. The concentration was reported in µg/L. For trace metals, the samples were filtered using 0.45 µm cellulose nitrate filter paper and preserved by adding ultrapure HNO_3 to a pH <2. Analysed the samples with AAS as per the Standard Analytical Procedures[14]. Lead, Copper, Zinc, Manganese, Cadmium and Arsenic metals were quantified.

Table-2: List of organo chlorine pesticides

1	alpha – HCH	16	Cis-Chlordane
2	beta – HCH	17	Trans – Chlordane
3	gamma - HCH (Lindane)	18	Heptachlor
4	delta - HCH	19	Heptachlor Epoxide
5	o, p^1 – DDT	20	Butachlor
6	p, p^1 – DDT	21	Alachlor
7	o, p^1 – DDE	22	Methoxychlor
8	p, p^1 – DDE	23	Endosulfan Sulfate
9	o, p^1 – DDD	24	Endrin Aldehyde
10	p, p^1 – DDD	25	Endrin Ketone
11	Endosulfan – Alpha	26	Chlorthalonil
12	Endosulfan – Beta	27	Dichlofluanid
13	Aldrin	28	Dicofol (Kelthane)
14	Endrin	29	Vinclozolin
15	Dieldrin	30	Chlorbenzilate

Table-3: List of organo phosphorus pesticides

1	Acephate	19	Mathamindophos
2	Azinphos – methyl	20	Mevinphos
3	Chlorfenvinphos	21	Omethoate
4	Chlorpyriphos	22	Methyl Paraoxon
5	Chlorpyriphos – methyl	23	Parathion – ethyl
6	Coumaphos	24	Parathion – methyl
7	Dichlorvos	25	Prothiofos
8	Diazinon	26	Phorate
9	Dimethoate	27	Phorate sulfone
10	Disulfoton	28	Phorate sulfoxide
11	Ethoprophos	29	Profenfos
12	Ethion	30	Phosalone
13	Fenchlorphos	31	Phosphamidon
14	Fenitrothion	32	Quinalphos
15	Iprobenphos	33	Triazophos
16	Monocrotophos	34	Tridimefon
17	Malathion	35	Propargite
18	Malaoxon		

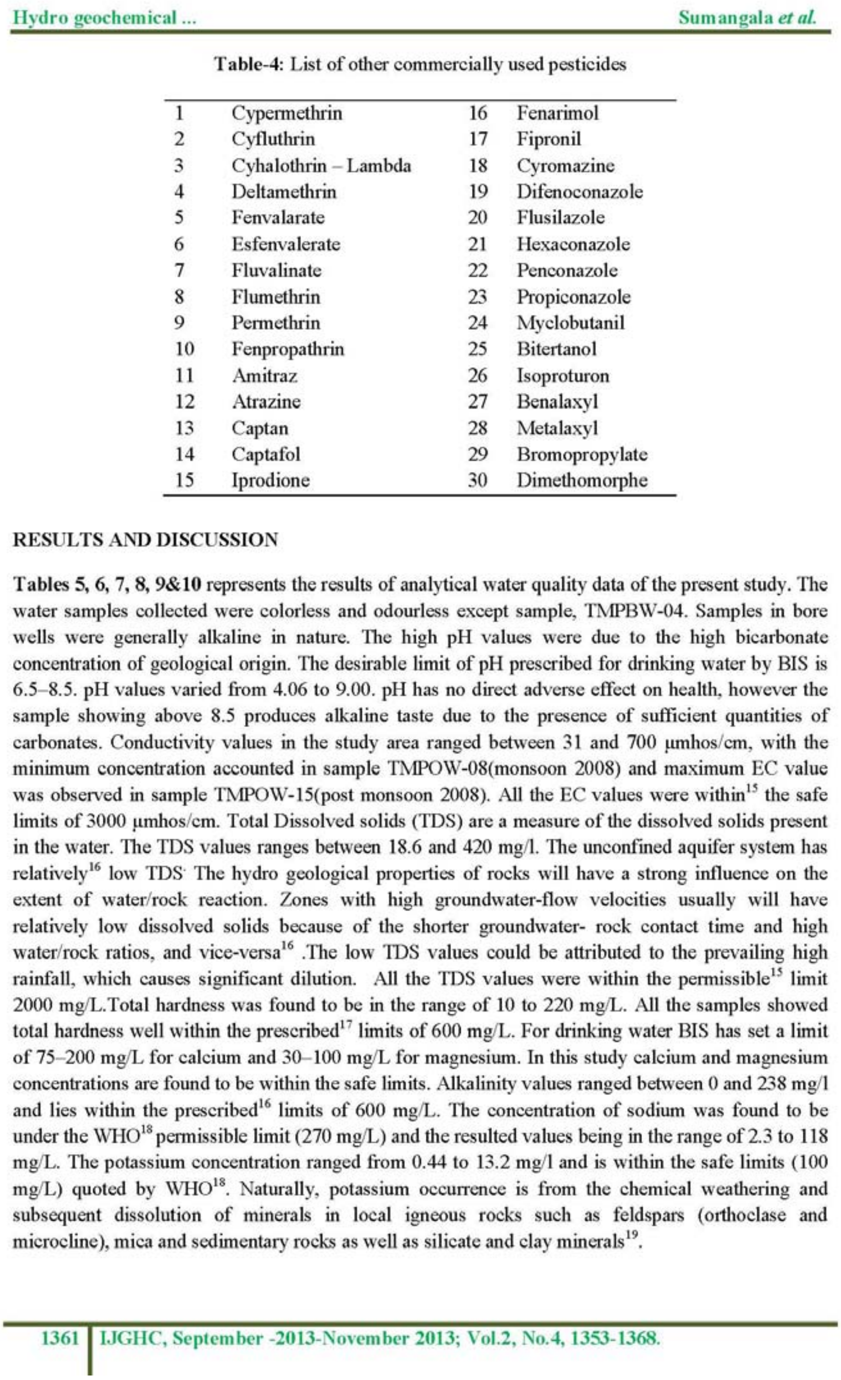


Table-4: List of other commercially used pesticides

1	Cypermethrin	16	Fenarimol
2	Cyfluthrin	17	Fipronil
3	Cyhalothrin – Lambda	18	Cyromazine
4	Deltamethrin	19	Difenoconazole
5	Fenvalarate	20	Flusilazole
6	Esfenvalerate	21	Hexaconazole
7	Fluvalinate	22	Penconazole
8	Flumethrin	23	Propiconazole
9	Permethrin	24	Myclobutanil
10	Fenpropathrin	25	Bitertanol
11	Amitraz	26	Isoproturon
12	Atrazine	27	Benalaxyl
13	Captan	28	Metalaxyl
14	Captafol	29	Bromopropylate
15	Iprodione	30	Dimethomorphe

RESULTS AND DISCUSSION

Tables 5, 6, 7, 8, 9&10 represents the results of analytical water quality data of the present study. The water samples collected were colorless and odourless except sample, TMPBW-04. Samples in bore wells were generally alkaline in nature. The high pH values were due to the high bicarbonate concentration of geological origin. The desirable limit of pH prescribed for drinking water by BIS is 6.5–8.5. pH values varied from 4.06 to 9.00. pH has no direct adverse effect on health, however the sample showing above 8.5 produces alkaline taste due to the presence of sufficient quantities of carbonates. Conductivity values in the study area ranged between 31 and 700 µmhos/cm, with the minimum concentration accounted in sample TMPOW-08(monsoon 2008) and maximum EC value was observed in sample TMPOW-15(post monsoon 2008). All the EC values were within[15] the safe limits of 3000 µmhos/cm. Total Dissolved solids (TDS) are a measure of the dissolved solids present in the water. The TDS values ranges between 18.6 and 420 mg/l. The unconfined aquifer system has relatively[16] low TDS. The hydro geological properties of rocks will have a strong influence on the extent of water/rock reaction. Zones with high groundwater-flow velocities usually will have relatively low dissolved solids because of the shorter groundwater- rock contact time and high water/rock ratios, and vice-versa[16] .The low TDS values could be attributed to the prevailing high rainfall, which causes significant dilution. All the TDS values were within the permissible[15] limit 2000 mg/L.Total hardness was found to be in the range of 10 to 220 mg/L. All the samples showed total hardness well within the prescribed[17] limits of 600 mg/L. For drinking water BIS has set a limit of 75–200 mg/L for calcium and 30–100 mg/L for magnesium. In this study calcium and magnesium concentrations are found to be within the safe limits. Alkalinity values ranged between 0 and 238 mg/l and lies within the prescribed[16] limits of 600 mg/L. The concentration of sodium was found to be under the WHO[18] permissible limit (270 mg/L) and the resulted values being in the range of 2.3 to 118 mg/L. The potassium concentration ranged from 0.44 to 13.2 mg/l and is within the safe limits (100 mg/L) quoted by WHO[18]. Naturally, potassium occurrence is from the chemical weathering and subsequent dissolution of minerals in local igneous rocks such as feldspars (orthoclase and microcline), mica and sedimentary rocks as well as silicate and clay minerals[19].

Table-5: Physical and chemical characteristics of groundwater samples in Ernakulam District during Monsoon 2007

Sl. No	well No	Type of Well	pH	EC, nicromhos /cm	TDS, mg/L	TH(as mg $CaCO_3$/L)	Ca, mg/L	Mg, mg/L	Na, mg/L	K, mg/L	TA(as mg $CaCO_3$/L)	CO_3, mg/L	HCO_3, mg/L	Cl, mg/L	SO4, mg/L	NO_3-N, mg/L	NO_3, mg/L	NO_2, ppb	PO_4, ppb	F ,mg/L	SiO_2 ,mg/L	DO, mg/L	Fe, mg/L
Desirable limit (BIS)			**6.5-8.5**	---	**500**	**300**	**75**	**30**	---	---	**200**	---	---	**250**	**200**	**10**	**45.00**	**30**		**1**			**0.3**
Permissible limit (BIS)			**6.5-8.5**	---	**2000**	**600**	**200**	**100**	---	---	**600**	---	---	**1000**	**400**					**1.5**			**1**
1	TMPOW-01	OW	6.91	58	34.8	10	4	0	5.8	1.85	8	0	9.8	9.8	1	1.7	7.53	1.56	0.14	0.23	2.89	2.1	ND
2	TMPOW-02	OW	5.37	41	24.6	10	2	1.2	3	1	4	0	4.9	5	1	3.3	14.61	2.5	0.09	0.01	2.6	3.22	0.0035
3	TMPOW-03	OW	7	114	68.4	34	5.6	4.9	6.8	2.3	16	0	14.6	12.7	4.17	4.9	21.70	2.19	3.01	0	4.96	5.04	0.0473
4	TMPBW-04	BW	6.81	111	66.6	30	8	2.4	7.3	6	14	0	17.1	14.7	3.54	4.6	20.37	25.48	0.222	0.27	4.55		0.3
5	TMPOW-05	OW	7.19	54	32.4	15	4	1.2	4.8	1.2	14	0	17.1	7.8	2.29	0	0.00	0	0.1	0.03	5.82	0.56	0.1986
6	TMPOW-06	OW	7.4	84	50.4	30	10	1.2	3.9	1.49	34	0	41.5	7.8	3.8	0	0.00	2	0	ND	6.4	4.48	0.689
7	TMPOW-07	OW	5.53	59	35.4	10	2	1.2	4.4	1.23	4	0	4.9	5.9	1.25	1.8	7.97	2.5	0.32	0	2.15	3.36	0.021
8	TMPOW-08	OW	4.76	31	30.4	10	2	1.2	1.64	0.8	4	0	4.9	6.9	1.04	1.5	6.64	1.47	0	0.14	2.4	3.64	0.1
9	TMPOW-09	OW	6.08	50	36	20	4	2.4	3.2	1.84	16	0	19.5	7.8	1.46	0.3	1.33	2.19	5.53	0.2	5.12		0.089
10	TMPBW-10	BW	8.3	320	192	125	32	11.1	24.4	3.9	154	4.8	178	13.7	4.58	0	0.00	4.06	1.09	0.37	31.72		0.744
11	TMPOW-11	OW	5.7	49	29.4	15	2	2.4	2.7	0.48	14	0	17.1	6.9	0.83	0	0.00	1.56	0.41	0	6.52	1.96	0.039
12	TMPBW-12	BW	8.85	420	252	15	4	1.2	118	1.25	232	4.8	273.3	3.9	1.25	0	0.00	0.94	0.51	0.43	28.19		0.019
13	TMPOW-13	OW	8.53	370	222	180	64	4.9	12.2	5.7	174	9.6	192.8	15.7	11.46	0	0.00	2.35	7.91	0.2	9.02	3.5	0.147
14	TMPOW-14	OW	8.7	330	198	170	58	6.1	6.8	2.4	158	7.2	178.1	13.7	7.64	0	0.00	7.31	0.54	0.28	6.64	2.38	0.192
15	TMPOW-15	OW	8.23	500	300	220	64	14.6	19.8	5.5	196	0	239.1	23.5	33.37	0	0.00	16.06	3.09	0.22	10.33	7	0.259

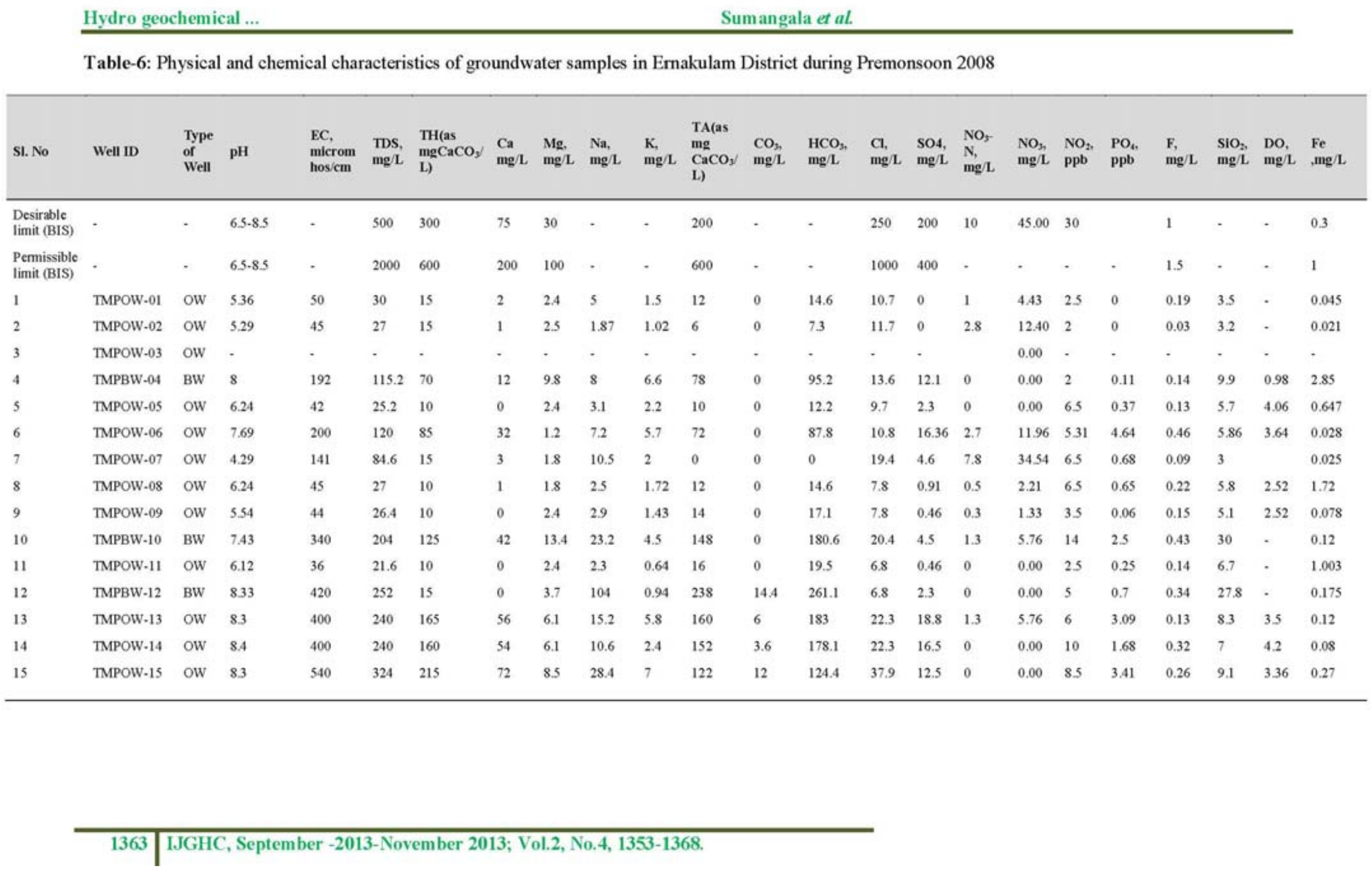


Table-6: Physical and chemical characteristics of groundwater samples in Ernakulam District during Premonsoon 2008

Sl. No	Well ID	Type of Well	pH	EC, microm hos/cm	TDS, mg/L	TH(as mgCaCO$_3$/ L)	Ca mg/L	Mg, mg/L	Na, mg/L	K, mg/L	TA(as mg CaCO$_3$/ L)	CO$_3$, mg/L	HCO$_3$, mg/L	Cl, mg/L	SO4, mg/L	NO$_3$-N, mg/L	NO$_3$, mg/L	NO$_2$, ppb	PO$_4$, ppb	F, mg/L	SiO$_2$, mg/L	DO, mg/L	Fe ,mg/L
Desirable limit (BIS)	-	-	6.5-8.5	-	500	300	75	30	-	-	200	-	-	250	200	10	45.00	30		1	-	-	0.3
Permissible limit (BIS)	-	-	6.5-8.5	-	2000	600	200	100	-	-	600	-	-	1000	400	-	-	-	-	1.5	-	-	1
1	TMPOW-01	OW	5.36	50	30	15	2	2.4	5	1.5	12	0	14.6	10.7	0	1	4.43	2.5	0	0.19	3.5	-	0.045
2	TMPOW-02	OW	5.29	45	27	15	1	2.5	1.87	1.02	6	0	7.3	11.7	0	2.8	12.40	2	0	0.03	3.2	-	0.021
3	TMPOW-03	OW	-	-	-	-	-	-	-	-	-	-	-	-	-		0.00	-	-	-	-	-	-
4	TMPBW-04	BW	8	192	115.2	70	12	9.8	8	6.6	78	0	95.2	13.6	12.1	0	0.00	2	0.11	0.14	9.9	0.98	2.85
5	TMPOW-05	OW	6.24	42	25.2	10	0	2.4	3.1	2.2	10	0	12.2	9.7	2.3	0	0.00	6.5	0.37	0.13	5.7	4.06	0.647
6	TMPOW-06	OW	7.69	200	120	85	32	1.2	7.2	5.7	72	0	87.8	10.8	16.36	2.7	11.96	5.31	4.64	0.46	5.86	3.64	0.028
7	TMPOW-07	OW	4.29	141	84.6	15	3	1.8	10.5	2	0	0	0	19.4	4.6	7.8	34.54	6.5	0.68	0.09	3		0.025
8	TMPOW-08	OW	6.24	45	27	10	1	1.8	2.5	1.72	12	0	14.6	7.8	0.91	0.5	2.21	6.5	0.65	0.22	5.8	2.52	1.72
9	TMPOW-09	OW	5.54	44	26.4	10	0	2.4	2.9	1.43	14	0	17.1	7.8	0.46	0.3	1.33	3.5	0.06	0.15	5.1	2.52	0.078
10	TMPBW-10	BW	7.43	340	204	125	42	13.4	23.2	4.5	148	0	180.6	20.4	4.5	1.3	5.76	14	2.5	0.43	30	-	0.12
11	TMPOW-11	OW	6.12	36	21.6	10	0	2.4	2.3	0.64	16	0	19.5	6.8	0.46	0	0.00	2.5	0.25	0.14	6.7	-	1.003
12	TMPBW-12	BW	8.33	420	252	15	0	3.7	104	0.94	238	14.4	261.1	6.8	2.3	0	0.00	5	0.7	0.34	27.8	-	0.175
13	TMPOW-13	OW	8.3	400	240	165	56	6.1	15.2	5.8	160	6	183	22.3	18.8	1.3	5.76	6	3.09	0.13	8.3	3.5	0.12
14	TMPOW-14	OW	8.4	400	240	160	54	6.1	10.6	2.4	152	3.6	178.1	22.3	16.5	0	0.00	10	1.68	0.32	7	4.2	0.08
15	TMPOW-15	OW	8.3	540	324	215	72	8.5	28.4	7	122	12	124.4	37.9	12.5	0	0.00	8.5	3.41	0.26	9.1	3.36	0.27

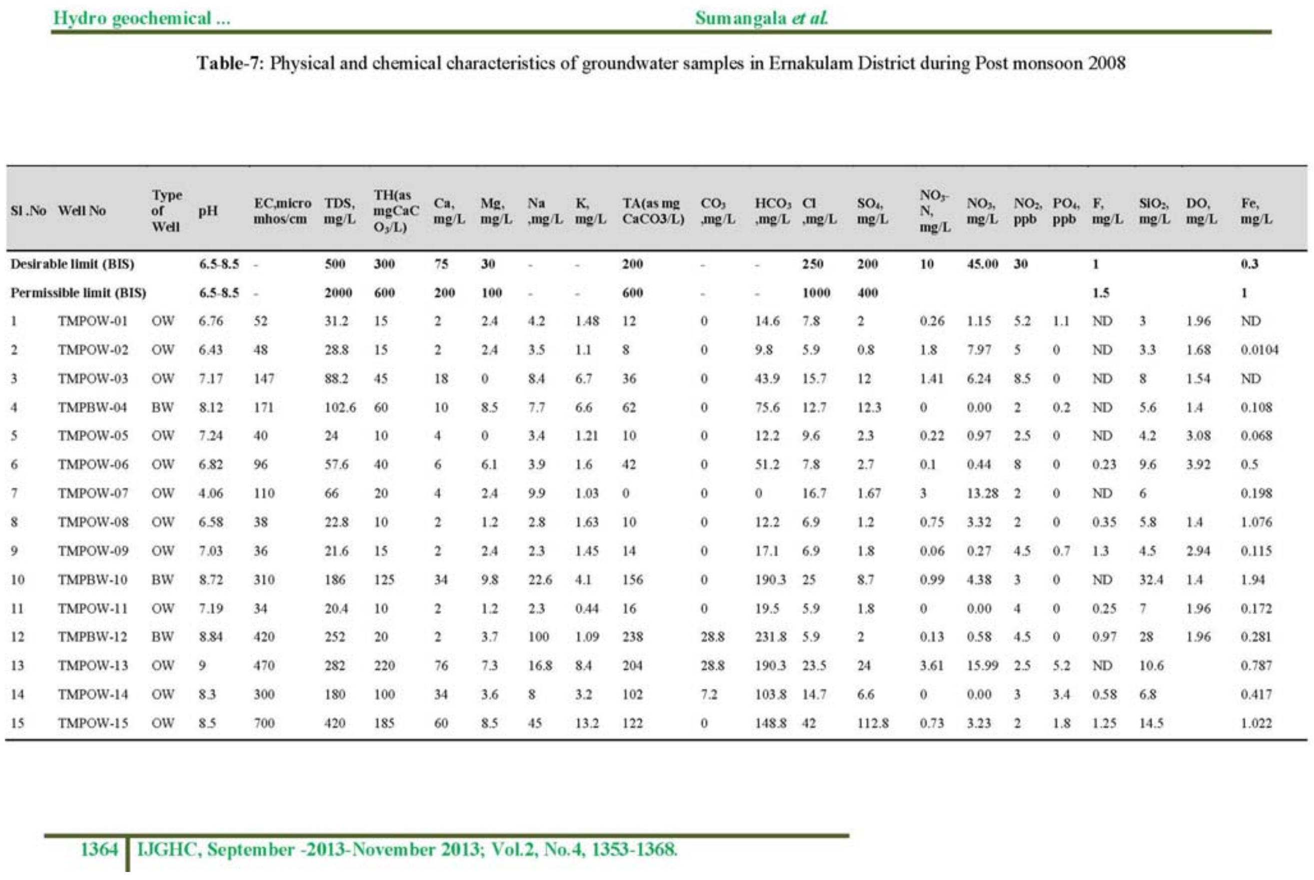


Table-7: Physical and chemical characteristics of groundwater samples in Ernakulam District during Post monsoon 2008

Sl .No	Well No	Type of Well	pH	EC,micro mhos/cm	TDS, mg/L	TH(as mgCaCO_3/L)	Ca, mg/L	Mg, mg/L	Na ,mg/L	K, mg/L	TA(as mg CaCO3/L)	CO_3 ,mg/L	HCO_3 ,mg/L	Cl ,mg/L	SO_4, mg/L	NO_3-N, mg/L	NO_3, mg/L	NO_2, ppb	PO_4, ppb	F, mg/L	SiO_2, mg/L	DO, mg/L	Fe, mg/L
Desirable limit (BIS)			**6.5-8.5**	-	**500**	**300**	**75**	**30**	-	-	**200**	-	-	**250**	**200**	**10**	**45.00**	**30**		**1**			**0.3**
Permissible limit (BIS)			**6.5-8.5**	-	**2000**	**600**	**200**	**100**	-	-	**600**	-	-	**1000**	**400**					**1.5**			**1**
1	TMPOW-01	OW	6.76	52	31.2	15	2	2.4	4.2	1.48	12	0	14.6	7.8	2	0.26	1.15	5.2	1.1	ND	3	1.96	ND
2	TMPOW-02	OW	6.43	48	28.8	15	2	2.4	3.5	1.1	8	0	9.8	5.9	0.8	1.8	7.97	5	0	ND	3.3	1.68	0.0104
3	TMPOW-03	OW	7.17	147	88.2	45	18	0	8.4	6.7	36	0	43.9	15.7	12	1.41	6.24	8.5	0	ND	8	1.54	ND
4	TMPBW-04	BW	8.12	171	102.6	60	10	8.5	7.7	6.6	62	0	75.6	12.7	12.3	0	0.00	2	0.2	ND	5.6	1.4	0.108
5	TMPOW-05	OW	7.24	40	24	10	4	0	3.4	1.21	10	0	12.2	9.6	2.3	0.22	0.97	2.5	0	ND	4.2	3.08	0.068
6	TMPOW-06	OW	6.82	96	57.6	40	6	6.1	3.9	1.6	42	0	51.2	7.8	2.7	0.1	0.44	8	0	0.23	9.6	3.92	0.5
7	TMPOW-07	OW	4.06	110	66	20	4	2.4	9.9	1.03	0	0	0	16.7	1.67	3	13.28	2	0	ND	6		0.198
8	TMPOW-08	OW	6.58	38	22.8	10	2	1.2	2.8	1.63	10	0	12.2	6.9	1.2	0.75	3.32	2	0	0.35	5.8	1.4	1.076
9	TMPOW-09	OW	7.03	36	21.6	15	2	2.4	2.3	1.45	14	0	17.1	6.9	1.8	0.06	0.27	4.5	0.7	1.3	4.5	2.94	0.115
10	TMPBW-10	BW	8.72	310	186	125	34	9.8	22.6	4.1	156	0	190.3	25	8.7	0.99	4.38	3	0	ND	32.4	1.4	1.94
11	TMPOW-11	OW	7.19	34	20.4	10	2	1.2	2.3	0.44	16	0	19.5	5.9	1.8	0	0.00	4	0	0.25	7	1.96	0.172
12	TMPBW-12	BW	8.84	420	252	20	2	3.7	100	1.09	238	28.8	231.8	5.9	2	0.13	0.58	4.5	0	0.97	28	1.96	0.281
13	TMPOW-13	OW	9	470	282	220	76	7.3	16.8	8.4	204	28.8	190.3	23.5	24	3.61	15.99	2.5	5.2	ND	10.6		0.787
14	TMPOW-14	OW	8.3	300	180	100	34	3.6	8	3.2	102	7.2	103.8	14.7	6.6	0	0.00	3	3.4	0.58	6.8		0.417
15	TMPOW-15	OW	8.5	700	420	185	60	8.5	45	13.2	122	0	148.8	42	112.8	0.73	3.23	2	1.8	1.25	14.5		1.022

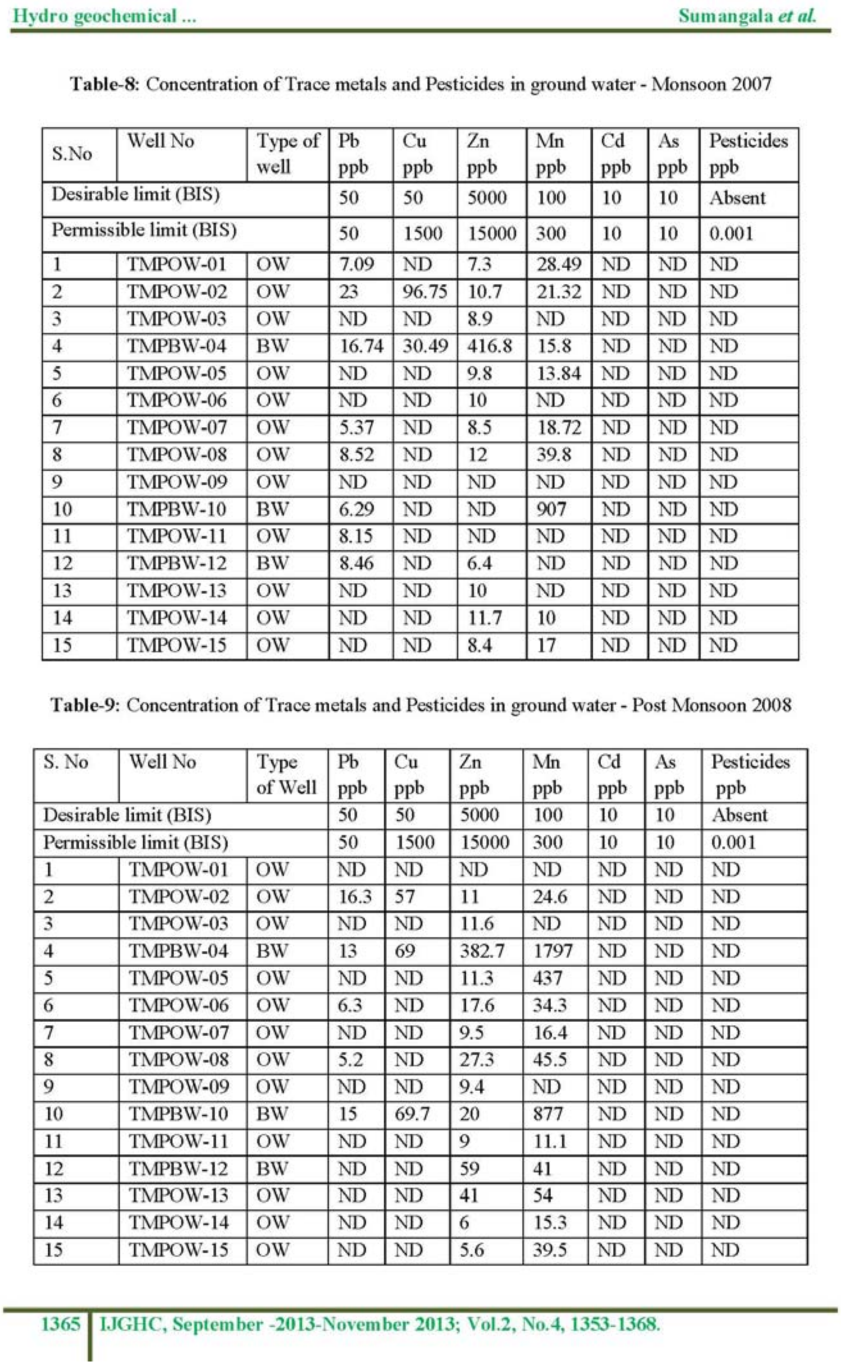


Table-8: Concentration of Trace metals and Pesticides in ground water - Monsoon 2007

S.No	Well No	Type of well	Pb ppb	Cu ppb	Zn ppb	Mn ppb	Cd ppb	As ppb	Pesticides ppb
Desirable limit (BIS)			50	50	5000	100	10	10	Absent
Permissible limit (BIS)			50	1500	15000	300	10	10	0.001
1	TMPOW-01	OW	7.09	ND	7.3	28.49	ND	ND	ND
2	TMPOW-02	OW	23	96.75	10.7	21.32	ND	ND	ND
3	TMPOW-03	OW	ND	ND	8.9	ND	ND	ND	ND
4	TMPBW-04	BW	16.74	30.49	416.8	15.8	ND	ND	ND
5	TMPOW-05	OW	ND	ND	9.8	13.84	ND	ND	ND
6	TMPOW-06	OW	ND	ND	10	ND	ND	ND	ND
7	TMPOW-07	OW	5.37	ND	8.5	18.72	ND	ND	ND
8	TMPOW-08	OW	8.52	ND	12	39.8	ND	ND	ND
9	TMPOW-09	OW	ND	ND	ND	ND	ND	ND	ND
10	TMPBW-10	BW	6.29	ND	ND	907	ND	ND	ND
11	TMPOW-11	OW	8.15	ND	ND	ND	ND	ND	ND
12	TMPBW-12	BW	8.46	ND	6.4	ND	ND	ND	ND
13	TMPOW-13	OW	ND	ND	10	ND	ND	ND	ND
14	TMPOW-14	OW	ND	ND	11.7	10	ND	ND	ND
15	TMPOW-15	OW	ND	ND	8.4	17	ND	ND	ND

Table-9: Concentration of Trace metals and Pesticides in ground water - Post Monsoon 2008

S. No	Well No	Type of Well	Pb ppb	Cu ppb	Zn ppb	Mn ppb	Cd ppb	As ppb	Pesticides ppb
Desirable limit (BIS)			50	50	5000	100	10	10	Absent
Permissible limit (BIS)			50	1500	15000	300	10	10	0.001
1	TMPOW-01	OW	ND	ND	ND	ND	ND	ND	ND
2	TMPOW-02	OW	16.3	57	11	24.6	ND	ND	ND
3	TMPOW-03	OW	ND	ND	11.6	ND	ND	ND	ND
4	TMPBW-04	BW	13	69	382.7	1797	ND	ND	ND
5	TMPOW-05	OW	ND	ND	11.3	437	ND	ND	ND
6	TMPOW-06	OW	6.3	ND	17.6	34.3	ND	ND	ND
7	TMPOW-07	OW	ND	ND	9.5	16.4	ND	ND	ND
8	TMPOW-08	OW	5.2	ND	27.3	45.5	ND	ND	ND
9	TMPOW-09	OW	ND	ND	9.4	ND	ND	ND	ND
10	TMPBW-10	BW	15	69.7	20	877	ND	ND	ND
11	TMPOW-11	OW	ND	ND	9	11.1	ND	ND	ND
12	TMPBW-12	BW	ND	ND	59	41	ND	ND	ND
13	TMPOW-13	OW	ND	ND	41	54	ND	ND	ND
14	TMPOW-14	OW	ND	ND	6	15.3	ND	ND	ND
15	TMPOW-15	OW	ND	ND	5.6	39.5	ND	ND	ND

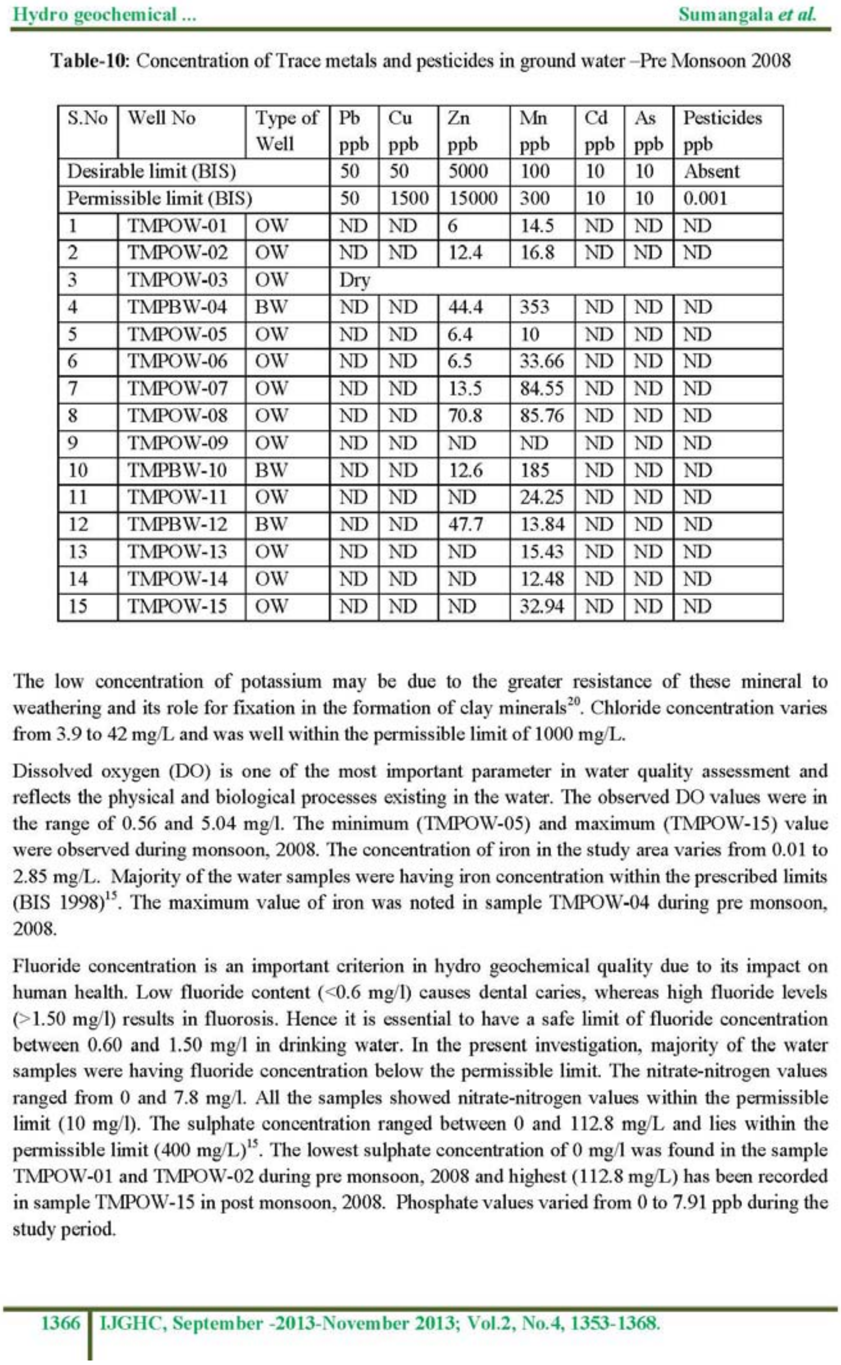


Table-10: Concentration of Trace metals and pesticides in ground water –Pre Monsoon 2008

S.No	Well No	Type of Well	Pb ppb	Cu ppb	Zn ppb	Mn ppb	Cd ppb	As ppb	Pesticides ppb
Desirable limit (BIS)			50	50	5000	100	10	10	Absent
Permissible limit (BIS)			50	1500	15000	300	10	10	0.001
1	TMPOW-01	OW	ND	ND	6	14.5	ND	ND	ND
2	TMPOW-02	OW	ND	ND	12.4	16.8	ND	ND	ND
3	TMPOW-03	OW	Dry						
4	TMPBW-04	BW	ND	ND	44.4	353	ND	ND	ND
5	TMPOW-05	OW	ND	ND	6.4	10	ND	ND	ND
6	TMPOW-06	OW	ND	ND	6.5	33.66	ND	ND	ND
7	TMPOW-07	OW	ND	ND	13.5	84.55	ND	ND	ND
8	TMPOW-08	OW	ND	ND	70.8	85.76	ND	ND	ND
9	TMPOW-09	OW	ND	ND	ND	ND	ND	ND	ND
10	TMPBW-10	BW	ND	ND	12.6	185	ND	ND	ND
11	TMPOW-11	OW	ND	ND	ND	24.25	ND	ND	ND
12	TMPBW-12	BW	ND	ND	47.7	13.84	ND	ND	ND
13	TMPOW-13	OW	ND	ND	ND	15.43	ND	ND	ND
14	TMPOW-14	OW	ND	ND	ND	12.48	ND	ND	ND
15	TMPOW-15	OW	ND	ND	ND	32.94	ND	ND	ND

The low concentration of potassium may be due to the greater resistance of these mineral to weathering and its role for fixation in the formation of clay minerals[20]. Chloride concentration varies from 3.9 to 42 mg/L and was well within the permissible limit of 1000 mg/L.

Dissolved oxygen (DO) is one of the most important parameter in water quality assessment and reflects the physical and biological processes existing in the water. The observed DO values were in the range of 0.56 and 5.04 mg/l. The minimum (TMPOW-05) and maximum (TMPOW-15) value were observed during monsoon, 2008. The concentration of iron in the study area varies from 0.01 to 2.85 mg/L. Majority of the water samples were having iron concentration within the prescribed limits (BIS 1998)[15]. The maximum value of iron was noted in sample TMPOW-04 during pre monsoon, 2008.

Fluoride concentration is an important criterion in hydro geochemical quality due to its impact on human health. Low fluoride content (<0.6 mg/l) causes dental caries, whereas high fluoride levels (>1.50 mg/l) results in fluorosis. Hence it is essential to have a safe limit of fluoride concentration between 0.60 and 1.50 mg/l in drinking water. In the present investigation, majority of the water samples were having fluoride concentration below the permissible limit. The nitrate-nitrogen values ranged from 0 and 7.8 mg/l. All the samples showed nitrate-nitrogen values within the permissible limit (10 mg/l). The sulphate concentration ranged between 0 and 112.8 mg/L and lies within the permissible limit (400 mg/L)[15]. The lowest sulphate concentration of 0 mg/l was found in the sample TMPOW-01 and TMPOW-02 during pre monsoon, 2008 and highest (112.8 mg/L) has been recorded in sample TMPOW-15 in post monsoon, 2008. Phosphate values varied from 0 to 7.91 ppb during the study period.

Concentration of Lead, Zinc, Cadmium and Arsenic were below the permissible limits as per BIS[17]. For TMPOW-02 concentration of Copper was above the desirable limits but it was below the permissible limit during the monsoon and post monsoon periods during the sampling period. Concentration of Manganese was above the permissible limit for TMPBW-04 (1797 ppb). For TMPBW-10, the concentration of manganese was 907 ppb during monsoon, 2007 and 887 ppb during post monsoon, 2008 **(Table 9).**

Nationwide reports for groundwater contamination with pesticides have been documented [10,21-24] and convey that microgram per liter levels of several commonly used pesticides could reach the groundwater even from the routine applications in the field for various crop protection. Even though present study region is also under severe threat of pesticide application, the concentrations of pesticide residues were below the detected level for the entire groundwater sample analysed, which indicates the good recharging of aquifers in these region.

CONCLUSION

Out of the 15 Observation stations (12 Open wells and 3 Bore wells), it is concluded that none of them are affected by the influence of pesticides as they are well protected groundwater structures. The pH of the bore wells and the wells situated near the coastal area are high which could be due to the high bicarbonate concentration. Conductivity value ranged between 31 and 700 µmho/cm which is well within the limit. The concentration of iron varies from 0.01 to 2.85 mg/l. Majority of the samples was having iron concentration within the prescribed limit of BIS. Fluoride concentration was found to be well within the maximum permissible limit. An important observation is that copper was above desirable limit for site TMPOW-02 and it was below the permissible limit during monsoon 2007 and post monsoon 2008. Concentration of Mn was above permissible limit for site TMPBW-04 during pre monsoon and post monsoon, 2008. For TMPBW-10, the concentration level of Mn was above the permissible limit during monsoon, 2007 and post monsoon, 2008.

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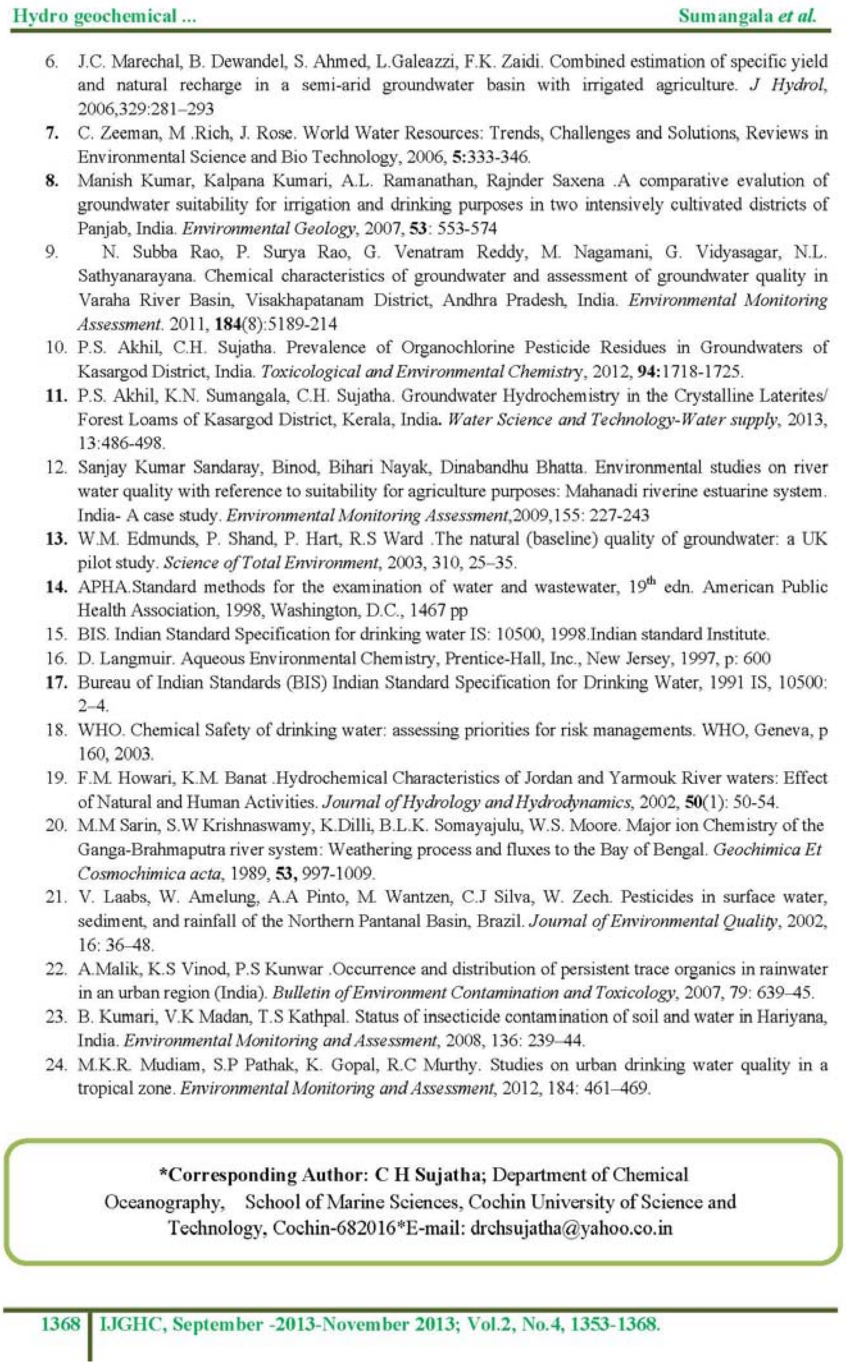

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Prevalence of organochlorine pesticide residues in groundwaters of Kasargod District, India

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The Kasargod District is the northernmost district of Kerala State and is bound between the north latitudes 12°02′27″ and 12°47′35″ and east longitudes 74°51′54″ and 75°25′25″. The present study highlights the contamination levels of organochlorine pesticides in open wells of the Kasargod District from 2010 to 2011. Maximum contamination of organochlorine pesticides (OCP's) was observed for endosulfan followed by hexachlorobenzene (BHC). Contamination levels of α-endosulfan were higher at Panathur ($58\,\mu g\,L^{-1}$) and next to Periya ($37\,\mu g\,L^{-1}$) in the postmonsoon season of 2010. During premonsoon 2011, the residue levels of α-endosulfan were higher at Panathady ($56\,\mu g\,L^{-1}$) followed by Rajapuram ($40\,\mu g\,L^{-1}$). Contamination levels of the BHC isomers exhibit the order of γ-BHC > α-BHC > β-BHC, showing that γ-BHC represents 62% of the total OCP residues in premonsoon 2010. Among the studied OCP's, concentration levels of DDT were below detection limit. Maximum concentrations of the sum of all OCP residues were observed at Mulleria and Cheemeni (premonsoon 2010), followed by Panathur and Periya (postmonsoon 2010), and lowest in Panathady and Rajapuram (premonsoon 2011). Residues of OCP's were lowest in Paettikundu and Cheravatur in all the three seasons.

Keywords: Kasargod District; Kerala; organochlorine pesticides; open well; ground water contamination

Introduction

Pesticides are synthetic organic chemicals used to control unwanted or harmful pests, such as insects and mites that feed on crops. Their resistance to degradation has resulted in their being almost universal presence contaminants in water, soil, and food (Kumar, Singh, and Gopal 1995; Caldas et al. 1999; Hans et al. 1999; Kim and Smith 2001; Singh 2002; Singh, Malik, Mohan, and Takroo 2005; Singh, Malik, Mohan, and Sinha 2005; Lamers et al. 2011). Nationwide reports for groundwater contamination with pesticides have been documented (Bakra, Misra, and Bhatnagar 1990; Kumari et al. 1996; Calder, Coelho, and Souza 1999; Laabs et al. 2002; Malik, Vinod, and Kunwar 2007; Kumari, Madan, and Kathpal 2008; Mudiam et al. 2012) and convey that microgram per liter levels of several commonly used pesticides can reach groundwater even from routine applications in the field. The cashew plantations owned by the Plantation Corporation of Kerala (PCK) in Kasaragod District has been aerially sprayed with the organochlorine pesticide endosulfan

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between 1978 and 2001 regularly three times every year. Recently, the exposure of the general public to endosulfan in Kerala State had high priorities in newspapers. People in the district are complaining from peculiar and complex diseases hitherto unknown. Therefore, knowledge on the contamination levels of pesticide residues in groundwater is in demand. Earlier reports infer that these organochlorine pesticides may cause deleterious effect not only in the environment but also for humans. Due to the persistence of organochlorine pesticides in soil and water, they can adversely affect the health of pedospheric (Kammenga et al. 2000) and aquatic biocoenoses and the quality of drinking water (Kumar, Singh, and Gopal 1995). Most of the organochlorine pesticides including DDT, aldrin, hexachlorocyclohexane (HCH), endrin, and isodrin remain stable in the environment for many years after use (Ritter 1990; Jani et al. 1991).

Therefore, this article highlights the presence of OCP residues in groundwater collected from different areas of Kasargod district in 2010 and 2011. Kasaragod is the northernmost district of Kerala, bordering Karnataka State. It is divided into two taluks (Kasargod and Hosdurg) and 75 villages with a mainly agrarian population. The major crops raised are rice, coconuts, areca nuts, tapioca, pepper, cashew nuts, rubber, and tobacco. Amongst the plantation crops, cashew is most dominant, followed by rubber and areca nut. Other major crops include pepper and spices.

Water samples were collected from different cropping fields, public wells, along with private wells used only for house hold activities in the Kasargod District. Most of the area is based on crystalline rock of Archean age, at the coastal belt sedimentary rocks of tertiary and recent age. Besides, the major geological formations are alluvial, laterites, and crystalines. Aquifer in the district offers very good potential in the deeper fractured rock zone. Groundwater arise under water table conditions in alluvium, laterites and weathered mantle of the crystallines, where as in the deeper fractured crystallines it occurs under semi confined to confined conditions. Alluvium occurs as narrow strips parallel to the coast and the width increases from the northern to southern part of the district. The area is drained by nine west flowing rivers and the average rainfall is 3294 mm.

Materials and methods

Sampling was undertaken covering the entire region of Kasargod district. Groundwater samples were collected from 13 representative open wells from Kasargod District in 2010 and 2011 (Figure 1).

One liter of the filtered water sample (GF/F 0.45 μm) was extracted thrice with 50 mL portions of n-hexane (HPLC grade, Glaxo, Mumbai, India) and the combined extract were dried over anhydrous sodium sulfate (AR grade, Glaxo-Mumbai, India). The extract was concentrated to about 5 6 mL by means of a rotary evaporator at 50 60°C and was subjected to a clean up procedure involving elution through a Florisil column (60 cm × 22mm i.d) with 100 mL *n*-hexane. The elute was concentrated to a final volume 5 mL for further analysis. Separation and analysis of the OCP's were performed on a gas chromatograph (GC) (model 7890A, Agilent, Waldbronn, Germany) with a Ni-63 ECD and equipped with capillary column (HP-35, 30 m × 0.320 mm × 0.5 μm) using nitrogen as carrier gas(1.5 mL min^{-1}). Details of experimental methodology adopted have been described earlier (Sujatha et al. 1993; Mudiam et al. 2012).The GC was calibrated with a standard solution of a pesticide mixture (Supelco, USA) prepared in HPLC grade *n*-hexane. Solvent blanks were used to confirm the absence of any pesticide residues. Analytical reproducibility was checked by replicate measurements. Identification and

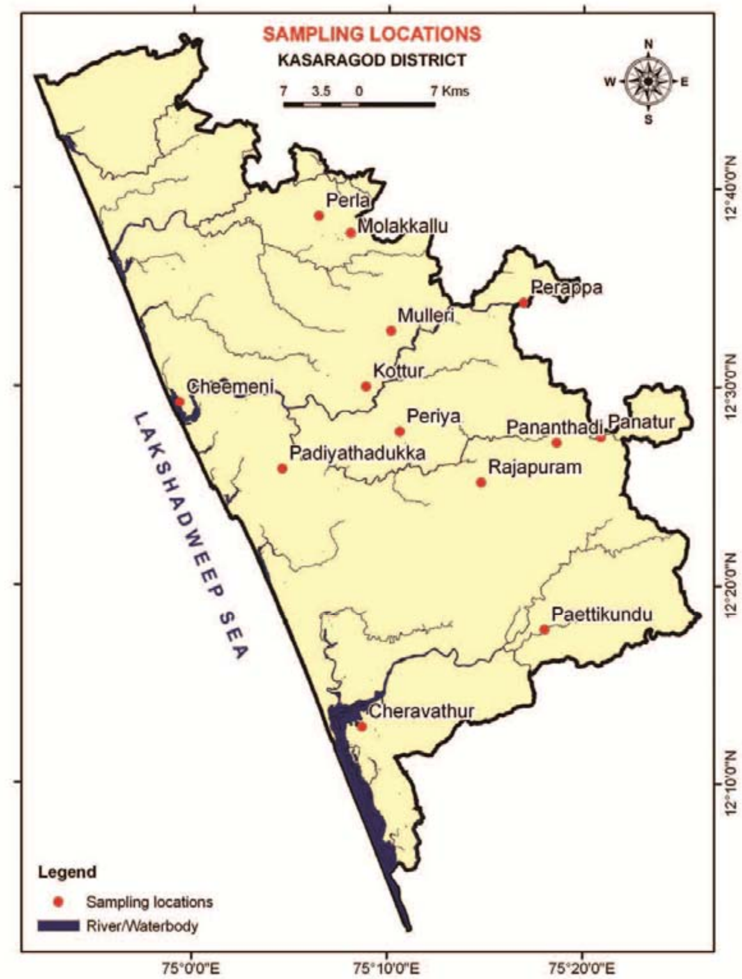

Figure 1. Sampling locations.

quantification of OCP's were accomplished by using reference solutions supplied by EPA (USA) and Supelco (USA). For recovery experiments, a known amount of standard pesticide mixture were spiked into both 1000 mL groundwater samples and high purity Milli-Q water which were extracted and analyzed in a similar manner. The minimum detection limits of OCP's in samples were determined as the concentration of analyte in a sample that gives rise to a peak with a signal-to-noise ratio (S/N) of 3. The detection limit was lowest for aldrin (0.00004 $\mu g\,L^{-1}$) and highest for endrin and 4,4′-DDT (0.0007 $\mu g\,L^{-1}$), while the detection limit of other analytes lies within the range. The average recoveries ($n = 3$) for OCP's revealed an efficiency of 95 100%. The relative standard deviations (RSD) were below 5.0% and fall within the requirement criteria of US-EPA (Recovery: 70 130%, RSD is $<30\%$).

The GC conditions are as follows: injection port temperature 250°C, detector temperature 350°C, oven temperature program: 110°C (5 min) at 5°C min^{-1} to 190°C (2 min) at 15°C min^{-1} to 280°C (10 min).

The following organochlorine pesticides were quantified.

α-hexachlorobenzene (BHC), β-BHC, γ-BHC, heptachlor, aldrin, heptachlor epoxide (B), 4,4′-DDE, dieldrin, endrin, 2,4′-DDD, 4,4′-DDD, 2,4′-DDT, 4,4′-DDT, α-endosulfan, and β-endosulfan. 1 μL of aliquot samples were injected onto the column.

Results and discussion

The findings of this research work constitute the first judicious base line data set for the ground waters of Kasargod District. The residual level of different OCP's in groundwater samples were estimated in the Kasargod District. From the analytical data, endosulfan showed the maximum concentration followed by BHC and are depicted in Table 1. These observations clearly revealed that organochlorine insecticides particularly high concentration of endosulfan and BHC was still persisting in the environment even after their restricted use/ban in the agricultural and public sectors. The occurrence of relatively low proportions of β isomer of BHC is due to the recalcitrant action, vapor pressure and different time intervals in the existence of these isomeric compounds. Earlier report also supports the above inference (Kaushik 1989). The pesticide residues which remained in the soil due to earlier application become a source of pesticide pollution to the water body through land runoff, leaching and ultimately contaminate the drinking water resource. In India, the main drinking water sources are surface water and groundwater. Contamination of drinking water supply is alarmingly increasing and causes threat to the public health. Adoption of the European Union permissible limit of individual pesticide in drinking water as 0.1 and 0.5 $\mu g\,L^{-1}$ for total pesticides has been currently enforced in India (Anonymous 2003). According to the Bureau of Indian Standards (BIS 10500: 1991), the maximum permissible limit of pesticides in drinking water is 1 $\mu g\,L^{-1}$. At various laboratories in India, the pesticide residues were detected in different brands of mineral water. Total BHC concentration as 24.1 $\mu g\,L^{-1}$ (Prakash et al. 2004) and lindane concentration as 4.2 $\mu g\,L^{-1}$ in various brands of soft drinks (CSE 2003). Similarly, contamination levels of the BHC isomers in the present study exhibit the order of γ-BHC $>$ α-BHC $>$ β-BHC, showing that γ-BHC represents 62% of the total OCP residues in premonsoon 2010. Avoidance from these obnoxious and ubiquitous chemicals requires an urgent need to regulate these pollutants that would contaminate both surface and groundwater resources.

The concentration of p,p′-DDT was below detectable level. p,p′-DDT undergoes slow degradation to p,p′-DDE and p,p′-DDD in natural environment by chemical and biological processes (Baxtor 1990). Contamination level of 4,4′-DDE (0.39 $\mu g\,L^{-1}$), 2,4′-DDE (0.14 $\mu g\,L^{-1}$) was detected at Cheemeni and 4,4′-DDD (0.51 $\mu g\,L^{-1}$) was found at Malakkallu in premonsoon 2010. During postmonsoon 2010, residues of 4,4′-DDE was detected at Periya (0.13 $\mu g\,L^{-1}$) and Padiyathadukka (0.04 $\mu g\,L^{-1}$). Also, 0.02 $\mu g\,L^{-1}$ of 2,4′-DDD was detected at Panathur. Residue levels of 0.09 $\mu g\,L^{-1}$ (4,4′-DDE) and 0.05 $\mu g\,L^{-1}$ (2,4′-DDD) was detected at Perla and Rajapuram, respectively, during premonsoon 2011. The ratio of (p,p′-DDE + p,p′-DDD)/p,p′-DDT further provides an indication of the extent of recent release of DDT into the environment, with the increasing ratio over time as DDT degraded. The ratio above unity point out the old use of DDT

Table 1. Mean concentration of BHC and endosulfan isomers detected in the groundwater's of Kasargod District.

Sampling stations	α-BHC ($\mu g\,L^{-1}$)			β-BHC ($\mu g\,L^{-1}$)			γ-BHC ($\mu g\,L^{-1}$)			α-endosulfan ($\mu g\,L^{-1}$)			β-endosulfan ($\mu g\,L^{-1}$)		
	Premonsoon 2010	Postmonsoon 2010	Premonsoon 2011	Premonsoon 2010	Postmonsoon 2010	Premonsoon 2011	Premonsoon 2010	Postmonsoon 2010	Premonsoon 2011	Premonsoon 2010	Postmonsoon 2010	Premonsoon 2011	Premonsoon 2010	Postmonsoon 2010	Premonsoon 2011
Mullria	7.9[a]	BDL	BDL	0.24	0.05	0.06	33	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Padiyathadukka	BDL	BDL	BDL	BDL	0.13	0.15	BDL	BDL	BDL	BDL	3.6	BDL	BDL	BDL	BDL
Parappa	4.2	BDL	BDL	0.18	BDL	0.06	12	BDL	BDL	7.8	BDL	BDL	BDL	BDL	BDL
Perla	1.8	BDL	BDL	0.08	0.56	0.06	15	BDL	BDL	BDL	BDL	6.3	BDL	BDL	BDL
Kottur	BDL	BDL	BDL	2.3	BDL	0.02	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Paettikundu	BDL	BDL	BDL	BDL	0.26	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Cheemeni	8.8	BDL	BDL	0.65	0.15	0.02	33	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Panathady	BDL	0.72	BDL	BDL	0.26	BDL	BDL	BDL	BDL	BDL	BDL	56	BDL	BDL	BDL
Panathur	4.5	BDL	BDL	0.17	BDL	0.24	16	BDL	BDL	BDL	58	BDL	BDL	BDL	BDL
Rajapuram	3.9	BDL	BDL	0.18	0.03	0.32	11	BDL	BDL	3.1	BDL	40	BDL	BDL	BDL
Periya	5.1	BDL	BDL	0.28	BDL	0.31	20	BDL	BDL	BDL	37	BDL	BDL	BDL	BDL
Malakkallu	2.4	0.02	BDL	0.1	0.03	0.007	11	BDL	BDL	BDL	BDL	BDL	BDL	0.05	BDL
Cheravathur	BDL	BDL	BDL	BDL	BDL	0.26	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

Notes: BDL: below detection limits.

[a] Values are as microgram per liter based on triplicate analysis.

and below unity refers to the current use of DDT in these area. Singh (2001) earlier reported that a 50% contribution of p,p′-DDE in ΣDDT concentration in groundwater from Agra (India), whereas p,p′-DDD and p,p′-DDT constituted 10% and 40%, respectively. The p,p′-DDE and p,p′-DDD found in drinking water might be due to metabolic conversion and dechlorination (Matsumura 1973). The groundwater aquifers of Gangetic plains of India in Unnao District of Uttar Pradesh were found to have a maximum concentration of p,p′-DDD (BDL-0.240 μg L^{-1}) followed by p,p′-DDE(BDL-0.073 μg L^{-1}), whereas p,p′-DDT ranged between BDL and 0.013 μg L^{-1} (Singh, Malik, Mohan, and Sinha 2005). Mukherjee and Gopal (2002) reported that, most of the samples from villages and agricultural fields in the national capital of Delhi were contaminated with p,p′-DDD metabolite only and showing the rate of metabolic action.

Aldrin, the probable carcinogen is mainly used as an insecticide for the underground control of termites. In the present study, residue level of aldrin was high (0.55 μg L^{-1}) at Cheemeni and Rajapuram in premonsoon 2010. Apart from these observation appreciable concentration 0.08 μg L^{-1},0.32 μg L^{-1} and 0.39 μg L^{-1} were detected at Panathady, Panathur, and Periya, respectively, in the same season. Similarly, 0.12 μg L^{-1}, 0.02 μg L^{-1} concentrations of aldrin were also noted in postmonsoon 2010. During premonsoon 2011, the concentration of aldrin were 0.15 μg L^{-1} and 0.03 μg L^{-1} at Panathady and Rajapuram, respectively. Though aldrin was detected in pre and postmonsoon 2010 at Cheemeni, unique observation as "aldrin free zone" was noted in premonsoon 2011. The results showed that instead of restriction in usage, excessive and indiscriminate adoption of these are still continuing due to the low cost and popularity of the insecticide formulations among the local people. Contamination level of dieldrin (0.13 μg L^{-1}) and endrin (2.8 μg L^{-1}) was prominent at Panathady in premonsoon 2011. Comparatively low levels of dieldrin was recorded at Panathur (0.08 μg L^{-1}); Periya (0.07 μg L^{-1}) in postmonsoon 2010; and in premonsoon 2011 at Kottur (0.003 μg L^{-1}). Whereas, endrin recorded as 0.04 μg L^{-1} at Padiyathadukka (premonsoon 2010), 2.13 μg L^{-1} at Panathur and 0.005 μg L^{-1} at Cheravatur in postmonsoon 2010. The residue levels of heptachlor was recorded (0.15 μg L^{-1}) at Rajapuram in premonsoon 2010 and in postmonsoon 2010 at Panathur (0.96 μg L^{-1}). In premosoon 2011 at Rajapuram (0.56 μg L^{-1}) and Cheravathur (0.21 μg L^{-1}) heptachlor were also quantified.

In premonsoon 2010, residue levels of α-endosulfan was 7.8 μg L^{-1} and 3.1 μg L^{-1} at Parappa and Rajapuram, respectively. Contamination level of α-endosulfan was highest at Panathur (58 μg L^{-1}) and next to Periya (37 μg L^{-1}) during postmonsoon 2010. The residue level was maximum at Panathady (56 μg L^{-1}) followed by Rajapuram (40 μg L^{-1}) in premonsoon 2011 and may be attributed to the illegal usage of these pesticides for the agricultural purposes. Different studies illustrates the high concentration of β-endosulfan in water samples from agricultural fields (Kumari, Madan, and Kathpal 2008). From soils, the α-isomer of endosulfan disappears more rapidly as it is more volatile than the beta-isomer (UNEP/FAO 2007) and it photo-isomerizes to beta-isomer (Walia and Dureja 1993). However, the elevated concentration of α isomer may be due to the recent usage of these pesticides in these studied area. Most of these OCP's are sparingly soluble in water; they leach into the lower soil profiles under the influence of water moving toward the sub-soil (Kaushik 1991).

Conclusions

Maximum concentrations of the sum of all OCP residues were observed at Mulleria and Cheemeni (premonsoon 2010), followed by Panathur and Periya (postmonsoon 2010), and lowest in Panathady and Rajapuram (premonsoon 2011). Above findings outweighs the existence of hot spot areas for persistent OCP residues like endosulfan and BHC. As compared to surface water, the character of non turbulence, limited experience of dilution and also the anaerobic conditions contributes the enrichment of these OCP's in groundwater. Soils become the reservoir of pesticides from their previous usage and the prolonged illegal practice in these area steadily transfer them to the groundwater. Besides, synergic action with the residues of other pesticides which are still in use pose a health hazard to local residents consuming these potable groundwater. Some of the isomers/metabolites detected might be the result of their prolonged persistence in the environment and the promotion by agriculture sector through expanding the market for pesticides and other agro chemical fertilizers. There is a need for awareness among farmers so that illegal use could be controlled. Strict action against sellers of banned or spurious pesticides and adoption of integrated pest management practices could be a possible way to overcome/bring down the present residue levels in the future. Frequent monitoring studies are encouraged to advocate regular water quality assessment with special attention to these xenobiotic OCP's.

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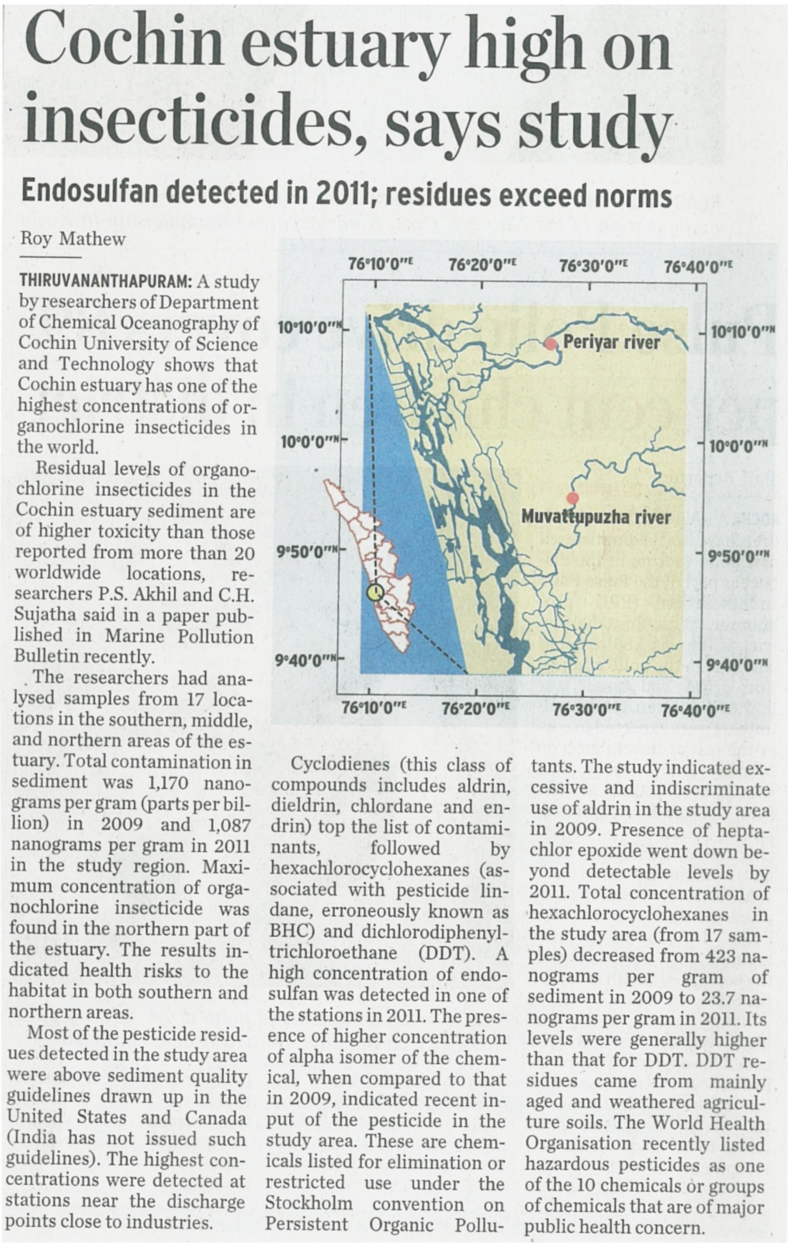
B. Articles Reported in Media

1. ***Cochin Estuary High on Insecticides, Says Study***. The Hindu National Daily News Paper, Published on 20th January 2014.



Cochin estuary high on insecticides, says study

Endosulfan detected in 2011; residues exceed norms

Roy Mathew

THIRUVANANTHAPURAM: A study by researchers of Department of Chemical Oceanography of Cochin University of Science and Technology shows that Cochin estuary has one of the highest concentrations of organochlorine insecticides in the world.

Residual levels of organochlorine insecticides in the Cochin estuary sediment are of higher toxicity than those reported from more than 20 worldwide locations, researchers P.S. Akhil and C.H. Sujatha said in a paper published in Marine Pollution Bulletin recently.

The researchers had analysed samples from 17 locations in the southern, middle, and northern areas of the estuary. Total contamination in sediment was 1,170 nanograms per gram (parts per billion) in 2009 and 1,087 nanograms per gram in 2011 in the study region. Maximum concentration of organochlorine insecticide was found in the northern part of the estuary. The results indicated health risks to the habitat in both southern and northern areas.

Most of the pesticide residues detected in the study area were above sediment quality guidelines drawn up in the United States and Canada (India has not issued such guidelines). The highest concentrations were detected at stations near the discharge points close to industries.

Cyclodienes (this class of compounds includes aldrin, dieldrin, chlordane and endrin) top the list of contaminants, followed by hexachlorocyclohexanes (associated with pesticide lindane, erroneously known as BHC) and dichlorodiphenyltrichloroethane (DDT). A high concentration of endosulfan was detected in one of the stations in 2011. The presence of higher concentration of alpha isomer of the chemical, when compared to that in 2009, indicated recent input of the pesticide in the study area. These are chemicals listed for elimination or restricted use under the Stockholm convention on Persistent Organic Pollutants. The study indicated excessive and indiscriminate use of aldrin in the study area in 2009. Presence of heptachlor epoxide went down beyond detectable levels by 2011. Total concentration of hexachlorocyclohexanes in the study area (from 17 samples) decreased from 423 nanograms per gram of sediment in 2009 to 23.7 nanograms per gram in 2011. Its levels were generally higher than that for DDT. DDT residues came from mainly aged and weathered agriculture soils. The World Health Organisation recently listed hazardous pesticides as one of the 10 chemicals or groups of chemicals that are of major public health concern.

2. ***Groundwater remains polluted in Kasargod Villages.*** The Hindu National Daily News Paper, Published on 7th October 2012.

Groundwater remains polluted in Kasaragod villages

Cusat study finds high concentration of insecticides in the environment

Roy Mathew

THIRUVANANTHAPURAM: Fresh evidence has emerged about prevalence of endosulfan residues in the groundwater of Kasaragod district and, possibly, recent use of the pesticide in the area.

A study by P.S. Akhil and C.H. Sujatha of the Department of Chemical Oceanography of Cochin University of Science and Technology (Cusat) reported that organochlorine insecticides, particularly high concentrations of endosulfan and BHC (hexachlorobenzene), were persisting in the environment. This was despite restrictions on use of BHC, and ban imposed by the High Court and the government on use of endosulfan.

The pesticide residues which remained in the soil from earlier application become the source of pollution of water bodies through land runoff, leaching and ultimately contaminate drinking water sources.

The study, published in the journal *Toxicological and Environmental Chemistry* this month, found that contamination by alpha isomer of endosulfan was the highest at Panathur (58 microgram per litre) followed by Periya (37 mcg/L) in the post-monsoon season of 2010. Before monsoon in 2011, the residue levels in water were highest at Panathady (56mcg/L), followed by Rajapuram (40mcg/L). Endosulfan residues have been detected at Parappa and Perla also.

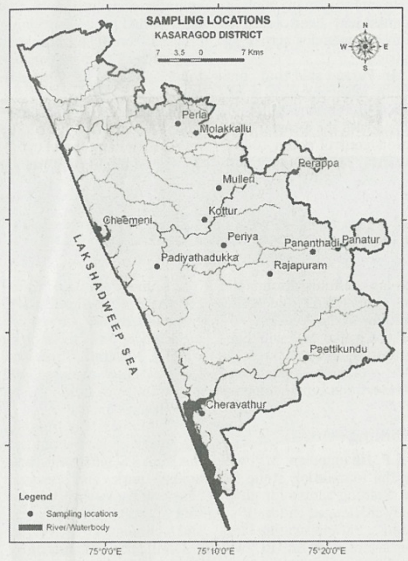
Water samples for the study were collected from different cropping fields, public and private wells across the district. High levels of alpha isomer found in water at places such as Panathady and Rajapuram suggest continued illegal use of the pesticide in the area. For, alpha isomer disappears from the environment faster than the beta isomer. (Both isomers are present in commercial endosulfan. However, it was notable that beta isomer was not detected in water except at one place, Malakkallu; that too in very low concentration. The exact reason for this is not known, though it may have something to do with solubility and binding of the isomer with soil sediments.)

The study found high levels of pesticide Aldrin (used for underground control of termites) also in water at places such as Cheemeni and Rajapuram in 2010. Highest concentrations of total residues of all organochlorine pesticides were observed at Mulleria and Cheemeni (pre-monsoon 2010), followed by Panathur and Periya (post-monsoon 2010). High levels of BHC were detected in water in these areas in 2010.

'Protected water supply'

It is notable that the study did not test soil samples which are likely to contain higher concentrations of endosulfan residues. Though the presence of endosulfan in soil sediments had long been known, the government has not taken any steps so far to decontaminate the areas. Arrangements for protected water supply are also lacking in many areas.

Though quite a large number of rural drinking water projects were taken up in Kasaragod district in recent years, priority was not accorded to endosulfan-affected villages. Even the second phase of Jalanidhi scheme skipped many of those areas.



C. CONFERENCES /SYMPOSIUMS ATTENDED

A. International

- Participated in **5th International Symposium on Biological and Environmental Chemistry of DMSP and related compounds** during 19-22 October 2010, **NIO**, Goa, **India**.
- Participated in **International Council for the Exploration of the Sea (ICES)** organized **Annual Science Conference 2010** at **Nantes, France**, on 20-24 September, and presented a poster entitled " Analysis and Identification of Biological production of Dimethyl Sulphide (DMS) and Dimethyl Sulphoniopropionate(DMSP) by Phytoplankton in the Cochin Estuarine System"

B. National

- Participated in National Conference of Ocean Society of India (OSICON'13) and presented two papers entitled **"Characterization of Organic Matter in the core sediments of Cochin Estuarine System**" and "**Geochemical Assessment of Metal contamination in the Core Sediments of Cochin Estuarine System**" held during 25th November to 28th November 2013at Indian Institute of Tropical Meteorology, Pune, India.
- Participated in Regional Seminar on "Water Quality Assessment and Management of Kerala State" and presented a paper entitled **"Soil Geochemical Facsimile of Kasargod District with special reference to Ground water Quality"** held during 5-6 February 2013 organized by National Institute of Hydrology, at Trivandram, Kerala.

- Participated in National Conference on "Mangrove wetlands and near shore marine ecosystems : from sustainability issues to management & restoration" and presented a paper entitled **"Core Sediment Biogeochemistry in Specific Zones of Cochin Estuarine System (CES)"** held during 5-6 March 2012 at Jawaharlal Nehru University, **New Delhi**, India.
- Participated in National Conference of Ocean Society of India (OSICON'11) and presented a paper entitled **" Spatial and Vertical Transmission pattern of Pigments and their Assimilation with Nutrients in the Southern Ocean Water Mass"** held during 13-15 July 2011 at National Institute of Ocean Technology, **Chennai,** India.
- Participated in National Conference of Ocean Society of India (OSICON'11) and presented a Poster entitled **"Core Sediment Organic Matter Distribution in the Coastal Region of Antarctica"** held during 13-15 July 2011 at National Institute of Ocean Technology, **Chennai,** India.
- Participated in **"National Seminar on biodiversity"** Organized by Swadeshi Science Movement on 17 December , 2010 at School of Marine Sciences, CUSAT, Kochi, **Kelala,** India.
- Participated in **"Symposium on Indian Ocean Marine Living Resources (IndoMLR)"** Organized by Centre for Marine Living Resources& Ecology(CMLRE) on 2-3 December 2010 at **Ernakulam,** Kerala**,** India.
- Participated in National Seminar on **"Chemistry and Environment"** and presented a paper entitled **"Groundwater Quality Assessment in Selected Areas in Mattancherry of Cochin Corporation, Kerala, India"** conducted by St. Pouls College on 2-4 September 2010, at **Ernakulam,** Kerala, India