GEOCHEMICAL METAL FRACTIONATION PROFILE OF THE CORE SEDIMENT IN THE COCHIN ESTUARINE SYSTEM

Thesis Submitted to
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
for the Award of the Degree of
DOCTOR OF PHILOSOPHY
in
MARINE CHEMISTRY
UNDER THE FACULTY OF MARINE SCIENCES

MANJU .P. NAIR
Reg.No.4233

Research Supervisor
Dr. SUJATHA C.H

DEPARTMENT OF CHEMICAL OCEANOGRAPHY
SCHOOL OF MARINE SCIENCES
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
KOCHI –682016

June 2014

Geochemical Metal Fractionation Profile of the Core Sediment in the Cochin Estuarine System

Ph.D. Thesis under the Faculty of Marine Sciences

Author

Manju .P.Nair
Research Scholar
Department of Chemical Oceanography
School of Marine Sciences
Cochin University of Science and Technology
Kochi - 682016
Email: manjupnaircsp@yahoo.com , manjupnaircod@gmail.com,
manjupnaircod@cusat.ac.in

Supervising Guide

Dr. Sujatha C.H
Associate Professor & Head
Department of Chemical Oceanography
School of Marine Sciences
Cochin University of Science and Technology
Kochi - 682016
Email: drchsujatha@yahoo.co.in, drchsujatha2012@gmail.com

Department of Chemical Oceanography
School of Marine Sciences
Cochin University of Science and Technology
Kochi – 682016

June 2014

Dedicated to My Beloved Parents and Teachers……………

Dedicated to My Beloved Parents and Teachers……………

Cochin University of Science and Technology
School of Marine Sciences
Department of Chemical Oceanography
Dr. Sujatha C.H
Associate Professor

Fine Arts Avenue
Cochin, Kerala – 682 016, India.
Tel: +91 484 2382131(0)
Mob: 9995991778
Fax: +91 484 2374164
E-mail: drchsujatha@yahoo.co.in

Certificate

This is to certify that the thesis entitled “Geochemical Metal Fractionation Profile of the Core sediment in the Cochin Estuarine System” is an authentic record of the research carried out by ***Ms. Manju.P.Nair*** *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 recommendations by doctoral committee of the candidate have been incorporated in the thesis.*

Kochi - 682016
June 2014

Dr. Sujatha C.H
(Supervising Guide)

Declaration

I hereby declare that the thesis entitled ***"Geochemical Metal Fractionation Profile of the Core sediment in the Cochin Estuarine System"*** *is an authentic record of the research carried out by me under the supervision and guidance of* ***Dr. Sujatha C.H,*** *Associate Professor and 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, associate-ship, fellowship or any other similar title or recognition.*

Kochi - 682016
June 2014 ***Manju.P.Nair***

Acknowledgements

I will always remain grateful to the **God Almighty** for the ample blessings during the entire course of the study.

I am deeply grateful to my supervising guide, **Dr Sujatha C.H, Associate Professor and Head,** Department of Chemical Oceanography, for guiding the research programme, constant encouragement, valuable suggestions and for the continuous support throughout the course of this thesis work. I express my deep and sincere gratitude to my guide for conceptualization and implementation of this research topic, in addition to her peerless guidance and motivation all the way throughout my doctoral research.

My sincere thanks goes to **Professor (Dr.) N. Chandramohanakumar, Professor (Dr.) S. Muraleedharan Nair** and **Professor (Dr.) Jacob Chacko** (Rtd), for their support, valuable advice and encouragement through the course of my research.I express my sincere thanks to all the administrative staff of Department of Chemical Oceanography.

I am thankful to **Professor (Dr.) H.S. Ram Mohan**, former Dean and Director and Director School of Marine Sciences, Professor (Dr.) **Sajan .K,** Dean, Faculty of Marine Sciences for the facilities provided.

I am grateful to **Mr. P.J. Manuel**, Librarian and staff members, School of Marine Sciences, CUSAT for valuable advice and encouragement through the course of my research. With gratitude I thank **Mr. Anilajen**, Staff, School of Industrial Fisheries, CUSAT for his help during sampling.

This research work cannot be produced without substantial financial support, and I would like to thank the **Cochin University of Science and Technology** *for providing the University Fellowships which gave me the financial capacity to devote the past three years to this research.*

I would like to take the opportunity to express a few words of thanks to my best Colleagues and friends.

My colleague Mr. Akhil P.S was always at the helping end and I cherish his timely helps which lessened much of my tasks to meet.

I acknowledge the help and encouragement rendered by my colleagues Dr. Ratheesh Kumar C.S, Dr. Sumangala K.N, Dr. Aneesh Kumar N, Dr. Pratheesh V B, Dr. Nify Benny, ,Mrs. Gayathree Devi P.K ,Dr. Ranjitha Raveendran, Mr. Byju K, Mrs. Athira Sreekanth, Dr. Shaiju P, Mr.Prashob Peter K.J, Mr. Jose Mathew, Ms. Manju M.N, Mr. Salas P.M, Mr. Jyothish kumar, Mrs. Dayala V.T, Mr. Mrudulrag S K,, Mr. Eldhose Cheriyan, and all other research scholars in the Department of Chemical Oceanography, CUSAT. I would like to thank for whoever being with me in all times of need and helping me in keeping my spirits up.

It is a pleasure to express my gratitude wholeheartedly to my guide's husband, Mr.Sathyachandran P.V and children Jithu.S and Aishwarya.S for their co-operation and prayers, to complete my work in a best manner.

I indebted to my parents for their inseparable support and prayers. My father, **Mr. C.S. Prabhakaran Nair**, *in the first place is the person who actuated me always, fed valuable suggestions, advice and urged me to grasp his dream of my doctoral ship. My mother,* **Mrs. Valsala Devi O.K**, *is the one who sincerely raised me with her caring and love. I am also very much grateful to both for being supportive and helped me to sort out the problems I faced and also for the assistance in the technical fulfilment of* *the research work. I owe them, for being unselfishly let their patience, aptitude, passion and ambitious collective with mine. I extend my deep sense of gratitude to my* ***Grandparents (late)*** *for the unlimited blessing, love and support throughout my life. I express my gratitude towards my Husband* ***Mr.Prasanth.P*** *for his love, care, motivation and support during the final stages of my research work.*

I would like to thank all, unnamed in credits without whom the work would ever have not been conceived.

Manju .P.Nair

Preface

The world oceans are in the brink of ecological collapse due to powerful forces like overfishing, rapid industrialization creating the marine ecosystem as an ultimate trash bin for dumping toxic chemicals including both inorganic and organics. Without swift action, ocean systems will continue to deteriorate and have been associated to human health such as cancer, birth defects and brain impairments. Reducing or eliminating these toxic components in the products we buy, the air we breathe, the food we eat and the water we drink can help to reduce the fall of human disease and suffering. Safeguard and protection of the environment requires high quality science that is free from conflicts of interest. The appropriate conservation and sustainable development strategies attempt to recognize the diversity in life on Earth as being integral and it enhance ecosystem productivity. As we enter the 21st century, swelling demand and changing climate pattern, clean water as the world biggest health requirement for public are continuous to threaten both quality and life. Estuarine water bodies in many densely populated region of the world are subjected to inducing multiple anthropogenic impacts. Biological activities convert organic compound to CO_2 and H_2O. But inorganics mainly metals are continuously accumulating in marine environments, except for a minor portion that may be taken away along with marine food and other products. Metals if present in higher amount than normal concentration are toxic to marine biota and humans. Many catastrophic events of human health significance have occurred in the past based on metal pollution. A sense of avoidances of such unfortunate incidents has led to a great extent in monitoring of toxic metal concentration in the marine environment.

Metal pollution of the natural environment is a universal problem as metals are indestructible and most of them have toxic effect when they exceed threshold levels. Metals are recognized as an important indicator of aquatic environment degradations. Huge amounts of metals are entering the environment each year as contaminants from anthropogenic-related processes by the ways of untreated industrial wastewater, municipal sewage effluent, surface run-off , so on. Population growth and the resultant acceleration of domestic , municipal, industrial, agricultural and recreational activities are the primary cause of anthropogenic pollution of the marine relam. Metals in the environment pose a variety of very interesting scientific questions. The field of work involved cover a wide range of disciplines, showed as an interdisciplinary field of work ranging from geology, mineralogy , geochemistry (origin and natural occurrence is concerned) analytical, physical and colloid chemistry (comes to the detection of metals and their interactions with environmental media such as water, ground water ,soil ,rock and air) biology ,ecology ,ecotoxicology medicine (concerned with their impact on global ecosystems and their effects on human and animal health) and finally the remediation of metals requires cooperation of several engineering disciplines such as environmental ,chemical and civil engineering.

Metal pollution in the estuarine and coastal sediments is an important component in understanding the exogenic cycling as well as in assessing the effect of antropogenic influence on marine ecosystem. In recent years, increasing attention was given in the level of metals in the sediment band. Thus, understanding the transport, distribution and characterization of trace metals in the sediments of the estuaries is a challenging area of research for environmental chemists. Stoichiometric regulation of aquatic ecosystem structure occurs at the sediment interface via altered biogeochemical processes and benthic food webs. Sediments constitute the environment, a solid frame work for geochemical reactions during early diagenesis that occur in the pore space between the particles in the water –sediment boundary layer. Marine sediments can be sensitive indicators for monitoring contaminants in aquatic environments. The bottom sediments serve as a reservoir for heavy metal and therefore deserve special consideration in the planning and design of aquatic pollution studies. Core sediments can be used to study the pollution history of aquatic ecosystem and comprises information data set regarding the events that occurred in a precultural time in the estuary. Sediments have been used frequently in the initial phase of environmental assessment to locate areas of possible concern and trace historical changes because they give an integrated picture of contaminants over time. Sediment cores are a pricey and exclusive resource of immense scientific value and are extremely useful gadget for the geochemical studies. The sediment core analysis is interesting as the bottom sediment records the past changes in the aquatic system. It establishes both the effect of anthropogenic and natural processes occur in the environment.

Cochin Estuarine System (CES), one of the largest tropical estuaries in south western side of Indian peninsula faces gross pollution problems following the release of untreated effluents from industries and domestic sectors. Considering the importance of metal estimations in the pollution assessment study in recent years there has been a great spuet of renewed activities were carried out in CES, but there is scanty literature available in the core sediment geochemistry. Sediment core analysis can be used as a gauge of the quality control in the CES and would provide a clear cut idea about the environmental dynamics of the studied site. No systematic research activities have been conducted in the characterization of metal fractions in the core sediment of the CES. Most of the studies are based on one time or seasonal sampling during a year of sample collection from areas known for environmental pollution. Though in any area in which distribution of inorganic pollutant in sediments collected with a considerable time period can provide a clue for change in the environment and such studies are limited. In this context the present work entitled "**GEOCHEMICAL METAL FRACTIONATION PROFILE OF THE CORE SEDIMENT IN THE COCHIN ESTUARINE SYSTEM"** mainly intends to remove the gap in the core sediment chemistry by characterizing metal fractions of the core sediment from different hotspot sites of the CES.

The thesis is divided in to six chapters.

Chapter 1 –ENVIRONMENTAL GEOCHEMISTRY OF ESTUARINE CORE SEDIMENT comprises a brief introduction deals with literature survey of the environmental geochemistry of estuarine sediment leading to the motivation and problem statement.

Chapter 2 –METHODOLOGY deals details of the methodology, the criteria for selection of sampling stations and the precautions adopted for sampling and analysis of each constituent are discussed .

Chapter 3 – METAL FRACTIONATION OF THE SURFACE SEDIMENT IN CES describes the spatial distribution and fractionation of metals in the surface sediments of Cochin estuarine system. Also explains the result in comparison with hydrographic parameters and sediment characteristics.

Chapter 4- METAL DISTRIBUTION IN THE SPECIFIC CORE SEDIMENTS OF COCHIN ESTUARINE SYSTEM (CES) depicts the information of the vertical distribution of metals in the core sediments of Cochin estuarine system and illustrates the depth variation profile with other components under study.

Chapter 5 – GEOCHEMICAL METAL FRACTIONATION OF SPECIFIC CORE SEDIMENTS IN THE CES comprises the geochemical fractionation of metals in the core sediment of Cochin estuarine system along with the evaluation of the risk and mobility associated with these fractions.

Chapter 6- SUMMARY gave précis of overall results and the outcomes derived are presented with comprehensive explanations.

Contents

List of Figures

List of Tables

List of Abbreviations

AAS	Atomic Absorption Spectrometer
AF	Anthropogenic Factor
BDL	Below Detectable Limit
CA	Bound to Carbonate Fraction
CES	Cochin Estuarine System
CF	Contamination Factor
EF	Enrichment Factor
EXC	Exchangeable Fraction
GCI	Geochemical Chemical Indices
ICTT	International Container Transshipment Terminal
IGEO	Geo accumulation index
KNRF	Non residual enrichment factor
MF	Mobility Factor
OM	Bound to Organic Matter Fraction
PCA	Principal Component Analysis
PLI	Pollution load index
RAC	Risk Assessment Code
RES	Residual Fraction
SQG	Sediment Quality Guidelines
SEP	Sequential Extraction Procedure
TOC	Total Organic Carbon

Chapter 1

ENVIRONMENTAL GEOCHEMISTRY OF ESTUARINE SEDIMENT

Contents

1.1 Environmental Geochemistry

Atmosphere, earth and water are the three prominent environmental ecosystems. More than 100,000 different forms of chemical compounds are released per annum into these ecosystems as a result of rapid industrialization and economic development. The fate of a chemical substance depends on its chemical forms, its rate of application, physico-chemical properties, in combination with the characteristics of the environment where it is released. Metals are one of the most abundant classes of contaminants generated and are continuing to be introduced to the aquatic system, thereby create a real hazardous situation for marine ecosystems and organisms health. Although these metals are man-made, they rush into the water body through effluent and sewage or are directly discharged from industries placed on the sea water front. A great number of factors influence the dose-effect and dose-response relationships between metals and organisms; their tolerance and finally the consumption of trace metals for various purposes reflect the sea water concentrations. These metals are one of the serious pollutants in the natural environment due to their toxicity, persistence and bioaccumulation problems (Chakraborty et al. 2010.).

Now a day the qualities of the water have become significant topic of concern for researchers in association with various scientific disciplines. Therefore, the present thesis encounters environmental geochemistry, which deals with the application of chemical principles for predicting the fate of pollutants especially metals in the earth's compartments. It envisages areas that could be at threat from natural and anthropogenic chemical intrusion and extends in to the realm of assessing physical, chemical and biological remediation technologies. Metal pollutants have low residence time in the water, so the measurements are not decisive owing to water discharge fluctuations. It has been reported that estuarine sediments are contaminated with both inorganic and organic pollutants including metals and acting as filter or reservoirs (Chapman and Wang. 2001). The enrichment of chemicals in sediment by anthropogenic pollution must account for a number of geologic, minerologic, hydrologic and biological processes controlled by both internal and external factors. Geochemical investigations of sediments have recently been practice in quality exploration and provide a valuable information document of on altering natural balance (Manju and Sujatha. 2012; Manju and Sujatha. 2013 a,b; Manju et al. 2013.**).** In estuarine sediment, concentration of metals can be elevated due to high inputs from natural, as well as anthropogenic sources. Although metals are natural constituents of the earth’s crust and are present in all ecosystems, their concentrations have been dramatically increased by human activities.

A thorough knowledge on these is essential to assess the overall effect on the ecosystem. Hence, the goal of environmental chemists is to understand the transport and distribution of metals in estuaries and the exact picture of contamination history of metal residue which can be revealed from sediment analysis collected from varying estuarine conditions.

1.2 Sediment Cores

Sediment is a naturally occurring material that is broken down by processes of weathering and erosion, and is subsequently transported by the action of wind, water, ice, or by the force of gravity acting on the particle itself. Sediments are the reserve of environmental variation and their analysis gives the diverse nature of the environmental chemical pattern. The nature and extent of fluctuation in the composition of sediments can indicate the rate of stress on aquatic environments. 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. The underlying principle behind the use of geochemistry to aid the study of sediments is that the different geochemical composition is reflected in the chemistry of sediments. The anthropogenic metal load of sediment to estuaries can be estimated from sediment geochemistry. Enough literature exists on details of sediment as the focal theme of pollution assessment but scanty data are available on core sediment geochemistry. Estuarine core sediment geochemistry allows extrapolating pollution histories to be studied and judged. Sediment cores are an extremely useful tool used in conjunction with environmental studies.

Sediment core analysis is interesting because the bottom of a 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. 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.

1.3 Importance of Metal Analysis

1.3. 1 Total Metal

The universal use of metals in human society has significantly changed their original distribution patterns in natural environments. Metals are recognized as an important indicator for the degradation of aquatic environments (MacDonald et al. 1996; Allen Burton. 2002). Huge amounts of metals are entering the aquatic system as contaminants from anthropogenic-related processes by the ways of untreated industrial wastewater, municipal sewage effluent, surface run-off and so on. In aquatic environments, many metals are transported predominantly in association with particulate matter, which makes sediments, the most important repository for metal pollutants that enter the water bodies (Ridgway and Shimmield. 2002). Sediment total metal analysis have been used frequently in the initial phase of environmental assessment to locate areas of possible concern and trace historical changes because they give an integrated picture of contaminants over time.

Geochemical studies of surficial sediment as well as sediment cores are helpful in the assessment of pollution (Holm. 1988; Geetha et al. 2008; Al-Juboury. 2009; Chibunda. 2009; Chibunda et al. 2010; Ahmad et al. 2010), changes in climatic conditions (Faganelli, et al. 1987; Karbassi and Amirnezhad. 2004; Karbassi and Shankar. 2005), accumulation or mobilization of trace elements in the various phases of aquatic environment (Al-Masri. 2002). Sediments act as sinks and sources of contaminants in aquatic systems because of their variable physical and chemical properties (Rainey et al. 2003; Marchand et al. 2006*;* Pekey. 2006*;* Priju and Narayan. 2007; Praveena et al. 2008; Sundararajan et al. 2009; Sundararajan and Usha Natesan. 2010). Core sediments provide useful information on the changes in the quality of the estuary from a past period. The pollution history of aquatic ecosystem by core sediments (Lopez and Lluch. 2000; Karbassi et al. 2005; Mohamed. 2005) have been used to study the behavior of metals (Lee and Cundy. 2001; Weis et al. 2001; Bellucci et al. 2003; Bertolotto et al. 2003). During their transport, the metals undergo numerous changes in their speciation due to dissolution, precipitation, sorption and complexation phenomena (Akcay et al. 2003; Abdel-Ghani et al. 2007; Abdel- Ghani and Elchaghaby. 2007; Praveena et al. 2008; Harikumar et al. 2009; Mohiuddin et al. 2010) which affect their chemical behavior and bioavailability.

Table1.1 shows the variations of the Pollution Load Index (PLI) in estuarine sediments from the Indian coast.

Table1.1 The pollution load index (PLI) value of the estuarine sediment around India

Estuary	References	PLI
Cauvery	Seralathan. (1987)	3.47
	Ramanathan et al. (1988)	1.78
	Subramanian et al. (1989)	3.27
	Ramanathan et al. (1993)	0.91
	Ramesh et al. (1999)	1.18
	Dhanakumar et al. (2013)	0.50
Cochin	Venugopal et al. (1982)	1.35
	Nair. (1992)	0.80
	Jayasree and Nair. (1995)	0.11
	Balachandran et al. (2005)	8.17
	Balachandran et al. (2006)	2.65
	Martin et al. (2012)	3.53
Ganges	Subramanian et al. (1988)	1.39
	Subramanian. (1993)	1.04
	Ramesh et al. (1999)	0.88
	Banerjee et al. (2012)	1.50
Godavari	Ramesh et al. (1999)	0.53
	Ray et al. (2006)	1.21
	Krupadam et al. (2007)	1.41
	Chakraborty et al. (2012)	11.04
Krishna	Subramanian et al. (1985)	1.27
	Ramesh et al. (1989)	1.31
	Ramesh et al. (1999)	1.70
Narmada	Subramanian et al. (1985)	1.06
	Sharma and Subramanian. (2010)	3.25
Tapti	Subramanian et al. (1985)	1.74
	Sharma and Subramanian. (2010)	3.55
Ulhas	Sahu and Bhosale. (1991)	3.35
	Rokade. (2009)	4.86
	Rokade. (2009)	4.54
	Rokade. (2009)	4.37

From the Table 1.1 it is clear that the Cochin Estuarine System (CES) is facing gross pollution problems following the release of untreated or partially treated effluents from industries and domestic sectors. Therefore sediment core analysis can be used as a gauge of the quality control in the CES and would provide a clear cut idea about the environmental dynamics of the studied site. The sediment characteristics in relation to changing hydrography of the CES have been investigated by Nair et al. 1993.

Extensive investigations have also been conducted on trace metal abundance, distribution and speciation in dissolved and particulate media, which highlight the role of numerous environmental factors, such as (a) the influence of riverine inputs of metals, regulated by dams/reservoirs, (b) the introduction of industrial effluents and sewage, (c) the modifications arising from anthropogenic activities and hydrographic changes related to complexity of water use (Shibu et al. 1990, 1995; Nair et al. 1990, 1991; Nair and Balchand. 1993). Earlier detailed descriptive studies have been carried out on the distribution of trace metals in CES (Ouseph. 1978; Saraladevi et al. 1979; Paul and Pillai. 1983; Rajendran and Kurian. 1986; Ouseph. 1987; Shibu et al. 1990; Rajamani. 1994; Mohapatra and Rangarajan. 2000 ; Kaladharan et al. 2011; Anju et al. 2011) in this enrichment of heavy metals in sediment due to industrialization and urbanization was recorded by several investigators (Paul and Pillai. 1976; Remani et al. 1983; Nair et al. 1990; Ouseph. 1992; Shajan. 2001; Balachandran et al. 2005; Kaladharan et al. 2005; Balachandran et al. 2006; Priju and Narayana. 2007; Harikumar et al. 2009; Ratheesh et al. 2010; Sudhanandh et al. 2011; Ramaswamy et al. 2012; Deepulal et al. 2012; Robin et al. 2012; Martin et al. 2012; Paneer Selvam et al. 2012; Manju and Sujatha. 2013 a,b.). and metals in organisms was studied deeply in CES (Remani et al. 1983; Gopalan et al. 1983; Saraladevi and Venugopal. 1989;

Rajendran and Kurian. 1986; Lakshmanan et al. 1989; Saraladevi et al. 1992; Rajamani et al. 1994; Pillai and Valsala. 1995; Kaladharan et al. 2005; Martin et al. 1998; Jiya et al. 2011; Ranjitha and Sujatha. 2011; Bijoy Nandan et al. 2013; Ciji and Bijoy Nandan. 2014) but there is a scanty literature available on metal fractionation.

1.3.2 Metal Fractionation

Contamination of metals in the environment is of prime importance because of their potential toxicity and threat to the ecosystems (Purves. 1985). Metals interact with sediment matrix through different binding mechanisms, including adsorption to mineral surfaces, associated with carbonates, Fe/Mn oxyhydroxides, organic matter, sulfides and the lattice of refractory crystalline minerals, such as silicates (Das et al. 1995; Tack and Verloo. 1995; Gleyzes et al. 2002; Sahuquillo et al. 2003). The mobility of metals in sediments is environmentally controlled and dependent on several factors such as pH, cationic exchange capacity, nutrient status, carbonates- organic matter contents, redox potential and texture (Sahuquillo et al. 2003). Therefore, besides measuring their total concentrations, determining the geochemical fractionation of metals in sediments is equally important in assessing their potential toxicity and threat to the ecosystems (Das et al. 1995; Quevauviller. 1998; Sahuquillo et al. 2003).

1.4 Aim and Scope

CES is the confluence of six rivers, has a length about 70 Km and width varied between few 100 m to about 6 Km. Numerous problems faced by CES include pollution due to industrial, agricultural and domestic effluents. Around the CES, the industries were situated in hindered areas near the backwaters or the bank of the rivers. These industries liberate heavy load of effluents to the system which are rigorously toxic in nature. The review of geochemical research carried out in core sediment so far on and off the west coast reveals that considerable amount of work still remains to be done with regard to geochemistry and metal pollution load and their association with the counter ions in these sediments. However, no previous reports were available on the core sediment metal fractionation in the CES. Therefore, this study provides the first detailed monograph of the environmental quality assessment of sediment cores from the prominent region of CES, which would inculcate to assess the geochemical quality of the estuary. Furthermore, the study will help to evaluate the risk and mobility associated with these metal fractions .These results of the core sediment profile enable to obtain a global picture of the historic sediment quality of CES. A number of investigations in recent years on surface sediment metal were carried out in the CES (Shajan. 2001; Balachandran et al. 2005, 2006; Renjith and Chandramohanakumar. 2009; Ratheesh Kumar et al. 2010; Paneer Selvam et al. 2012), but there is scanty literature available in the detailed core sediment geochemistry (Harikumar et al. 2009; Harikumar and Nasir.2010). Most of the studies are based on one time or seasonal sampling during a year sample collection from areas known for environmental pollution. Though in any area in which the distribution of inorganic pollutant in sediments collected over a considerable time period can provide a clue for change in the environment and such studies are limited. The present effort mainly intends to remove the gap in the core sediment chemistry by characterizing metal fractions in the core sediment from different hotspot sites of the CES. The main objectives of the study are

- To analyze the concentrations and the distribution of metals in the 17 surface sediment and selected core sediments of the CES.
- Metal fractionation in the surface and core sediment in the three zones of the CES.
- Develop a comprehensive explanation and the interrelationships between the environmental components.

****

Chapter 2

METHODOLOGY

Contents

2.1 Study Area

Cochin Estuarine System (CES), 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 CES (Gopalan et al. 1983). The development activities in and around the CES have added all the complexities and environmental dilemmas in this coastal niche. 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 rapid growth in the region accompanied by very high population growth, housing shortages, haphazard industrial and commercial improvement along transportation corridors has greatly increased the problems of urban development.

The study area was situated in the CES and divided into three zones viz south, middle, and north (Figure 2.1).

South Zone: The zone situated in the fresh water region, originated from the southern bough of the Moovattupuzha. Major source of pollution is from sewage and agricultural runoff. This zone is far from the industrial effluents.

Middle Zone: 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. With the advent of ICTT (International Container Transhipment Terminal) project, this area has become the backbone of the economy of the State of Kerala. 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 was 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.

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 pollutants in the Periyar River.

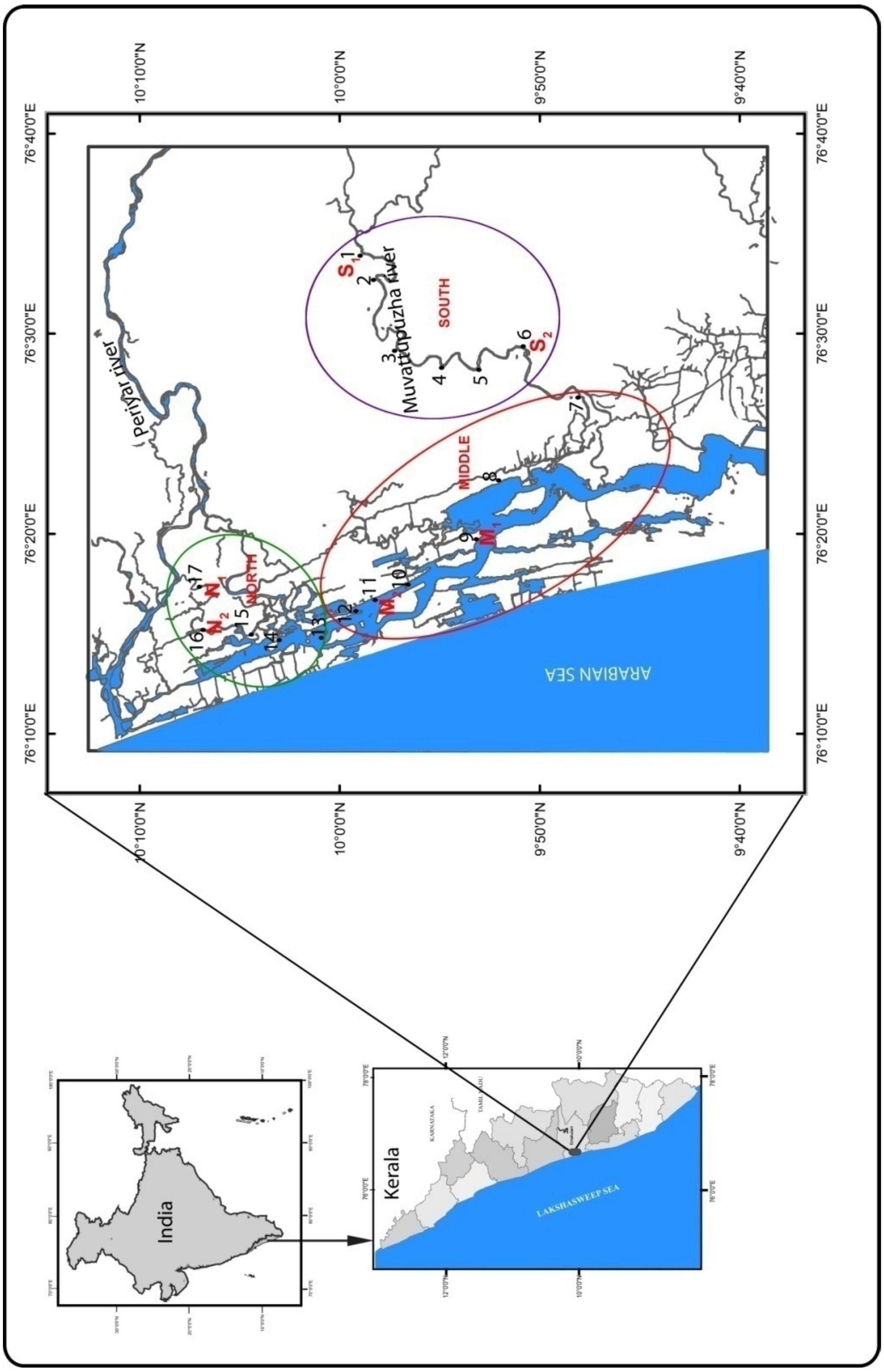


Figure 2.1 Zonal classification of Cochin Estuarine System

2.2 Sampling and Methods

Surface and bottom water samples were collected from 17 stations (Figure 2.2) of Cochin estuary during November 2009 and 2011. Surface water samples are collected by clean bucket and bottom water by a Niskin sampler. Surface sediments (Figure 2.2) (top 0-5 cm) were collected from 17 locations of CES during November 2009 and 2011 (Post monsoon). This was performed using a stainless steel grab sampler and 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 the samples were kept in ice chest boxes on board during transportation. The sediment samples were preserved at 4^0C until analysis. The sediment cores (Figure 2.3) were collected at low tide by pushing a hand held PVC pipe (150 cm long with a diameter of 6.3 cm) in November 2009 and 2011(Table 2.1) by the help of a skin diver at the prominent zones of the CES, with varying depths (1-3.50 m) of the water body. The sediment cores were sliced according to lithology, transferred to plastic vessels. The pH (Thermo Orion 420A+ model) of the sub samples was immediately measured and then they were frozen at 4^oC for further analysis. These subsamples were air dried, finely powdered 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 and Rantala. 1992) and metal concentration was analyzed by AAS (Perkin Elmer 3110). Physicochemical parameters were determined according to standard procedures. Total organic carbon (TOC), CHNS were determined using respective analyzers.

Sequential extraction procedures (SEP) are operationally defined methodologies that are widely applied for assessing metal mobility in sediments (Stephens et al. 2001; Svete et al. 2001), soils (Mossop and Davidson. 2003) and waste materials (Alvarez et al. 2002). Single extractions are thus used generally to provide a rapid evaluation of the exchangeable metal fraction in soils and sediments (Sahuquillo et al. 2003). Fractionation of metal was carried out according to Tessier et al. 1979.The following five fractions were selected:

Fraction 1. Exchangeable

This fraction involves weakly adsorbed metals retained on the surface by relatively weak electrostatic interaction, metals that can be released by ion-exchangeable processes etc. Remobilization of metals can occur in this fraction due to adsorption desorption reactions and lowering of pH. Exchangeable metals are a measure of those traces metals which are released most readily to the environment. Corresponding metals in the exchangeable fraction represent a small fraction of the total metal content in soil, sewage sludges and sediments and can be replaced by neutral salts.

Fraction 2. Bound to Carbonates

The carbonate fraction is a loosely bound phase and viable to changes with environmental factors such as pH. The time lag for the complete solubilisation of carbonates depends on some factors such as the type and amount of the carbonate in the sample, particle size of the solid. Extraction of metals from carbonates phases enhances the leaching of metals specifically sorbed to organic and inorganic substrates. In general this fraction would be susceptible to changes of pH.

Fraction 3. Bound to Iron and Manganese Oxides

This fraction is referred to as sink for metals. This can occur as a combination of the precipitation, adsorption, surface complex formation and ion exchange. Scavenging by these iron and manganese oxides exist as nodules, concretions, cement between particles, or simply as a coating on particles; these oxides are excellent scavengers for metals and are thermodynamically unstable under anoxic conditions.

Fraction 4. Bound to Organic Matter

Metals may be bound to various forms of organic matter: living organisms, detritus, coatings on mineral particles, etc. The complexation and peptization properties of natural organic matter (notably humic and fulvic acids) are well recognized, as is the phenomenon of bioaccumulation in certain living organisms. Under oxidizing conditions in natural waters, organic matter can be degraded, leading to a release of soluble metals.

Fraction 5. Residual

Residual phase contain mainly primary and secondary minerals, which may hold metals within their crystal structure. These metals are not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature. This serve as a useful tool in the assessment of the long-term potential risk of toxic metals entering the biosphere. Residual phase give an estimate of the maximum amount of elements that are potentially mobilisable with changes environmental conditions.

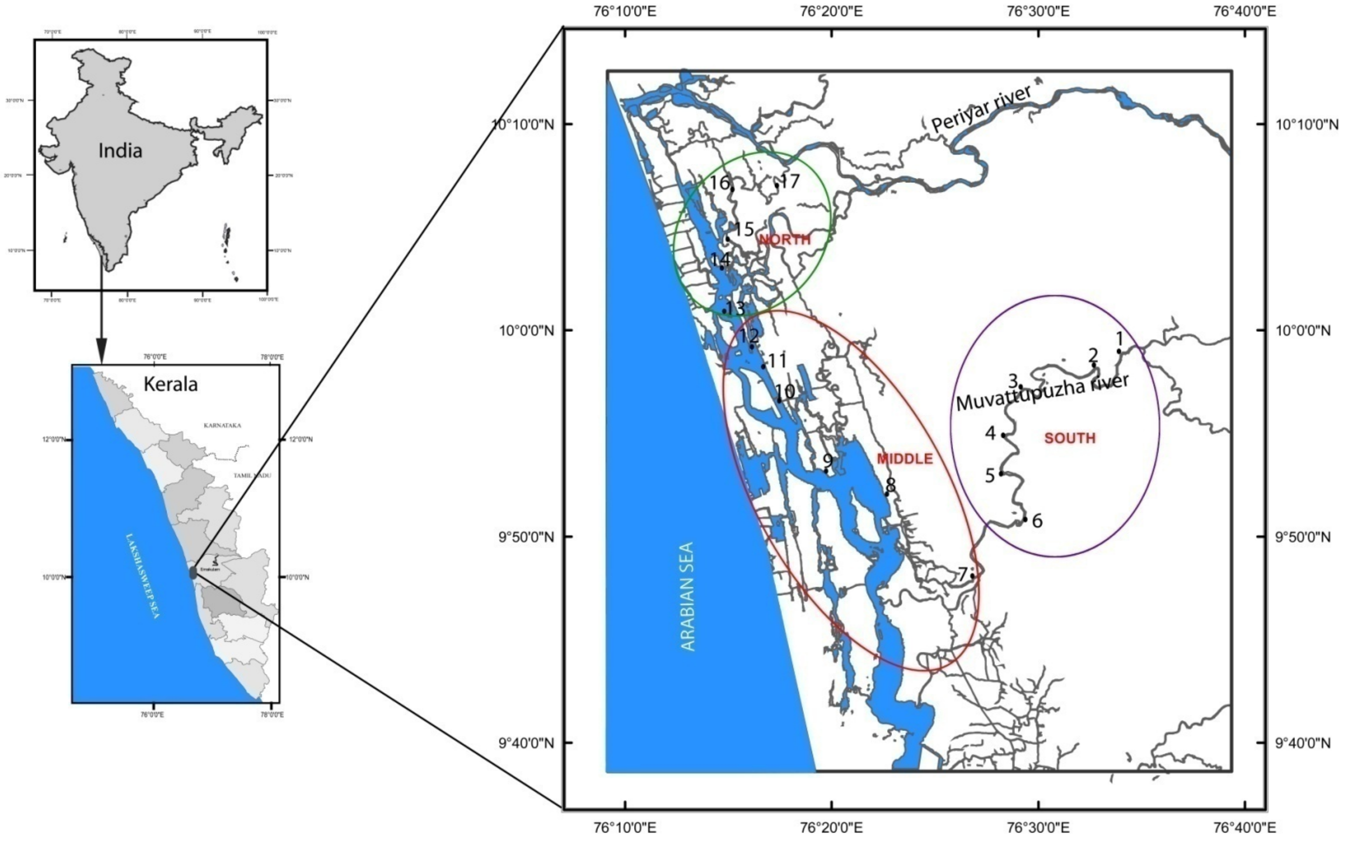


Figure 2.2 Surface sediment sampling stations

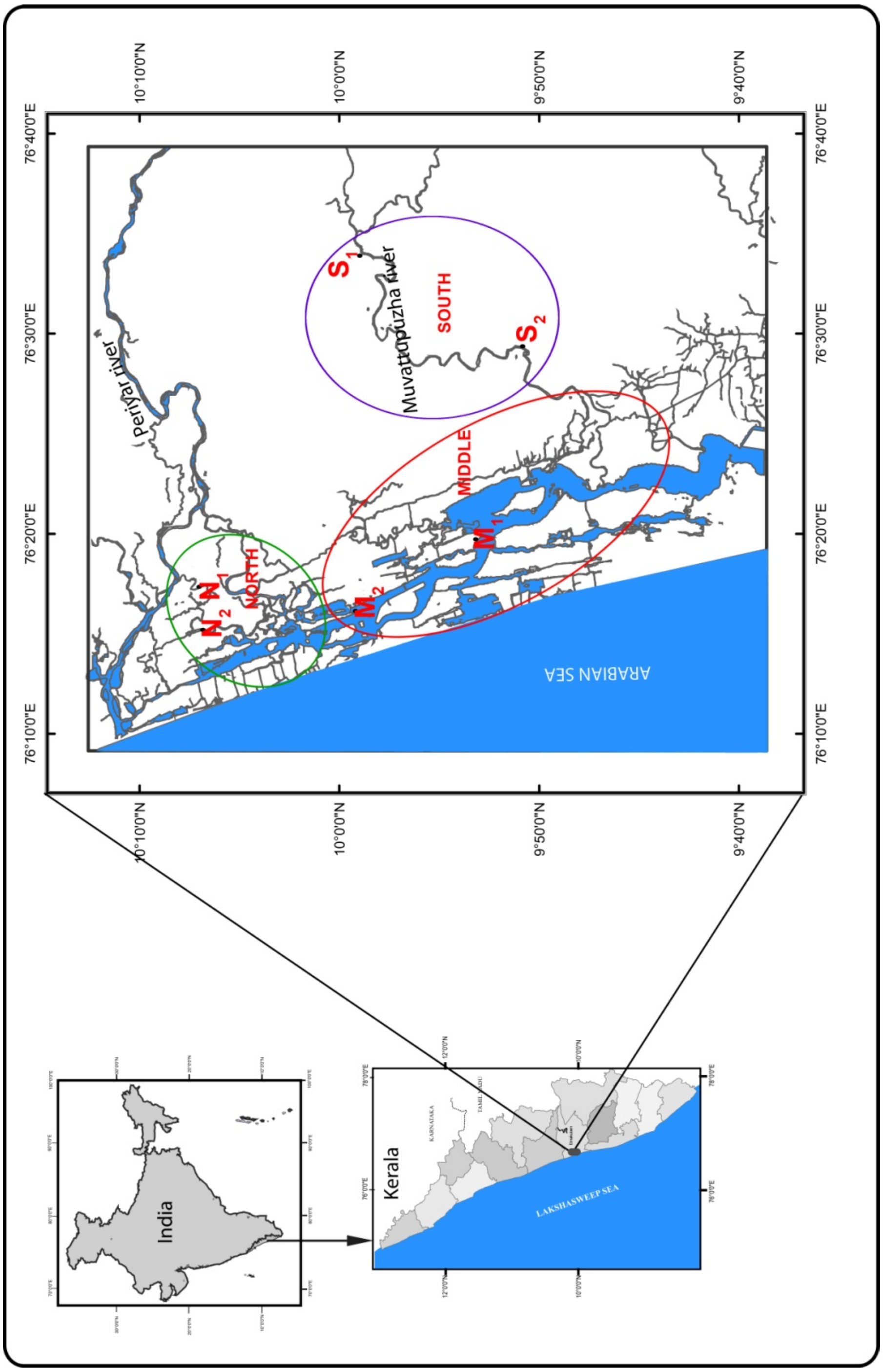


Figure 2.3 Core sediment sampling stations

Table 2.1 Core sampling description

Zones	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	

2.3 Sediment Quality Guidelines (SQG)

Sediment quality guidelines (SQG) are to protect the aquatic environment by setting safe levels for pollutants. The guidelines are designed to help Environmental Managers - Ministry Officials and Environmental Consultants to make decisions on a whole range of issues that affect the quality of sediment. The different SQGs used in the study listed in Table 2.2.

Table 2.2 Sediment Quality Guideline

SQG	LEVELS	Cd ppm	Co Ppm	Cr ppm	Cu ppm	Fe %	Mg%	Mn ppm	Ni ppm	Zn ppm	Pb ppm
ELEMENTAL BACKGROUND		0.2	20	100	55	4.72	1.5	950.0	75.0	70.0	12.5
USEPA	NP	-----	-----	<25	<25	-----	-----	-----	<20	<90	<40
	MP	-----	-----	25-75	25-50	-----	-----	-----	20 - 50	90 - 200	40-60
	HP	-----	-----	>75	>50	-----	-----	-----	>50	>200	
ONTARIO MOE	LEL	0.6	-----	-----	16	-----	-----	460	16	120	31
	SEL	10	-----	-----	110	-----	-----	1110	50	820	250
NOAA SQG	ERL	1.2	-----	-----	34	-----	-----	-----	20.9	150	46.7
	ERM	9.6	-----	-----	270	-----	-----	-----	51.6	410	218
FDEP SQG	TEL	0.68	-----	-----	18.7	-----	-----	-----	15.9	124.0	30.2
	PEL	4.20	-----	-----	110	-----	-----	-----	43	271	110
CCME	IGM	0.6	-----	-----	35.7	-----	-----	-----	123	-----	35
	PEL	3.5	-----	-----	197	-----	-----	-----	315	-----	91.3
ANZECC	ISQG	0.7	-----	52.3	18.7	-----	-----	-----	-----	124	-----
WHO			2.0	25	25	-----	-----	30	20	123	-----
CBSQG		0.99	-----	43	32	-----	-----	460	23	120	36

NP:Non Polluted ,MP: Moderately Polluted, HP: Heavily Polluted, LEL:Lowest effect level, SEL:Severe effect level, ERL:Effect range low,ERM:Effect range median,TEL:Threshold effect level,PEL:Probable effect Level,IGM:Interiem sediment Quality goals

Precisions of the analytical procedure were checked using a triplicate analysis of a certified reference material (BCSS-1) from the National Research Council of Canada (Table 2.3). The results were mostly comprised within the uncertainty associated to certified concentration.

Table 2.3 Comparitive values of BCSS-1 in the present study

Concentration (ppm)	Cd	Cr	Co	Cu	Pb	Fe	Mg	Mn	Ni	Zn
Metal extracted[a]	0.3	123	11.4	18.5	22.7			229	55.3	119
Metal extracted[b]	0.291	133	9.2	18.2	19.6	29200		209.8	61.1	114.6
Accuracy (± %)	3	9	10	2	20			8	11	4

[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.

2.4 Geo Chemical Indices (GCI)

2.4.1 Enrichment Factor (EF)

Enrichment factor were interpreted as suggested by Birth. 2003 for metal studied with respect to natural background concentration. The enrichment factor (EF) for elements in the sediment and cores were calculated according to the formula

$$EF = (C_x / C_{Fe})_s / (C_x / C_{Fe})_c$$

where C_x and C_{Fe} refer to the concentrations of element *x* and Fe in the sediments (*s*) and earth's crust (*c*) respectively. Iron is used here as the reference element.

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.

2.4.2 Anthropogenic Factor (AF)

The anthropogenic factor (AF) for the cores were calculated by using the formula (Morillo et al. 2004).

$$AF = C_s/C_d$$

where C_s and C_d are the concentrations of the element in the sediments and sediments at depth in the sediment column. If AF > 1 for a particular metal means contamination exist. AF < 1 there is no metal enrichment of anthropogenic origin.

2.4.3 Contamination Factor (CF) and Pollution Load Index (PLI)

To assess the extent of metal contamination, contamination factor was calculated for sediments using measured concentration of metals and respective world shale average reported by Turkian and Wedephol. 1961. However, the pollution levels in the sampling sites were calculated based on Tomlinson et al. 1980 developed Pollution Load Index (PLI).

$$CF = C_m / C_b$$

$$PLI = n\surd\ (CF_1 \text{ x } CF_2 \text{ x } CF_3 \text{ x} \dots\dots\dots \text{x } CF_n)$$

Where CF=contamination factor, n =number of metals; C_m = metal concentration in polluted sediments; C_b = background value of that metal.

CF was classified into four groups in Hakanson. 1980: CF < 1, low contamination factor; 1 < CF < 3, moderate contamination factor; 3 < CF < 6, considerable contamination factor; and CF > 6, very high contamination factor.

The PLI value of > 1 is polluted whereas < 1 indicates no pollution.

2.4.4 Geoaccumulation Index

The geoaccumulation index (IGEO) described by Salomons and Fo¨rstner. 1984; Howari and Banat. 2001 and Santos et al. 2003 is considered as a measure of the contamination by metals. This index is acquired by means of computing the base two logarithm of the quotient of the total concentration of the element obtained in each sample (C_n) over the average of the total concentration measured in the uncontaminated zone (B_n) multiplied by 1.5 (a correction factor for background values), this is: IGEO = $\log_2 C_n/(1.5\ B_n)$. Seven classes of geoaccumulation index is present in sediments (Muller. 1969), where *I*geo < 0 refers to unpolluted, IGEO = 0-1 refers to unpolluted to moderately polluted, IGEO = 1-2 refers to moderately polluted, IGEO = 2-3 refers to moderately to heavily polluted, IGEO = 3-4 refers to heavily polluted, IGEO = 4-5 refers to heavily to extremely polluted, and IGEO > 5 refers to extremely polluted.

2.4.5 Risk Assessment Code (RAC) and Mobility Factor (MF)

To evaluate the risk and metal mobility associated with labile fractions of metals, the relative index was applied to calculate the risk-assessment code (RAC) and mobility factor (MF) on the basis of the ratio of EXC and CA fractions to the sum of all fractions (Perin et al. 1985; Kabala and Singh. 2011).The risk assessment code (RAC) (Jain. 2004) which takes into account the mobility fraction of the metal and was evaluated in order to identify the extent of risk associated with the percentage of metals present in the sediments. The relative index of metal mobility was calculated as a mobility factor (Narwal et al. 1999, Kabala and Singh. 2011) assessed on the basis of absolute and relative content of fractions weakly bound to sediment components. A sediment containing less than 1% of exchangeable and carbonate fractions is considered safe for the environment; 1-10% of these fractions is regarded as low risk; medium risk category falls in 11-30% of these fractions; mobile fractions with values 31-50% and more than 50% are considered as high risk and very high risk categories respectively since the metals found in these fractions are bioavailable and it may easily enter into the food chain.

2.4.6 Non-Residual Fractions Enrichment Factor (KNRF)

In order to quantify the anthropogenic contamination of the metals according to the fractionation compositions, the *K*NRF approach is presented in this paper. The *K*NRF of the metals is calculated using the following formula. $K\mathrm{NRF} = (M\mathrm{NRF}(\mathrm{a})/\ M\mathrm{TOT}(\mathrm{a}))/(M\mathrm{NRF}(\mathrm{b})/M\mathrm{TOT}(\mathrm{b}))$ where *M*NRF(a) and *M*NRF(b) are the non-residual fractions concentrations of the metals in the interest and background sediments, *M*TOT(a) and *M*TOT(b) are the total concentrations of the metals in the interest and background sediments.

2.5 Statistical Analysis

Statistical analysis is particularly useful to process large amounts of data and report overall trends. It provides ways to objectively report on how unusual an event is based on historical data. In this principal Component Analysis (PCA) and correlation analysis (SPSS, 15.0) was done to understand the interrelationship between the parameters were utilized to assess the biogeochemical characteristics of the study region.

Annexure

Table 2.4: Expansions of SQGS

SQGS	EXPANSIONS
USEPA	United States Environmental Protection Agency
ONTARIO MOE	Ministry of the Environment
NOAA SQG	National Oceanic and Atmospheric Administration
FDEP	Florida Department of Environmental Protection
CCME	Canadian Council of Ministers of the Environment
ANZECC	Australian and New Zealand Environment Conservation Council
WHO	World Health Organization
CBSQG	consensus-based SQGs

****

Chapter 3

METAL FRACTIONATION OF THE SURFACE SEDIMENT IN CES

Contents

3.1 Introduction

The world population has increased almost thrice in the last 60 years and is estimated to increase from about six billion currently to 8.3 billion by 2025 (Bowen and Crumbly. 1999). Nearly, 60% of the world population is recorded to live in coastal areas and the present population of the coastal areas exceeds the global population of just 50 years ago. Majority of the people worldwide rely on seafood as the main source of protein in their diet and the consumption continues to increase globally. These food sources were contaminated from point source of pollution. Overpopulation, rapid urbanization and industrial revolution had discarded tremendous amounts of toxic pollutants into the ecosystem. Many of these wastes were potential sources for metal contamination that have the prospective threat for the balance of the aquatic environment. Metals that enter these environments will settle and become incorporated into the sedimentary reservoir (Salomons and Stigliani. 1995; Peng et al. 2009). Therefore, analysis of metal content in sediments can reflect the pollution level of the water body. Previous studies on assessment of metals in sediments from estuarine and coastal areas are useful to assess the varying pattern of pollution status in the marine environment (Bellucci et al. 2003; Pekey. 2006; Buccolieri et al. 2006; Anithamary et al. 2012). Metals have the ability to concentrate in organism directly from the water, then accumulate and finally lead to biomagnification in the food chains, causing higher trophic organisms in contamination with elevated levels of pollutants. Hence it is imperative to understand the geochemical distribution and transport of metals in the sediment stratum in order to develop pollution control strategies and adopt suitable approaches for water quality management in the estuarine area.

CES, one of the largest tropical estuaries of India, is facing gross pollution problems due to the untreated or partially treated effluents from industries and domestic sectors. A number of investigations in recent years in this estuarine system conducted (Shajan. 2001; Balachandran et al. 2005, 2006; Renjith and Chandramohanakumar. 2009; Ratheesh Kumar et al. 2010; Paneer Selvam et al. 2012; Deepulal et al. 2012) and revealed the high significance of this estuarine system for pollution studies. A review on these geochemical researches on sediment was carried out so far disclose that considerable amount of work still remains to entangle with regard to the metal geochemistry. Metal pollution levels in sediments of CES showed an increase in metal concentrations over the past several decades. The estuary potentially attributed to an annual loading of effluents from approximately 250 chemical industries situated in the northern part (Shibu et al. 1995; Paneer Selvam et al. 2012; Martin et al. 2012). Toxic elements released into the aquatic system are often clubbed to particulate matter, which eventually settles and incorporates into the sediments. However major portion of the sediment bound metals may remobilize and be released back to the water column with a change in environmental conditions, and pose adverse effects on living species. The reported high enrichment factors of metals place the study region CES as one among the impacted estuaries in the world (Balachandran et al. 2005). Similarly, Ratheesh et al. 2010 reported severe enrichment for Cd in the CES. Moreover, the geoaccumulation index of metals also showed very strong evidence for metal pollution condition in these estuarine sediments (Ratheesh et al. 2010; Deepulal et al. 2012). Most of the earlier studies in CES were based on one time or seasonal sampling during a year from these areas. Though in any area in which distribution of pollutants in sediments collected over a considerable time period can provide a clue for the change in the environment pattern and such studies are limited.

In this context, the present work attempted to highlight the first detailed monograph on biennial distribution and fractionation of metals in the surface sediments from selected prominent regions of CES. Thus, this primer is designed to acquaint the basic concentration of metal, their distribution and fractionation associated with the surface sediments collected from 17 stations situated in the CES. The link between geochemical indices and ecological risk assessment of these metals in the study area were also incorporated. These 17 surface sediment samples were grouped in to three zones – **south**, **middle** and **north** based on the environmental variability such as the physicochemical and sediment characteristics. The results discussed hither are on the basis of three zones.

3.2. Physicochemical and Sedimentary Characteristics

General physicochemical properties of overlying water and sedimentary parameters were studied which could help to understand the metal flux in the estuary. Brief descriptions of sedimentary parameters are given in Table 3.1. Salinity was ranged between 0.81 PSU to 32.95 PSU. Dissolved oxygen varied between 1.96 mg/L to 6.95 mg/L in the middle and north zone respectively. Sedimentary parameters showed that the pH values varied from 5.1 to 8.7 and highest value was noted at the middle zone in the first sampling campaign (2009) and a minor variation exhibited during the second sampling (2011). Eh ranged between -109 mV to +286 mV. Texture analysis showed a progressive increase of fine fractions at southern (96%) and northern part (80%) of the estuary and coarse grains dominated at the middle part of the CES (80-95%) during 2009 and it was found a mixed nature with minor fluctuations during 2011 sampling periods. Percentage of TOC ranged from 0.34 to 6.25 and was significantly higher at southern and northern part of the estuary (Figure 3.1).

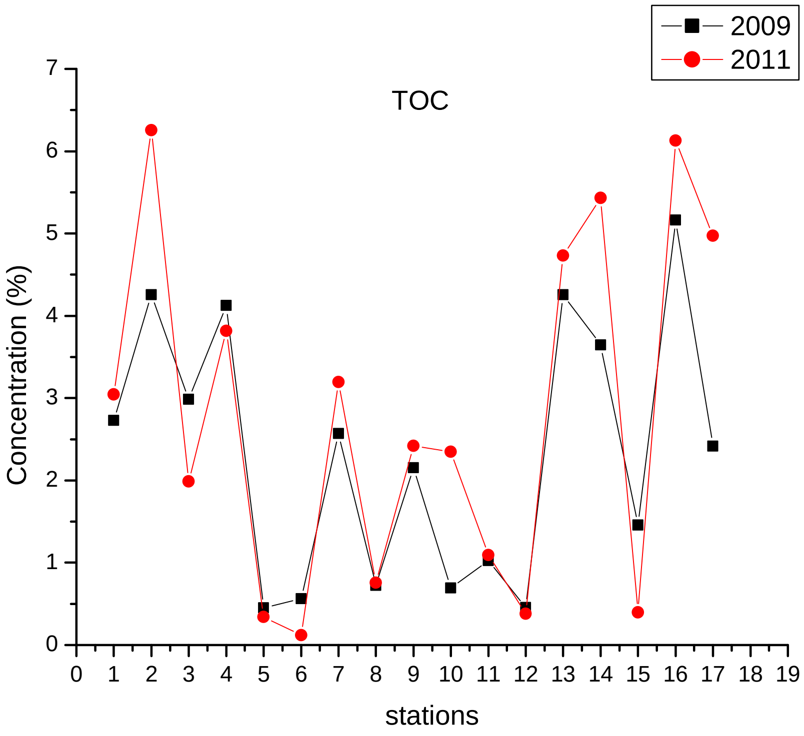


Figure 3.1 Spatial Variation of TOC

Table 3.1 Descriptions of 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

3.3 Biennial Metal Discrepancy in the Surface Sediments of CES

In recent years, CES has become one of the distinguished regions in India due to the vast industrial and urban development activities aroused in various sectors. As a part and parcel of this, a variety of chemicals in turn discharges enormous wastes thrown out into the aquatic system and contribute significant enhancement of metal levels.

Even though enough work has been carried out so far in this respect within the estuary (Shajan. 2001; Balachandran et al. 2005, 2006; Renjith and Chandramohanakumar. 2009; Ratheesh Kumar et al. 2010; Paneer Selvam et al. 2012), this research work also details the continuous monitoring of metal variations in a two year gap (2009-2011) period. The residual metal concentrations were given in Table 3.2.

Table 3.2 Table 3.2.Biennial comparison of metal concentration (mg/Kg) in the surface sediment of CES

Year	Metals	Zones																
		South						Middle						North				
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
2009	Cd	2.58	0.85	1.29	1.24	3.24	0.25	2.64	2	1.99	11.53	1.34	5.5	19.73	32.52	0.7	16.39	14.02
	Co	14.68	10.08	0	4.37	21.06	0	12.28	0	5.13	72.75	15.97	25.3	38.58	74.6	0	91.34	68.39
	Cr	79.76	34.48	0	132.41	47.55	75.15	0	125.8	51.54	0	35.57	0	0	0	54.17	0	0
	Cu	43.8	25.05	14.93	35.64	36.33	11.85	26.9	20.45	40.89	55.49	8.78	55.05	27.46	151.54	10.44	72.52	77.19
	Pb	114.09	135.23	104.17	111.83	109.78	113	142.22	123.5	133.47	112.28	109.62	79.7	80.71	97.61	99.4	117.82	131.21
	Fe	286.46	4347.55	4704.86	6843.94	12372.75	3152.5	10848.3	6131.25	5920.07	67465.07	3642.11	61001.24	64942.18	68544.57	2017.89	68303.22	68500.25
	Mg	64.98	60.38	18.35	26.64	39.32	23.3	110.03	63.35	75.3	264.12	28.97	277.57	306.94	243.97	27.73	249.55	240.51
	Mn	508.18	292.96	128.52	188.82	9.31	1.65	3.63	122.45	127.04	4.3	0.18	3.67	4.09	3.88	1.07	9.33	9.33
	Ni	53.75	49.22	53.61	57.19	49.81	45.58	53.12	42.38	51.11	480.12	56.51	228.61	434.56	496.75	56.18	493.81	431.57
	Zn	5.31	4.89	5.16	5.47	4.79	4.55	5.69	4.95	4.98	233.18	5.61	126.68	243.65	269.57	5.47	239.11	213.57
2011	Cd	6.23	5.97	5.4	5.48	3.5	2.67	6.24	3.49	4.72	11.37	7.11	6.69	38.02	41.47	5.99	6.9	10.54
	Co	27.57	39.05	31.93	31.63	9.07	4.55	35.41	7.73	3.3	25.2	54.5	13.63	30.87	34.81	5.59	54.68	39.16
	Cr	0	0	0	0	0	0	2.26	0	7.33	0	0	0	0	0	0	0	0
	Cu	29.1	24.21	26.98	36.97	2.32	0	0	35.14	37.2	26.77	14.87	2.51	56.26	157.64	0	42.01	58.47
	Pb	82.02	51.28	49.5	59.13	41.91	14.33	129.67	66.93	157.97	114.67	59.78	50.2	127.71	149.41	24.26	150.39	0
	Fe	50734.93	50449.95	52629.95	48377.4	9338.02	5673.17	51203.34	14025.59	41523.13	46352.12	39433.05	10580.71	41481.76	68447.98	68966.58	6872.53	61540.84
	Mg	0	9.08	0	0	0	0	19.16	2.65	56.92	12.87	3.67	0	0.2	0	0	0	0
	Mn	21.13	17.22	14.43	16	1.55	-0.75	11.98	6.55	5.68	5.34	6.75	1.39	7.82	7.22	1.49	26.44	4.37
	Ni	201.45	98.36	95.81	78.13	180.24	69.81	98.33	82.31	99.81	95.75	89.31	118.45	207.81	488.81	455.74	531.21	666.72
	Zn	5.61	10.93	5.21	1.69	3.59	3.05	8.93	4.9	8.37	26.7	14.83	11.58	4.43	4.93	9.74	17.03	27.93

Table 3.3 Comparison of metal concentrations (mg/Kg) in CES with Indian and globally impacted systems

Location	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Zn	References
CES	41.47	91.34	132.41	157.64	68,966.58	306.94	508.18	87.65	157.97	269.57	Present Study
CES	10.5	40.7	200.9	59.2	98000	NA	1,086	79.0	46.8	973.7	Paneer Selvam et al. 2012
CES	9.5	NA	V	166.14	115200	NA	NA	NA	221.37	1249.44	Mahesh Mohan et al. 2012
CES	40.7	NA	NA	123.5		NA	NA	NA	99.6	2233.0	Martin et al. 2012
CES	7.04	NA	NA	126.25	43421	NA	NA	60.70	31.41	248.79	Pratheesh. 2011
CES	0.22	23.08	90.22	39.12	58,300	17,800	315.32	69.35	39.5	455.68	Ratheesh Kumar et al. 2010
CES	0.08		0.71	243.60	NA	NA	29.47	1.93	23.62	554.23	Harikumar and Jisha. 2010
Zonguldack, Black Sea, Turkey		NA	NA	30.21		NA	NA	NA	39.14	84.6	Coban et al. 2009
Nile	2.42	NA	NA	13.3	46500	NA	NA	NA	89.61	106.38	Lasheen and Ammar. 2008
Ganga	NA	NA	NA	717.09	152700	NA	NA	NA	466.32	569.91	Purushothaman and Chrakrapani. 2007
CES	4.33	NA	NA	6.72	53000	NA	NA	NA	35.5	542.2	Balachandran et al. 2006
Achankovil	6	NA	NA	224	11900	NA	NA	NA	221.37	415	Prasad et al. 2006
CES	14.94	NA	NA	53.15	61800	NA	NA	NA	71.28	1266	Balachandran et al. 2005
Queensland, Australia	NA	NA	NA	19.19	NA	NA	NA	NA	29.31	80.02	Liaghati et al. 2003
Harbour and Mytilene Coast, Greece	NA	NA	NA	86.2	NA	NA	NA	NA	95	230	Aloupi and Angelidis. 2002
Mediteranian Sea, France	NA	NA	NA	82.6	NA	NA	NA	NA	509.3	393.6	Fernex et al. 2001
Jurujuba sound , Brazil	NA	NA	NA	51	13000	NA	NA	NA	61	158	Baptista Neto et al. 2000

NA-Not Available

Metal distribution in the first sampling campaign (2009) was detailed in the initial part of this section and the results were compared with the analysed concentration levels in the second sampling.

The concentration of Cd ranged from 0.25 mg/Kg to 3.24 mg/Kg in southern zone at stations 6 and 5 respectively. In middle zone, Cd content was varied between 1.34 mg/Kg (station no.11) to 11.53 mg/Kg (station no.10). Northern zone revealed as the minimum and maximum content of

Cd at station no.15, 0.7 mg/Kg and at station no.14, 32.52 mg/Kg. The cadmium concentration recorded in the present study was above the permissible limit (0.6- 10 mg/Kg) given by different SQGs listed in Table 2.2 in Chapter 2. Similar observations were reported (Padmalal et al. 1997) and noticed a high concentration of Cd in the same vicinity of the estuary. Other studies on Cd in estuarine sediments have reported for polluted areas like Mezica valley (Slovenia), had Cd concentrations in the range of 20.5–130.0 mg/Kg (Svete et al. 2001; Tack and Verloo. 1999), whereas in unpolluted areas, Arosa estuary NW Spain were within the range of 1.56–8.0 mg/Kg (Santamaria-Fernandez et al. 2005; Svete et al. 2001). On comparison with the earlier reports (Table 3.3) with in the CES and other impacted estuaries, Cd concentration was heavily magnified. Earlier results reported by Martin et al. 2012 also justify the above trend. These inferences of Cd distribution establishes severe contaminant load of Cd in the northern part of the estuary. These outcomes were strongly agrees with the previous published research reports (Ratheesh et al. 2010; Martin et al. 2012; Paneer Selvam et al. 2012). Finally, the sediment samples investigated in the study area are considered as moderate to severely polluted by Cd.

Among the southern zone stations, concentration of Co was higher at station no.5 (21.06 mg/Kg) and BDL at stations 3 and 6. Middle zone showed intensified value for Co at station no.10 (72.75 mg/Kg) and diminished to BDL at station no.8. In the north zone, Co content was high at station no.16 (91.34 mg/Kg) and BDL at station no.15. The concentration of Cobalt observed in the present study was above the permissible limit (2 mg/Kg) which resulted severe pollution in the northern part of the estuary and observed very high concentration as compared to the earlier reports of the same aquatic system (Ratheesh et al. 2010; Martin et al. 2011; Paneer Selvam et al. 2012).

In south zone, Cr content showed from BDL (station no.3) to 132.41 mg/Kg (station no.4). Concentration of Cr in the middle zone ranged between BDL (station nos. 7,10,12) to 125.8 mg/Kg (station no.8) and it was found only at station no.15 (54.17 mg/Kg) in the northern region of the estuary. Cr content was high at central part of the estuary. On comparison with the different SQGs (Table 2.2 in Chapter 2), the content of Cr was above the permissible limit (25-75 mg/Kg). Cr was found to be of elevated values as compared with other estuaries (Table 3.3). Paneer Selvam et al. 2012 reported a higher concentration (200.9 mg/Kg) than the above trend.

Southern zone showed greater content of Cu at station no.1 (43.80 mg/Kg) and diminished content at station no.6 (11.85 mg/Kg). Cu content was high (55.49 mg/Kg) and low (8.78 mg/Kg) at station no. 10 and 11 respectively in middle zone. In the northern region of the estuary Cu concentration was dominant at station no.14 (151.54 mg/Kg) and decreased at station no.15 (10.44 mg/Kg). Greater concentration of Cu was observed at northern part of the estuary. The Copper concentration cited in this study was moderately above the permissible limit (16- 270 mg/Kg) as given by different SQGs listed in Table 2.2 in Chapter 2. It has been reported that the concentration of Cu in polluted areas ranges from 20.0 to 343.0 mg/Kg, while in unpolluted areas, it will be between 1.0 and 13.0 mg/Kg (Santamaria-Fernandez et al. 2005; Spencer and MacLeod. 2002; Sulivan and Taylor. 2003). Cu concentration in this study revealed moderate pollution. The amount of Cu was increased in this study except two, one within the system reported by Mahesh et al. 2012 (166.14 mg/Kg) and other was from Ganga by Purushothaman and Chakrapani. 2007 (717.09 mg/Kg).

At station no.5 noted as high value for Fe (12372.75 mg/Kg) and low at station no.1 (286.46 mg/Kg) in the south zone of the estuary. In the middle region, increased Fe concentration was observed (10848.3 mg/Kg) and decreased the content as 3642.11 mg/Kg at station nos: 7 and 11 respectively. Northern zone exposed heavy Fe content (68544.57 mg/Kg) at station no.14 and less (2017.89 mg/Kg) at station no.15. Heavy load of Fe was found in the northern region of the estuary. Residual level of Fe was increased in the study area as compared to the previous reports (Table 3.3), but there are exceptions showing heavy concentration of these by Purushothaman and Chrakrapani. 2007 (152700mg/Kg) and Mahesh et al. 2012 (115200 mg/Kg).

Concentration of Mg in the south zone was high at station no.1 (64.98 mg/Kg) and low at station no.3(18.35 mg/Kg); middle zone ranged as 28.97 mg/Kg (station no.11) to 277.57 mg/Kg (station no.12) and in the northern region the concentration ranged between 27.73 mg/Kg (station no.15) and 306.94 mg/Kg (station no.13). These results showed that Mg was intensified in the north zone of the estuary. On comparison with Table 3.3, Mg showed a less amount for the present study than the previous report in CES by Ratheesh Kumar et al. 2010 (17200 mg/Kg).

Content of Mn in the southern zone showed lower (1.65 mg/Kg) at station no.6 and high (508.18 mg/Kg) at station no.1. In the middle zone, Mn content was dominant at station no.9 (127.04 mg/Kg) and lower at station no.11 (0.18 mg/Kg). In the northern part of the estuary, less concentration of Mn was found at station no.15 (1.07 mg/Kg) and greater was noted at station no. 16, 17 (9.93 mg/Kg). Mn content showed to be high in the southern part of the estuary. The Manganese concentration analysed in this study was moderately above the permissible limit (30 - 3000 mg/Kg) as given by different SQGs listed in Table 2.2 in Chapter 2. Concentration of Mn was high in this study as compared within the system and the other reports listed in the Table 3.3.

The southern part of the estuary showed greater Ni content at station no.1 (57.19 mg/Kg) and less at station no.6 (45.58 mg/Kg). Middle zone revealed high content of Ni at station no.10 (480.12 mg/Kg) and diminished at station no.8 (42.38 mg/Kg). In the North zone, Ni ranged between 56.18 mg/Kg (station no.15) and 496.75 mg/Kg (station no.14). Thus Ni revealed a high concentration in the southern part of the estuary, which was accounted by heavy sewage and domestic runoff. The Nickel concentration cited in this study was moderately above the permissible limit (16-315mg/Kg) given by different SQGs listed in Table 2.2 in Chapter 2. Concentration of Ni was enormous in this study as compared within the system and the other reports listed in the Table 3.3.

Pb concentration > 100 mg/Kg in most of the stations, south zone ranged from 104.17 mg/Kg (station no.3) to 135.23 mg/Kg (station no.2), middle zone ranged between 109.62 mg/Kg (station no.11) and 142.22 mg/Kg (station no.7), northern region, noted high concentration at station no.17 (131.21 mg/Kg) and low at station no.12 (79.70 mg/Kg). Earlier, high levels of Pb, 26–630 mg/Kg, were detected in the sediments of polluted areas (Aloupi and Angelidis. 2002; Leivuori. 1998; Everrarts and Fischer. 1992) and low levels of Pb, 0.5–60 mg/Kg, were found in the sediments of unpolluted regions (Leivuori. 1998) reported elsewhere. The Lead concentration cited in this study was above the permissible limit (12.5- 400 mg/Kg) given by different SQGs listed in Table 2.2 in Chapter 2. The Pb concentration recorded in the current study were highly intensified at the central part of the estuary. The Pb content was greater in this study except two previous reports, one within the system reported by Mahesh et al. 2012 (221.31mg/kg) and other was from Ganga by Purushothaman and Chakrapani. 2007 (466.32 mg/Kg).

The concentration of Zn varied from 4.55 mg/Kg to 5.47 mg/Kg in southern zone at stations 6 and 4 respectively. In the middle zone, Zn content was varied between 4.95 mg/Kg (station no.8) to 233.18 mg/Kg (station no.10). Northern zone revealed as a minimum content of Zn at station no.15 (5.47 mg/Kg) and maximum at station no.14 (269.57 mg/Kg). Northern and middle region were Zn enriched zones. Previous studies showed that Zn concentrations in the polluted sediments were up to 4,000 mg/Kg (Everrarts and Fischer. 1992; Spencer and MacLeod. 2002) and in unpolluted sites, it ranged from 9 to 162 mg/Kg (Ridgway et al. 2003). The Zinc concentration analysed was moderately above the permissible limit (70-820 mg/Kg) given by different SQGs listed in Table 2.2 in Chapter 2 and will lead to generate moderate pollution in the study area.

On comparing the concentration of metal obtained in the first sampling periods (2009) with that of second (2011) revealed that similar trend was observed for Cd, Co, Cu, Fe, Mn and Pb; but for Ni and Zn, there is a slight deviation in the distribution pattern. Ni and Zn had lower than that of the first sampling campaign (2009). The result obtained in biennial evaluation of metal concentration values in the present study with the earlier research reports in the estuary and the other recognized polluted area are given in Table 3.3. Comparison of metal concentration with the maximum values reported worldwide generate most of the inference that metals were of the same magnitude or even higher than those information for other polluted estuaries, placing the region as one among the impacted estuaries around the world.

Major enrichment for the metal concentration was observed in the northern and middle zone in both the sampling (2009 and 2011) periods. These are in close agreement with previous report as levels of Fe, Mn, Ni, Zn, Cd, Co, Cr, Cu and Pb in the surficial sediments of the estuary which rendered significantly high concentration in the northern parts of the estuary (Nair et al. 1990; Balachandran et al. 2005; Martin et al. 2012). Cr and Mn in the sediments of the first sampling showed exceptions, as they were intensified in the southern zone.

Metals such as Fe, Mn, Ni, Zn, Cd, Co, Cr, Cu and Pb generally exhibited higher levels in the northern and central regions of the estuary. This is due to the dynamic nature, whereas the northern and southern zone showed flow restrictions and hence showed more sensitive to the accumulation of contaminants (Balachandran. 2008). Due to the weak flow and the huge input of industrial effluents, higher levels of metals were found in the northern estuary (Thomson. 2002). On the contrary, consistent with a strong flow, moderate levels of metals were found in the central estuary, which receives both domestic and industrial effluents. Decreasing trends in metal levels were detected towards the central estuary as compared with north may be due to strong rectilinear current, which maintains an effective flushing (Balachandran. 2008). Likewise, in relation with weak flow and minor inputs, lower levels of metals were characterized in the southern estuary, which receives agricultural wastes from Kuttanad Paddy fields.

The observed results showed high organic matter content and metal concentrations in the northern part of the estuary revealing fine particle dependence of these parameters (Table 3.1). Generally, TOC> 5% indicate the polluted nature of the estuary. The poor dependence between organic carbon and the metals indicates that metal enrichment in the estuary may be initiated by inorganic processes, such as precipitation and scavenging by hydroxides of Fe and Mn. Fe and Mn in the estuary were accumulated and spatially segregated, as a consequence of their different flocculation properties. Furthermore, both the increased Eh and low pH values in the southern and northern part of the study region also favour the sorption of metals in the sediment (Table 3.1). TOC: TS ratio also well supports these results. The possible enrichment mechanism appears to be estuarine coagulation and flocculation of elements as colloids in association with hydrous iron oxides under fluctuating salinity in the entire study area. Inadequate flushing of pollutants released in the flow restricted water bodies could promote coagulation or co-precipitation of metals under the prevailing ionic (salinity) condition (Cobelo-Garcia and Prego. 2004). These processes could be critical in the study area, CES revealing fluctuating salinity between

0.81 PSU and 32.95 PSU which are characterized the intensification of metal content.

3.4 Evaluation of Sediment Pollution with Sediment Quality Guidelines (SQG)

The level of pollution in the aquatic system can be simply assessed by different worldwide used SQGs. Detailed distribution were given in Table 2.2 in Chapter 2 .The ranges of metals in their comparative assessment are given in Table 3.4.

Table 3.4 Comparative assessment of Biennial metal variation in the surface sediments of CES

METALS	BIENNAL VARIATION (mg/Kg)		SQG (mg/Kg)	
	2009	2011	ERL	ERM
Cd	0.25 - 32.52	3.5 - 41.47	1.2	9.6
Co	0 - 91.34	3.3 – 54.68	-	-
Cr	0 – 132.41	0-7.33	-	-
Cu	8.78-151.54	0-157.64	34	270
Fe	286.46- 68,544.57	10,580.71-68,966.58	-	-
Mg	18.35 – 306.94	0-56.92	-	-
Mn	0.18 - 508.18	0.75 -26.44	-	-
Ni	35.56-70.65	44.56- 87.65	20.9	51.6
Pb	79.7-142.22	0- 157.97	46.7	218
Zn	4.55- 269.57	1.69-27.93	150	410

In most of the stations, all the metals identified had found to be of elevated concentration as compared to different SQGs. The US National Oceanic and Atmospheric Administration (NOAA) guidelines were used as interim measures to assess whether the concentrations of metals in sediments could have adverse biological impacts. Long et al. 1995 suggested two guideline values, namely, the ERL (effective range: limit) and ERM (effective range: medium) delineating three concentration ranges of a particular metal. If a metal occurs in concentrations below ERL value, effects on the biota would rarely be observed. At concentrations ≥ ERL but < ERM, the biota could "occasionally" be affected by the pollutant, whereas at concentrations ≥ ERM, effects would be expected to occur "frequently". Concentration of Cd in both the periods of study was higher than ERM indicating the frequent chance of adverse effect to biota. The values of Cu and Pb exhibit between ERL and ERM limit generating an occasional effect to the biota. For Ni, showed in between ERL and ERM and also greater than ERM created occasional and frequent effect to aquatic biota. Zn concentrations were less than ERL and in between ERL to ERM which generate rare and occasional pollutant effect to the aquatic biota. Zonal comparison of the adverse effect to biota gave the order as North Zone > Middle Zone >South Zone.

3.5 Geochemical Chemical Indices (GCI)

Majority of studies on the sediment contamination with metals come down to the determination of their content in samples without considering the specificity of their random and systematic variations. A good indicator of environmental pollution of sediments by metals can be assessed by measuring geochemical indices (GCI). The different GCI used in this study are enrichment factor (EF), contamination factor (CF), geoaccumulation index (*Igeo*) and pollution load index (PLI).

3.5.1 Enrichment Factor (EF)

Enrichment factor was attempted to differentiate between the metals originating from human activity and those from natural weathering processes. It is a powerful tool for the regional comparison of metal content in sediments and can be applied to determine enrichment of the studied metals with respect to crustal average (Nolting et al. 1999). Since Al, Fe, and grain size all tend to co-vary, the use of a single normaliser can often represent several underlying geochemical relationships. In this work, EFs were computed by normalizing with Fe (Blomqvist et al. 1992). Iron is a conservative element during diagenesis (Berner. 1980) and its geochemistry is similar to that of many metals both in oxic and anoxic environments. Natural concentrations of Fe in sediments are more uniform than Al and beyond the influence of humans which justify its use as a normaliser (Daskalakis and O'Connor. 1995).

Mg has minimal enrichment (EF < 3) in all the studied zones in the first sampling period, 2009. Mn had high enrichment (EF > 50) in the stations, sampled from south zone and minimal enrichment (EF < 3) in the middle and north zone. An exceedingly high enrichment (EF > 50) for Ni was noticed in south zone. In the middle-north region it had moderate to significant enrichment (EF = 3-30). Zn had significant enrichment (EF = 1-9) in the south zone and in the remaining zones revealed a minimal enrichment (EF <3). Cd, Co, Cr, Cu and Pb had out of due proportion of enrichment (EF > 50) in the southern zone. Middle and northern zone had significant enrichment (EF = 1– 10) for Co, Cr and Cu. Both Cd and Pb terrify by its magnitude of their enrichment (EF > 50), Co and Cu had moderate enrichment (EF = 3-5) and Cr had significant enrichment (EF = 2-16).

In the second set (2011) Mg, Mn and Zn were showed minimal improvement (EF <3) where Ni had significant observation (EF = 1-11). For Cd showed rich in enrichment (EF > 50) was noticed in both the southern-northern region whereas very high enrichment (EF = 25-50) was noted in the middle zone. Co had moderate embellishment (EF = 3-5) in the southern zone and significant enrichment (EF =2-18) in middle and north zone. In all the zones, Cr specifically showed minimal enrichment (EF < 3). For Cu the study inferred high enrichment (EF > 50) in the south zone and significant in middle- north region. Pb showed significant enrichment (EF = 2-11) in south- middle sites and extreme enrichment (EF > 50) at the north zone. To unveil, the northern and southern part of the estuary was magnified with all the toxic metals and it had a close agreement with the previous reported EF in the estuarine system (Ratheesh et al. 2010. Martin et al. 2012) .This may be inferred due to the weak flow and the huge input of industrial effluents, which were the real picture in the northern estuary and earlier reports by Thomson. 2002 also support these results. An EF value less than 1.5 suggests that, the metals may be entirely from crustal materials or natural weathering processes (Zhang and Liu. 2002 and Feng et al. 2004). However, an EF value greater than 1.5 suggests that a significant portion of the metal is delivered from non-crustal materials, or non natural weathering processes (Feng et al. 2004). In both the sampling period, most of the metals (Mn, Ni, Zn, Cd, Co, Cr, Cu and Pb) had EF > 1.5 indicating the exogenic input of these metals.

3.5.2 Contamination Factor (CF)

The level of sediment contamination by a metal is often expressed in terms of a contamination factor calculated as: Contamination Factor (CF) = Metal content in the sediment/ Background level of metal, where $CF < 1$ refers to low contamination, $1 \geq CF \geq 3$ means moderate contamination, $3 \geq CF \geq 6$ indicates considerable contamination, and $CF > 6$ indicates very high contamination. Metals in the study area exposed moderate contamination (CF=1-3) for Ni and low contamination (CF <1) for Mg, Mn and Zn in both the sampling period. Contamination factor was high (CF > 6) for Cd, moderate (CF = 1-3) for Co and Cu, low (CF <1) for Cr and CF = 3-6 for Pb in the study area during first sampling (2009). However, the sediment collected in the next set (2011) showed low (CF < 1) contamination for Cr; but all the other metals had very high (CF > 6) contamination factor. On comparison between the zones, the northern region of the estuary was vulnerable for severe metal contamination especially for Cd and was supported by the earlier reports by Ratheesh et al. 2010, Martin et al. 2012 and Paneer Selvam et al. 2012.

3.5.3 Geoaccumulation Index (IGEO)

The geoaccumulation index, IGEO values were calculated for different metals as introduced by Muller. 1969 is as follows: $IGEO = \log_2 (C_n / 1.5 * B_n)$ Where C_n is the measured concentration of element ‘n’ in the sediment sample and B_n is the geochemical background for the element n.

The factor 1.5 is introduced to include possible variation of the background values that are due to lithogenic variations. IGEO studies in sediments collected in first sampling campaign (2009) revealed uncontamination (IGEO < 0) for Fe, Mg, and Mn in all the zones of the estuary. But Ni and Zn showed moderate to high (IGEO = 1-3) pollution load in north and middle zone of the estuary. South zone is uncontaminated (IGEO < 0) for Ni and Zn. Moderate to high (IGEO =1-3) contamination for Cd, moderate (IGEO = 1-2) with Pb, and uncontaminated to moderate (IGEO = 0-2) contamination for Cr, Co and Cu were observed at the south zone. Middle zone opened heavily to extremely contaminated (IGEO = 3-6) with Cd, moderately to heavily (IGEO = 1-5) contaminated with Pb and moderate (IGEO = 1-2) contamination for Co, Cr and Cu. North zone showed extreme contamination for Cd. For Co, Cr and Cu moderate (IGEO = 1-2) contamination were observed. Pb revealed as moderate to heavy (IGEO = 1-5) contamination. For sediments in the second sampling campaign (2011), Cd showed extreme contamination and all the other metals showed moderate contamination in the entire zones. Igeo studies confirm the contamination of the study area for Cd, Co, Cr, Cu, Pb and Zn. This was in agreement with results reported by Paneer Selvam et al. 2012.

3.5.4 Pollution Load Index (PLI)

The extent of pollution by metals has been assessed by employing the method based on Pollution Load Index (PLI). PLI = n√Product of n number of CF values, Where CF = contamination factor and n= number of metals. PLI provides a simple, comparative means for assessing a site or estuarine quality: a value of zero indicates perfection, a value of 1 indicates only baseline levels of pollutants present and values >1 would indicate progressive deterioration of the site and estuarine quality. The sampling period, 2009 sediment PLI exposed low contamination (PLI < 1) in the study area for major metals (Fe , Mg, Mn, Ni, Zn) and severe load (PLI >1) for minor metals (Cd, Co, Cr, Cu, Pb). But for the next set, PLI was high (PLI >1) revealing greater pollution load for all the metals. This also confirms the polluted nature of the estuary.

Thus GCI results establishes metal enrichment in the study area and support it as a seriously impacted estuary.

3.6 Statistical Analysis

Correlation analysis revealed a strong positive interrelationships among all the metals in sediments which indicate that the northern, central, and southern parts of CES are influenced by direct point sources of contaminants and earlier published research works also support these facts (Thomson. 2002; Martin et al. 2012). Metals have not shown any significant correlation with sediment texture. This is well supported by Paneer Selvam et al. 2012 who found that Zn and Cd were not controlled by any size fraction. The same results have also been observed by Padmalal et al. 1997. This shows that the lithogenic component is not a controlling factor for metals in sediments and the high concentrations were affected by anthropogenic discharges. The absence of any significant correlation of the metals with texture, TOC, total C and total N in the estuarine sediments also reflects that the input is not through the natural weathering processes. Most of the metals showed a significant increase in the estuarine sediments and justifies the point sources contamination. In both the sampling period (2009 and 2011) observed insignificant granulometric, organic matter and elemental dependence for the metals which confirmed their anthropogenic origin. Hence, the absence of a significant correlation between metals and any of the sediment is physico-chemical parameters might be owed to the high influx of contaminants from the industries, which forms organic complexes through flocculation (Zourarah et al. 2007). Previous works do not find any strong associations of metals with organic carbon in the sediments of the Cochin estuary, and thus it is still a matter of controversy that whether metal distributions result from grain size or organic matter content (Nair et al. 1990; CPCB 1996).

Principal component analysis (PCA) was widely used as multivariate statistical tool to assess the origin of metals in sediment. PCA was performed on the entire data set, in order to identify the major estuarine process that leads to the trace metal enrichment. PCA for the first set (2009) of 10 metal distribution reduced to 4 factors (Table 3.4) in which first factor contribute to 40.196% had strong positive loading of Cd, Co, Cu, Fe, Mg, Ni and Zn and negative loading for Cr, Pb, Mn and S. This reflects that the redox process controlling the metal distribution. Second factor positively loaded by Cd, clay, silt, Mn, TOC and C and negative for sand with a variance of 17.959%. This could be attributed to the flocculation and sedimentation of organic matter and granulometric dependence of these metals. Mn found to be made the third factor of variance 16.340% and was negatively loaded for Pb, C, H, N and S. The remaining factor, factor 4 has less importance on the total variance was accounted. The second set (2011), principal component analysis of 10 metal distribution reduced to 4 factors(Table 3.5), in which first factor contribute to 33.78% and is laden up of Cd ,Co ,Cu , Mn and Ni . Second factor burdened by Cr, Pb and Mg and had a variance of 16.192%. The third factor of variance, 13.876% found to be made of Cd and Cu .The remaining factor had less importance on the total variance was accounted.

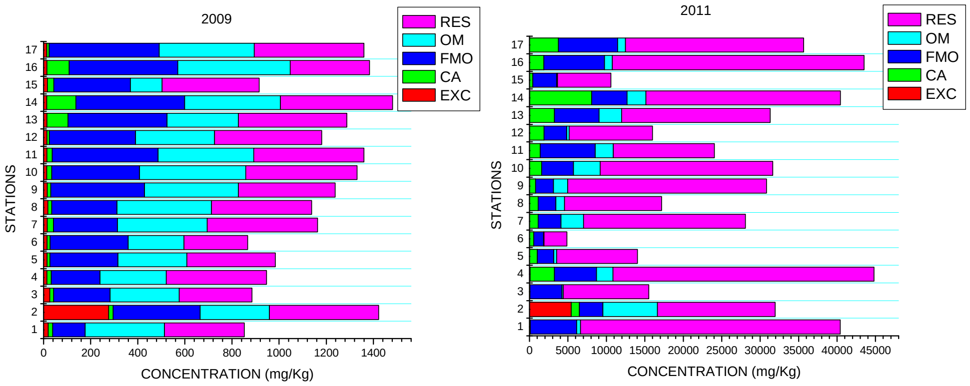
The overall results of metal distribution in the surface sediment of CES were concluded as:

- On comparing with the metal concentration in both sampling (2009 and 2011) periods showed major enrichment in the northern and middle zone.
- Similar trend was observed for Cd, Co, Cu, Fe, Mn and Pb in both the sampling periods; but for Ni and Zn there is a slight deviation in pattern. Ni had high value; whereas Zn had low value than that of the first sampling campaign (2009).

3.7 Metal Fractionation

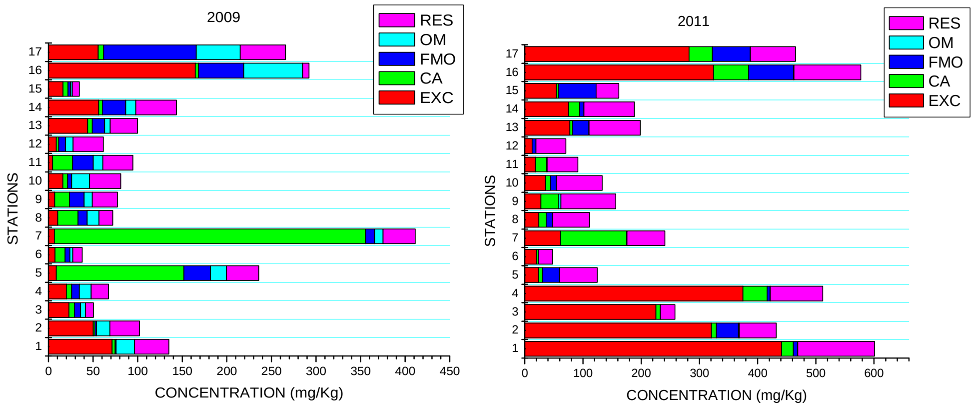
The first part of the study conveyed on the distribution of metal along the CES that demonstrate heavy rate of pollution in the studied estuarine system. GCI and statistical results established that CES is facing serious environmental pollution threat. Even though environmental protection measures are improving, the development rate of the Cochin city suggests that industrial, domestic, and agricultural pollutant sources are likely to increase enormously and cause serious health problems. The system contamination in detail can be confirmed by studying the chemical forms of metals in the sediment. As these different metal forms generally exhibit different chemical entities, the measurement of the total concentration of a particular metal provides little information regarding the potential interactions with the abiotic or biotic components present in the environment. The partitioning of sediment-bound metals could provide significant insight into the factors influencing the bioavailability of metals. Therefore adopting the selective sequential extraction procedure would help to assess the partitioning of sediment associated metal and their accumulation mechanisms in sediment which lead to the metal mobility, biological availability and chemical behaviour. The extent of pollution hazard and to understand the metal dynamics in the CES, the intensities of different chemical fractions in the sediment have to be looked further. Therefore, this section describes the geochemical distribution of metal fractions in the sediments of CES. Chemical fractionation of metals viz- exchangeable (EXC), bound to carbonate (CA), organic matter bound (oxidisable) (OM), iron and manganese bound (reducible) (FMO) and residual (RES) (Tessier et al. 1979; Salomons et al. 1988) forms were encountered and were depicted in **Figure 3.2.**

Figure 3.2. Fractionation of metals in the surface sediments of CES



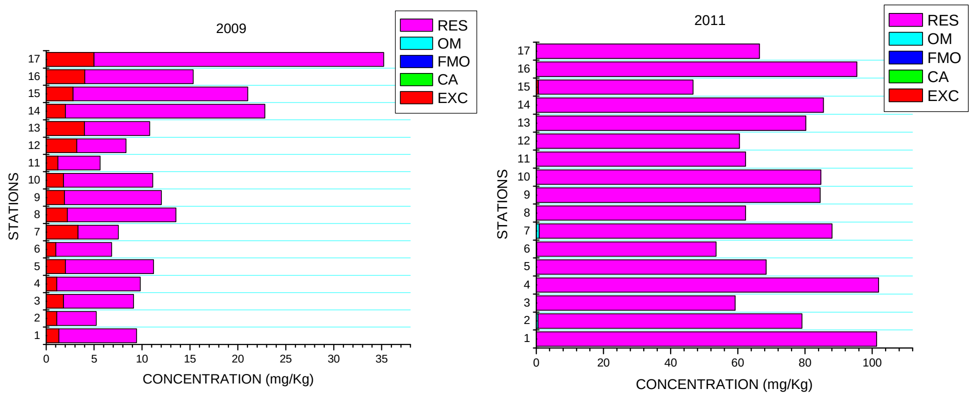
2009 **2011**

3.2. a. Iron



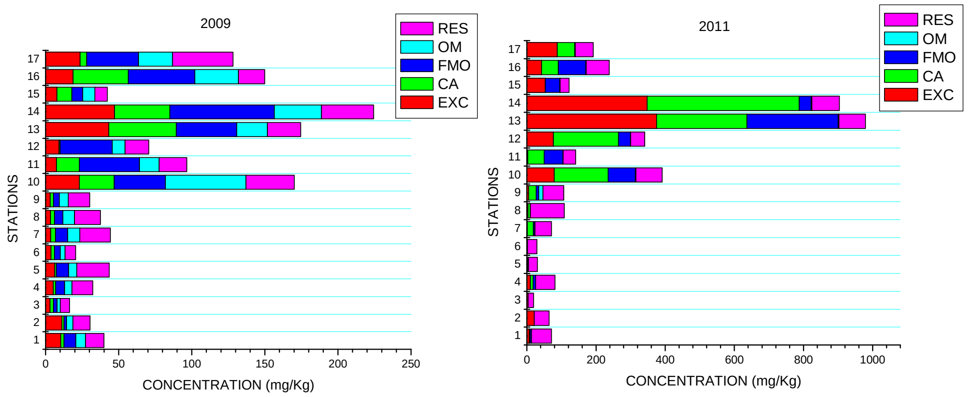
2009 2011

3.2. b. Manganese



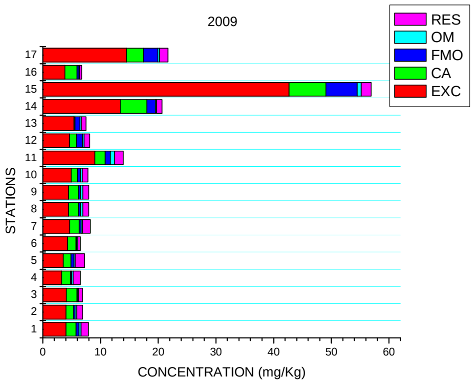
2009 2011

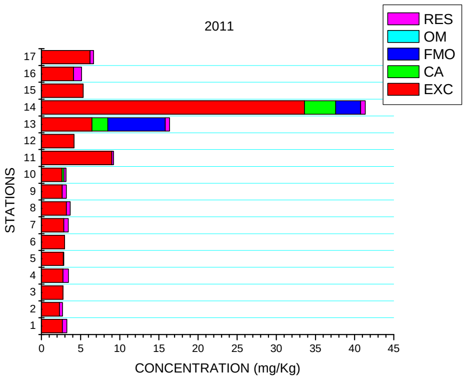
3.2. c.Nickel



2009 **2011**

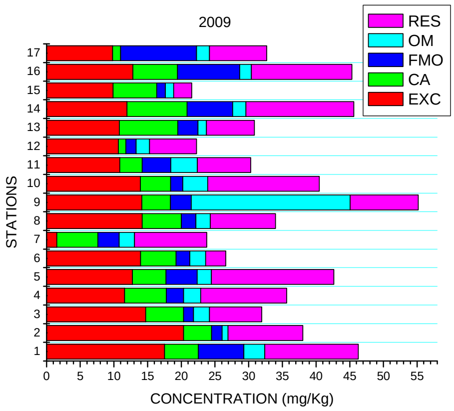
3.2. d. Zinc

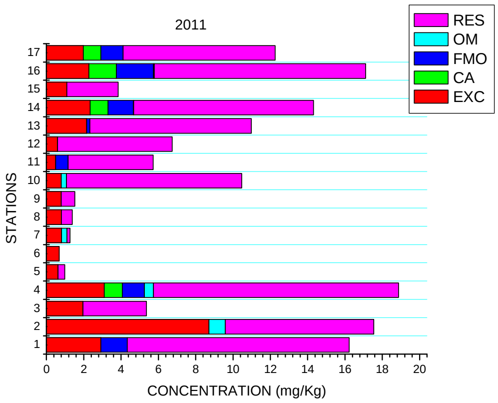




2009 **2011**

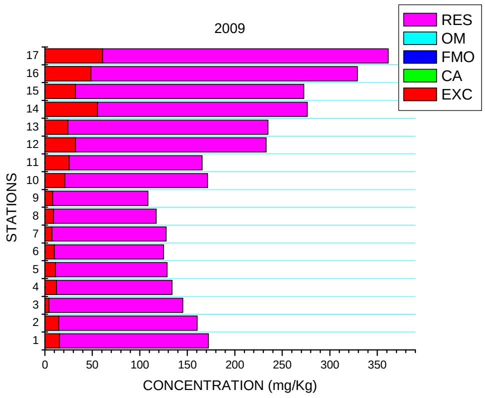
3.2. e. Cadmium

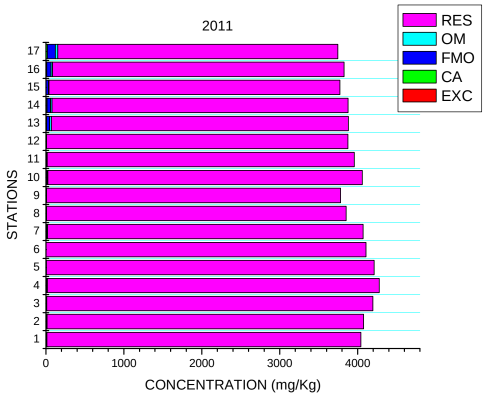




2009 **2011**

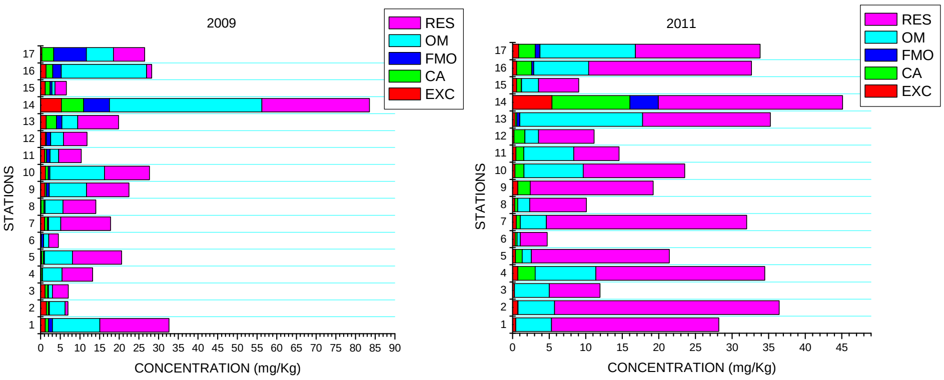
3.2. f. Cobalt





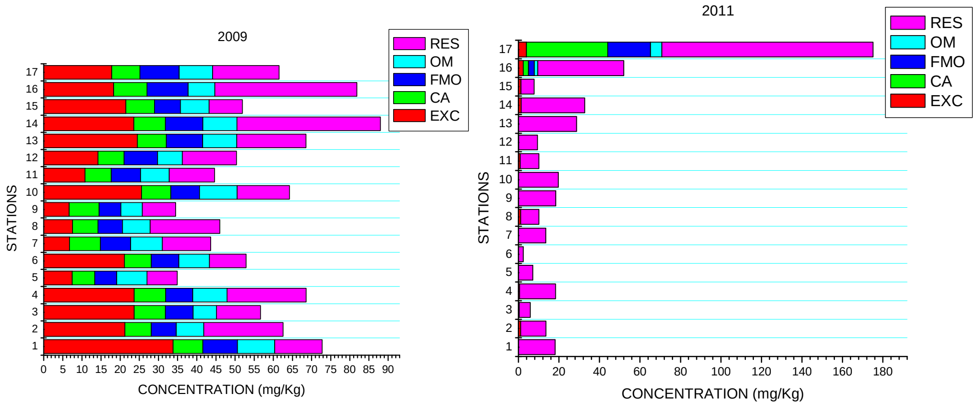
2009 2011

3.2. g. Chromium



2009 2011

3.2. h. Copper



2009 2011

3.2. i. Lead

Metal found in each fraction had specific and special features, in which exchangeable and carbonate fractions are considered to be weekly bound and are equilibrium with the aqueous phase and become readily available to the biological systems. Some amounts of metals are strongly bound to Fe and Mn oxides and organic matter, acting as internal reservoirs. On the other hand, the metals in the residual fraction are not available under normal conditions.

EXC fraction of metals can be easily released back to the water column which may cause secondary pollution and subsequent health risk to the sediment dwelling consumers in the aquatic niche. The amount of metals in this phase indicated the environmental conditions of the overlying water bodies. Metals in this fraction are the most mobile and readily available for biological uptake in the environment (Singh et al. 2005; Zakir et al. 2008). The exchangeable fraction recovered in the sediments of 2009 sampling period revealed major metal (Fe, Mn, Ni and Zn) distribution and expressed in the order as south zone: Fe > Mn > Zn > Ni; middle zone: Zn > Fe > Mn > Ni and north zone: Mn > Zn > Fe > Ni. Comparing the zones, samples in the first sampling campaign (2009) showed that the north zone is enriched with exchangeable fraction and identifies the threat to the environment. In this study, Cd is intensified in northern part of the estuary. Co had greater content in all the zones of the study area. Cr had increased values in the southern and northern zone of the estuary than the middle zone. Cu was analysed in greater content in north zone, then to the middle zone and finally to the south zone. In the northern region of the estuary, Pb was found in higher amount. In the next set (2011) middle and north region of the estuary had same variation as that of major metal as: Mn > Fe > Zn > Ni, but the southern zone, the dynamics showed as: Fe > Mn > Zn > Ni. Minor metal concentration in all the zones of the estuary was in the order Cd > Co > Cu > Pb > Cr.

CA fraction is initially present as metal salts in sediment and readily available following a slight lowering of pH (Turner and Olsen. 2000. Association of metals with this fraction is probably the best example of human-induced influence in the sediments of the study area. Sediment in the first sampling campaign (2009), Fe and Zn content in CA fraction was high at north zone, followed by middle and ends to the south zone. Mn content was higher in the middle zone and lower in the south and least in the north zone of the estuary. Ni in this fraction was found BDL. Cd and Cu content in this fraction was intensified at north zone, smaller to the middle and least to the south zone of the estuary. Co and Pb content was higher in the all regions of the estuary. Concentration of Cr in this fraction was BDL. All zones of the estuary in the second sampling (2011), the major metal distribution order is as: Fe > Mn > Zn > Ni; minor metals Cd ,Co, Pb were BDL in many of the stations of the estuary and found only in few stations of the northern region .Similarly Cu and Cr were also intensified in the northern part of the estuary.

Metal adsorbed in sediments are found in FMO fraction. These oxides become unstable by reduction or acidic transformation of sediments. Sediments in first (2009) sampling, Fe, Mn, Zn fractions were intensified in all the zones of the estuary. Ni in this fraction was BDL. Present study revealed that Cd, Co, Cu and Pb fractions were highest in the three zones of the estuary and Cr fraction was BDL. In the next set (2011), the major metal varied as Fe > Mn > Zn > Ni in all the zones of the estuary and strengthen in the northern region. All the minor metals were abundant in northern region of the estuary and showed as Cr > Co > Cu > Pb > Cd.

The affinity of metals for organic substances and their decomposition products are of great importance for the release of the metals into the water column. Metal bound to this fraction is in chelated form assumed to reflect strong association with sediment organic material and can be immobilized in both oxidizing and reducing condition. During the first sampling period (2009), Fe, Mn and Zn fractions showed similar enrichment in the three zones of the estuary. Ni was BDL in this fraction. The present effort showed that Cd and Co had less content compared to Cu and Pb in this fraction. But Cr was BDL in this fraction. Sediments collected in 2011sampling period revealed major metal distribution as Fe > Zn > Mn > Ni, for minor metal, Cd was BDL and others are in the order as Cr > Cu > Co > Pb.

The metal present in the residual fraction were in the form of metal precipitates which could be used as a baseline data for the assessment of the degree of contamination of the system. The association between metals and the residual fraction of uncontaminated sediments are so strong that metal association with non-residual fraction has been used as an indicator of anthropogenic enrichment (Sutherland et al. 2000; Zakir et al. 2008). The residual fraction is increased in all the three zones of the estuary. Residual fraction showed major metal abundance and was in the order as: Fe >Mn > Ni> Zn and that for minor metal the pattern of distribution was: Cr > Cu > Pb > Co > Cd. In the next sampling period (2011), all the metals heap on in this fraction. The major and minor metal variation illustrate as Fe > Mn > Ni > Zn and Cr > Pb > Cu > Cd respectively.

Comparison of sediment in two year gap revealed greater concentration of Cd and Mn in the exchangeable fraction for the sediment samples in 2011 sampling .Whereas Co, Cr, Cu, Fe, Ni and Pb were abundant in the residual fraction. On comparing the metal concentration between the sampling periods, greater concentration was found in the exchangeable fraction which revealed extensive pollution in the aquatic realm. Metal fractions were high in the residual form of the fraction during both years of study and proved mainly as anthropogenic enrichment component. All the fractions concludes greater content in the year 2009 than 2011.These revealed greater availability of the metals in the ecosystem, and in turn concentrate by the aquatic biota and finally create damage to the ecosystem.

3.8 Biennial Metal Fractionation Profile

The chemical partitioning trend was found to be different for each metal and discussed separately.

3.8.1 Cadmium:

The distribution of cadmium fractions biennially follows as:

Exchangeable fraction> Bound to carbonate fraction > Bound to Fe and Mn oxide > Residual fraction > Fraction bound to organic matters [2009].

Exchangeable fraction > Bound to Fe and Mn oxide > Residual fraction > Bound to carbonate fraction > Fraction bound to organic matters [2011].

High enrichment of Cd in the mobile fractions indicating its high mobilization potential in the study area. According to Muniz et al. 2004, the changing pH and redox conditions were of primary importance for the potential release of metals from sediment. Therefore, a great percentage of this metal can be mobilized from sediment to water with a decline in pH (from carbonate fraction) or a decrease of redox potential (from oxide fractions), due to the input of organic matter or the depletion of dissolved oxygen content (1.96 mg/L). In the present study, the northern and southern zones are vulnerable for this mechanism which in turn results release of Cadmium. Low organic and residual fractions of Cd in the entire study area illustrates the authigenic association with riverine sandy sediments (Nair et al. 1991). High Cd content in the exchangeable fraction was also found in the river sediments by Morillo et al. 2002 and marine sediments by Guevara-Riba et al. 2004 and Cuong and Obbard. 2006. Changes in the ionic composition, influencing adsorption- desorption reactions, or lowering of pH could cause remobilization of metals from this fraction (Marin et al. 1997). Previous studies have shown that Cd has a good capacity to form soluble Cd-Cl complexes ($CdCl^+$, $CdCl^-$(aq), $CdCl^{3-}$, $CdCl_4^{2-}$) with Cl^- even at low Cl^- concentrations, which could promote Cd desorption from sediment particles(Doner. 1987; Rasa et al. 2006) and enhance the extraction of the acid-soluble fractions (Makino et al. 2007). Therefore, it was assumed that the formation of Cd-Cl complexes in the studied sediments in the CES, with high Cl^- concentrations in the middle zone (32.95 psu), might induce Cd desorption from the sediments and hence result the Cd percentage increase in the exchangeable fraction.

3.8.2 Cobalt:

The relative distribution of different fractions of cobalt in the biennial sampling was in the order as:

Exchangeable fraction> Residual fraction > Bound to carbonate fraction > Bound to Fe and Mn oxide > Fraction bound to organic matters [2009].

Residual fraction > Exchangeable fraction> Bound to Fe and Mn oxide > Bound to carbonate fraction > Fraction bound to organic matters [2011].

Exchangeable and residual fraction were intensified in the study area resulting the anthropogenic effect with geogenic origin of these metal. Fractions bound to organic matter had minimum concentration in both years of the sampling sites. Low organic fractions in both periods of study indicate the authigenic association with riverine sandy sediments (Nair et al. 1991) and this had close agreement with the results of the middle region of the estuary which constitute the coarse texture and less organic carbon.

3.8.3 Chromium:

Chromium fraction distribution was following the order as

Residual fraction > Exchangeable fraction> Bound to carbonate fraction =Bound to Fe and Mn oxide =Fraction bound to organic matters [2009].

Residual fraction > Bound to Fe and Mn oxide > Fraction bound to organic matters > Bound to carbonate fraction > Exchangeable fraction [2011].

Cr was mostly concentrated in the residual fraction. Other studies carried out in Spain, in Singapore and in China (Martin et al. 1998; Morillo et al. 2004; Guevara-Riba et al. 2004; Cuong and Obbard. 2006; Yuan et al. 2004) also showed that Cr was found mainly in the residual fraction in all the samples. These results indicate that Cr has the strongest association with the crystalline structures of sediments. Biennial comparison of Cr fractions revealed a decline in the bioavailable fraction in the second sampling campaign (2011) which may be due to the absence of its carbonate fraction in the natural environment (Förstner and Wittmann. 1983). This establishes the inference as the bioavailable form of Cr in the system which is removed generating threat to the CES by biomagnification.

3.8.4 Copper:

Biennial variation of Copper was in the order as

Residual fraction > Fraction bound to organic matters > Bound to Fe and Mn oxide > Bound to carbonate fraction > Exchangeable fraction [2009].

Residual fraction > Fraction bound to organic matters > Bound to carbonate fraction > Exchangeable fraction > Bound to Fe and Mn oxide [2011].

The residual fraction and bound to organic matter were the dominant fractions in the entire study area. Residual fraction abundance generate less toxic behaviour of this metal. A significant amount of Cu is associated with the reducible fractions either by co-precipitation or by sorption onto pre existing coatings under physicochemical conditions (Panda et al. 1995). Ho. 2000 suggested that the high affinity of organic ligands create Cu in sediments more stable, leading to the suppression of diffusion and dispersion of Cu. In addition, organic compounds under the reduced condition may be more active to bind with Cu by complexation rather than by ion exchange (Balasoiu. 2001; Wu et al. 1999). This strong effect can also be attributed to the fact that copper easily forms complexes with the organic matter due to high stability constant of organic Cu compounds (Kotoky et al. 2004). Organic matter exhibits a high degree of selectivity for divalent ions and hence the organic bound Cu fraction is an important fraction in the sediments and is not available to the biological activity (Mcbride. 1994). Hence, the organic matter plays an important role in the immobilization of Cu, but mineralization of the host organic material under oxidizing conditions will release Cu into the overlying water column (Jain et al. 2007). Significantly high Cu concentration in organic and sulfide fraction in the sediments of Periyar River and Cochin estuary can be attributed to the high stability constant of organic-Cu compounds and the earlier studies of Lasheen and Ammar. 2008 establishes the same.

3.8.5 Lead:

The biennial variation in the partitioning pattern of Pb was different and the order is given as:

Exchangeable fraction> Residual fraction> Fraction bound to organic matters > Bound to carbonate fraction > Bound to Fe and Mn oxide [2009].

Residual fraction > Bound to carbonate fraction > Bound to Fe and Mn oxide > Exchangeable fraction > Fraction bound to organic matters [2011].

Residual and bio available fractions were intensified in the entire study area. The high concentration of Pb in residual fractions might be due to the incorporation of Pb in alumino- silicate minerals (Yuan et al. 2004). Greater content of Pb in the bioavailable fraction generate severe threat to the aquatic system. The significant concentrations of Pb in Mn-Fe-oxides are due to the formation of a stable complex (Lopez Sanchez et al. 1996; Jones and Turkie. 1997). The exchangeable lead content was intensified in the northern and southern zones of the estuary revealing the granulometric dependence of these fractions.

3.8.6 Iron:

Biennial variation of iron was in the order as

Residual fraction > Bound to Fe and Mn oxide > Fraction bound to organic matters > Bound to carbonate fraction > Exchangeable fraction [2009 and 2011].

Fraction of Fe accounts for greater metal content in the residual form and this level is toxicologically insignificant to cause any adverse effect on biota. This result was in good agreement with data reported by several research work carried out in other marine systems (Usero et al. 1998; Martin et al. 1998; Yuan et al. 2004; Takarina et al. 2004). Large amounts of Fe accumulate in the residual phase probably because it is basically of natural origin (it is the most common element in the earth's crust) and can exists as crystalline iron peroxides (goethite, limonite, magnetite, etc.). The major part of the remaining Fe is associated with the reducible phase. Singh and Subramaniam.1984 explained that Mn-Fe oxides act as efficient scavengers for Fe which supports the occurrence of it as second most abundant fraction in the present study.

3.8.7 Manganese:

Manganese varies biennially as:

Bound to carbonate fraction > Exchangeable fraction> Residual fraction > Bound to Fe and Mn oxide > Fraction bound to organic matters [2009].

Exchangeable fraction> Residual fraction > Bound to carbonate fraction > Bound to Fe and Mn oxide > Fraction bound to organic matters [2011].

Bioavailable and residual fractions were strengthened in the entire study area. Mn content was mostly present in the labile phase. This is probably because of the known intimate association of Mn with carbonates as endorsed by Dassenakis et al. 2003 and also by other earlier workers

(Kiratli and Ergin. 1996; Morillo et al. 2004). In this phase, weakly sorbed Mn retained on sediment surface by relatively weak electrostatic interactions which may be released by ion exchange processes and dissociation of Mn-carbonate phase (Tessier et al. 1979).

3.8.8 Nickel:

Biennial variation of Ni fractions was in the order as

Residual fraction > Exchangeable fraction> Bound to carbonate fraction =Bound to Fe and Mn oxide =Fraction bound to organic matters [2009].

Residual fraction > Fraction bound to organic matters > Exchangeable fraction > Bound to carbonate fraction = Bound to Fe and Mn oxide [2011].

In the aquatic sediment, Ni is present predominantly in the residual fractions (Staelens et al. 2000; Zhai et al. 2003). The dominant proportion of Ni in the residual phase in this study is in agreement with the results of other studies (Martin et al. 1998; Mester et al. 1998). This also infers the less toxicity of this metal to the study area.

3.8.9 Zinc:

Zinc fraction partitioned as follows

Bound to Fe and Mn oxide > Residual fraction > Fraction bound to organic matters > Exchangeable fraction > Bound to carbonate fraction [2009].

Bound to carbonate fraction > Exchangeable fraction> Residual fraction > Bound to Fe and Mn oxide > Fraction bound to organic matters [2011].

A major part of Zn is associated with Fe-Mn oxide phase, because of the high stability constant of Zn oxides. Fe oxides adsorb considerable quantities of Zn and these oxides may also occlude with Zn in the lattice structures (Banerjee. 2003). Singh and Subramaniam.1984 explained that Mn-Fe oxides act as efficient scavengers for Zn. Relatively higher concentration of Zn associated with this fraction is caused by the adsorption of these elements by the colloids of Mn and Fe (Jenne. 1968). The sorption of zinc with iron in the sediment may strongly hinder their mobility in the aquatic environment. In the present study minor amount of Zn is associated with carbonate and exchangeable fractions. Besides, Calcium carbonate forms complexes with zinc as a double salt ($CaCO_3 \cdot ZnCO_3$) in the sediment (Li et al. 2000). The association of the metals with the carbonate phase is less in first sampling campaign (2009) which may be due to the low carbonate in the sediment. Low concentration in exchangeable fractions indicates low bio-availability of Zn.

The results of the sequential extraction revealed that Cd, Cr, Cu, Fe, Mn and Ni had similar pattern as for the dominant content in both years of sampling. Cd and Mn were found in the bioavailable fraction (EXC, CA). Greater availability of these metals in the ecosystem, and in turn enters in to the aquatic biota and cause biomagnification through food chain and finally create damage to the ecosystem. Cr, Cu, Fe and Ni in these fractionation profiles intensified with residual fraction. Co and Pb showed high concentration in EXC and RES in first and second sampling periods respectively.

3.9 Risk Assessment Code (RAC) and Mobility Factor (MF)

The results of sediment fractionation expose the presence of metals in various fractions and facilitate to determine the mobility of the metals by evaluating the percentage of metals in the weakly bound fractions with the total metal content.

In this study, the Risk Assessment Code (RAC) which accounts the mobility of the metal was evaluated in order to identify the extent of risk associated with the percentage of metals present in the sediments. From RAC and MF, Fe showed as low risk in the sediment of the first sampling period (2009), but revealed to be of medium risk in the second sampling period (2011). Mn had very high risk effect in both the sampling period. Ni revealed high toxic nature in the sediment for the first set (2009) and in the next (2011), it had low toxic effect. Zn showed to be very high toxic nature in both the study periods. Sediment had very high risk with Cd and Co. Cr and Cu revealed as medium risk for the 2009 samples and no toxic effect for 2011. Pb showed high risk in the first set (2009) and medium risk for the next sampling year (2011). RAC and MF also confirmed as moderate to severe pollution behaviour in the estuary.

3.10 Non-Residual Fractions Enrichment Factor (KNRF)

In order to quantify the anthropogenic contamination of the metals, for the fractionation compositions, the KNRF approach is adopted and presented herewith. KNRF studies indicate extreme contamination in the surface sediment of the study area especially in the northern region of the estuary which revealed heavy anthropogenic pollution in these regions.

3.11 Conclusion

The cycling, mobility and biological effect of metals in the aquatic environment can be revealed from the knowledge of metal fractionation.

Therefore, the study highlights the analysis of total metal content and its fractions to generate the quality of the sediment. Results showed that the distribution of metals in the sediment was not uniform over the whole study area and revealed extreme metal contamination in CES. In general, the northern region of the study area showed higher values as compared to the southern region. The sediment quality guideline and previous literature comparison resulted drastic pollution in CES. Geochemical indices also support these outcomes. The factor analysis and geochemical index effectively differentiate the natural anthropogenic sources of metals. Fractionation profile showed intensified content of metal in non residual fraction, creating severe threat to the aquatic system. EXC and CA fractions dominated in the fractionation profile in most of the metals which gain attention due to their bioavailable nature and susceptibility to release back to the water column in the entire zones of the estuary. RAC and MF revealed that certain pockets of the three zones of the estuary are polluted by metal either from human activities and industrial wastes or sewage disposal influences. EF and KNRF revealed extreme contamination in these surface sediments. The high concentration and bioavailability of metals indicate that there is urgent need to conduct more detailed and continuous monitoring studies in this region and to take necessary steps to reduce the sources of pollution. Further, deterioration of geochemical parameters may enhance the bioavailability of metals and will adversely affect the aquatic system and health of human, as they are depend on the system for their livelihood. Hence, the findings in this study will indicate the need for proper industrial planning and the safe disposal of industrial and urban waste, which would otherwise lead high levels of pollutants into the coastal ecosystem of Kerala, and would greatly invite socioeconomic disaster. Thus, for getting a crystal clear idea about the pollution status, geochemical studies of the core sediment from prominent stations of the three zones were carried out and described in detail in Chapter 4.

Annexure

Table 3.5 Component matrix of the surface sediment (2009) using principle component analysis

	1	2	3	4
SAND	-.624	.455	.189	-.524
CLAY	.469	-.330	-.303	.683
SILT	.480	-.367	.079	-.001
Cd	.521	.010	.617	-.307
Co	.850	.015	-.409	-.067
Cr	-.203	.798	.305	.369
Cu	.685	-.002	.564	-.135
Fe	.465	.076	.103	.338
Pb	.439	.528	.423	.208
Mg	-.175	.849	.183	.399
Mn	.635	.138	-.339	.072
Ni	.533	-.359	.349	-.136
Zn	.336	-.066	-.234	.220
TOC	.848	.275	.052	-.250
C	.916	.209	-.159	-.182
H	.294	.445	-.667	-.409
N	.891	.079	.298	.039
S	.242	.588	-.573	-.102

Table 3.6 Component matrix of the surface sediment (2011) using principle component analysis Component Matrix

	Component			
	1	**2**	**3**	**4**
SAND	-.301	-.865	.232	-.125
CLAY	.257	.855	-.159	.167
SILT	.400	.577	-.500	-.129
Cd	.942	-.033	.059	.022
Co	.897	-.122	.269	.070
Cr	-.631	.199	-.036	-.050
Cu	.730	.011	.343	.245
Fe	.970	-.172	-.051	.109
Pb	-.323	-.149	.825	.137
Mg	.919	-.205	-.017	.155
Mn	-.451	.516	.262	.488
Ni	.970	-.119	.069	.054
Zn	.976	-.117	.014	.071
TOC	.270	.652	.309	.048
C	.212	.506	.635	-.440
H	-.079	-.279	.775	.004
N	.274	.375	.502	-.702
S	-.332	.276	.558	.469

****

Chapter 4

METAL DISTRIBUTION IN THE SPECIFIC CORE SEDIMENTS OF COCHIN ESTUARINE SYSTEM (CES)

Contents

4.1 Introduction

Coastal and estuarine waters are sensitive zones acting as important sinks for many persistent pollutants and they accumulate in bottom sediments (Szefer et al. 1995). Among the varying contaminants, metals in aquatic systems could be transported rapidly into the sediments, where they could be released according to the changing environmental conditions, ultimately resulting to a secondary contamination source affecting the ecosystem. Sediment cores provide information about the events that occurred in preindustrial time and can be used as a tool to assess and monitor the pollution history encountered in changing climatic conditions (Karbassi and Amirnezhad. 2004), rate of sedimentation (Karbassi. 1996), weathering trend and the source of pollution etc of the aquatic system (Lopez and Lluch. 2000, Karbassi et al. 2005, Ahmad et al.2010; Mohamed. 2005). Over the last few decades intensive research has been carried out on sediment cores for establishing the effects of anthropogenic and natural processes on depositional environments. Changes in metal concentration with depth in sediment cores can show long-term changes in the metal input trends and thereby imply pollution status. Vertical profiles of pollutant species in sediment cores have been commonly used as ‘‘pollution records’’ in the aquatic realm.

The geochemical research reviews on core sediment metal carried out so far on and off the west coast (Priju and Narayan. 2007; Harikumar et al. 2009; Harikumar and Nasir. 2010) reveals that considerable amount of work still remains to be done with regard to metal pollution. The sediment core analysis can be used as a gauge of the quality control in the CES and would provide a clear cut idea about the environmental dynamics of the studied site under consideration. This Chapter characterize the depth profile pattern of metals (Cadmium (Cd), Cobalt (Co), Chromium (Cr), Copper (Cu), Lead (Pb), Iron (Fe), Magnesium (Mg), Manganese (Mn), Nickel (Ni) and Zinc (Zn) in the core sediment collected from different hotspots in the CES. Anthropogenic Factor (AF), Contamination Factor (CF), Enrichment Factor (EF), Geoaccumulation Index (IGEO) and Pollution Load Index (PLI) were used to differentiate the typical metal sources. Statistical analyses were employed to understand the origin of metals in the core sediment samples.

4.2 Sediment Geochemistry

Estuaries are frequently conceptualized as large reactors of chemical wastes which are supplied, mixed, processed and transported along the salinity and suspended sediment gradient (Church. 1986).The fate of pollutant is a complex pattern, because estuaries are heterogeneous, chemically reactive and hydro dynamically variable and sedimentologicaly active. For getting an idea about the depth profile of pollutant behavior, geochemical analyses of metals in the sediment core were carried out in two year gap. In any environmental sampling, the water column depth and the respective core length of the same site may not be uniform; therefore the study cannot be related year wise. Therefore, this section only details the geochemistry of metal including the sedimentary characteristics, TOC and depth profile of metals in the two year gap (2009 and 2011) sampling period and discussed in separate sections as Part A and Part B.

4.2.1 Part A

This section describes the salient portrayal on the geochemical characteristics of six sediment cores collected during November 2009 from three specific zones of CES and are grouped as South, Middle and North. More details were discussed in Chapter 2. These core sediments are named as S_1, S_2, (South); M_1, M_2, (Middle); N_1 and N_2 (North).

4.2.1.1 General Sedimentary Characteristics

Colour, pH, Eh and texture for each core sediment are discussed as given below:

S_1: Varying colour combination in core sediment length 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. Values of Eh ranged from -263 to -107 mV and it was highest negative value in the bottom portion of the core. Clay content dominated in this core and showed a variation ranging from 3.2% to 97.8%. Along the core, as depth increases, clay fraction was noted both at the top and bottom portion of the core and in the middle section, sand content was dominated (48% to 70%).

S_2: Uniform black colour up to 12 cm and mixed black and grey colour up to 30 cm was noted. pH ranged from 7.53 to 8.75 and it was found to exhibit an increasing trend towards the bottom portion of the core. Values of Eh ranged from + 102 to +264 mV and it was high at the top portion of the core. Sand content dominated in this core, and it was observed a variation as 81.7 % to 95.5% to the entire core.

M_1: The whole core appeared blackish brown in colour. Values of pH ranged from 7 to 8. Values of Eh ranged from -324 to -263 mV 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.

M_2: Mixed black and grey colour at 0-36 cm and uniform black colour up to 63cm were noted. Values of pH ranged from 7.9 at 63 cm depth to 8.7 at 9 cm depth and exhibited a decreasing trend with minor fluctuations from surface to bottom. Values of Eh ranged from -412 to -310 mV and it was found highest negative value at bottom portion of the core. Sand content was intensified in this core. The textural variation was in the order; sand> clay> silt.

N_1: The entire core was blackish brown in colour. pH value ranged from 6.1 to 6.6 and it decreased towards the bottom. Values of Eh ranged from -376 to -252 mV and it was found 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.

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. Values of pH ranged from 5.6 to 7.54 and highest at bottom portions of the core. Values of Eh ranged from + 172 to +286 mV and it was found highest at top portion of the core. Clay content dominated in this core and showed a variation ranging from 2.2 % to 88.9 %. Along the core, as depth increases, clay fraction was also decreased.

4.2.1.2 TOC and CHNS

In core $S_{1,}$ the 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. Core S_2 showed percentage of TOC ranging from 0.44 to 0.56 and almost equal in the entire portions of the core. Core M_1 had TOC decreased from top (0.7%) to bottom (0.6%) of the core. Core M_2 revealed the content of TOC as 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. In the core N1, percentage of TOC ranged from 0.6 to 2.9. The maximum was noted at 12 cm depth and the minimum at 27 cm length of the core. Core N_2, had percentage of TOC ranged from 0.75 to 4.01, showing the lowest at bottom and highest at the top portions of the core.

A number of important bulk sediment parameters are available for the evaluation of OM sources and its fate within the marine sediments, in which C/N ratios are often used to differentiate marine from terrestrial OM (Redfield et al. 1963; Atkinson and Smith. 1983; Perdue and Koprivnjak. 2007), although selective degradation of the different minerals in sediments can affect the C/N ratios of OM (Muller. 1997). C/N values are typically lower for aquatic OM than for terrestrial OM (Meyers and Lallier-verges. 1999) and it ranges were 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 and justifying that the source of organic matter is allochthonous. It also suggests that less productive and terrestrial OM could be a dominant contributor in the study region. 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.

The ratio of total organic carbon (TOC) % to total sulfur (TS) % (TOC: TS), in the studied core sediments was determined. Their values ranged as: 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 cores N_2 and S_2 indicating that the amount of metabolizable organic matter were 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 and unused) organic matter content (TOC). Further, fresh water sediment have very high TOC/TS ratios because of the low sulphate concentrations in most fresh water bodies (Berner and Raiswell. 1983). In general, 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 cores viz; S_1, M_1, M_2 and N_1. These sites were under the threat of anthropogenic waste materials and were associated with the dredging, and piling activities. This region endure sulfate reduction below an oxygenated water column exhibiting TOC: TS ratios in the range: 1.5 to 5 and these results were well corroborated with the earlier works by Berner and Raiswell. 1983. Thus sediments from these stations (S_1, $M_{1,}$ M_2 and N_1) were characterized as 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 a significant effect on the degradation of sedimentary pigments. TOC/TS ratio > 5 in core S_2 and N_2 are considered as oxic sediment with oxygenated bottom water.

4.2.1.3 Depth Profile of Metals

S_1: Depth profile of metal was given in Figure 4.1. Cd content showed almost similar trend in the entire sections of the core. The content was diminished to 15-18 cm length of the core and increased towards the bottom. Concentration of Co was diminished in the top section of the core i.e up to 15 cm and increased towards the bottom section of the core. Cr showed a decline up to 15 cm length and intensified in mid and bottom section of the core. The top section of the core is concentrated with Cu and changes slightly from 15 cm to the bottom. Intensified Fe concentration was observed in the top (3-12 cm) and bottom section (24-33 cm) of the core. Pb showed high residual levels in the top and bottom section of the core. In the entire sections of the core, Mg had high content in top (12 cm) and bottom (33 cm). Mn revealed larger content in the top section (up to 15 cm) of the core and diminished in the bottom. Concentration of Ni was highest in the bottom section of the core. Zn also revealed greater content in the top and bottom section of the core and less in the middle part.

High content of Fe, Mn and Cu were present in the top section of the core and indicated bottom layer anoxia. The Eh and TOC: TS values also support the increased anoxia along the bottom portion of the core. All the metals analyzed revealed an increase in concentration at the top and bottom section of the core, clearly reveals the granulometric dependence as intensified by clay content in the top and bottom part of the core.

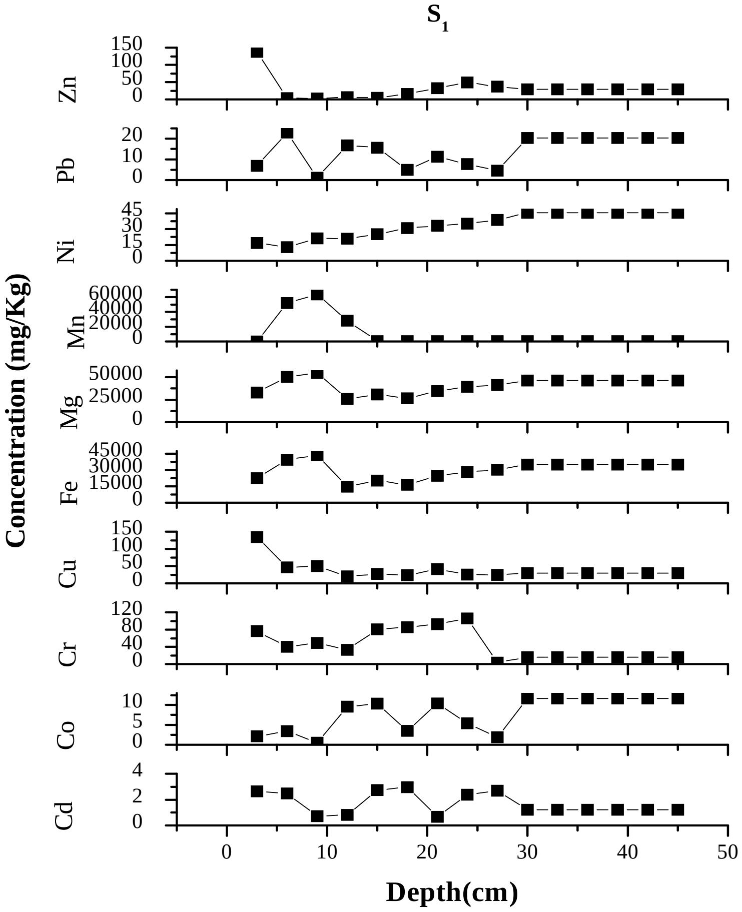


Figure 4.1 Discrepancy of metals in core S_1 (2009)

S_2: Distribution of metal was given in Figure 4.2. Cd content showed prevailing trend in the top - bottom section and lessen in the mid portion. Depth increased Co content also reduced. Cr content declined as depth increased up to 6 cm and again intensified towards 27 cm and later diminished up to 33 cm. Cu showed somewhat similar pattern in all the sections of the core. Fe and Mg showed same pattern revealing a heavy load in the top and bottom section of the core. Pb content was intensified in the top and bottom section of the core. Mn and Ni showed the same trend as metals were enriched in the top and bottom section. Zn content was diminished at the top and mid section of the core and intensified in the bottom region.

Cd, Cu, Fe, Mg, Mn, Pb and Ni content showed intensified concentration in the top and bottom section of the core. Cr and Zn had shown high concentration in the bottom section of the core. Sand content was dominant in the core and showing granulometric independence, revealing anthropogenic origin of these metals. Similarly Eh and pH value had no significant impact on the metal distribution in the core.

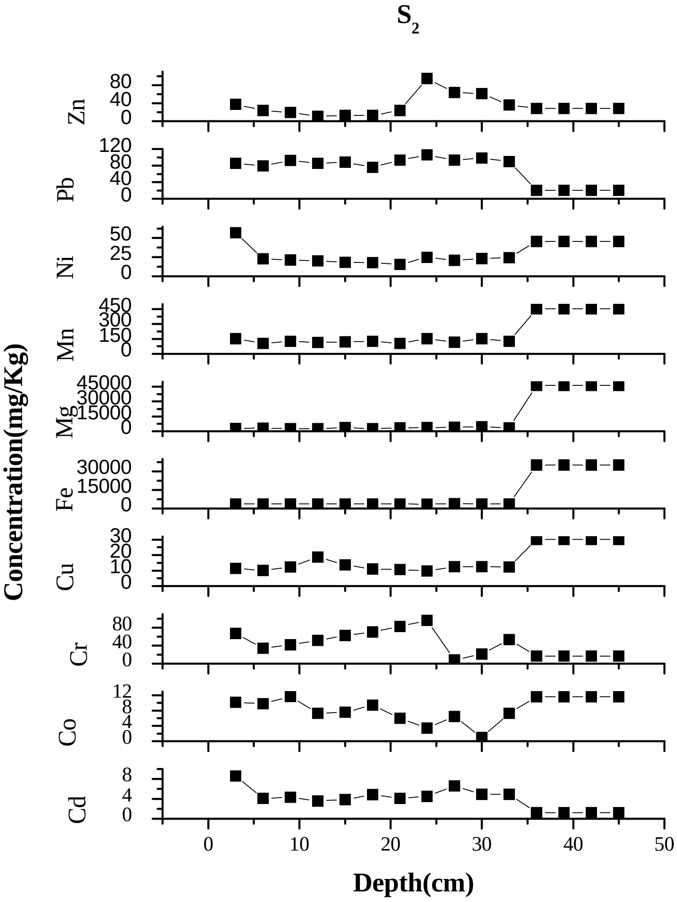


Figure 4.2 Discrepancy of metals in core S_2 (2009)

M_1: Discrepancy of metal given in Figure 4.3. Cd, Co, Cr, Fe, Mg, Mn, Ni and Zn were directly related to depth where Cu and Pb were concentrated to the middle then decreased towards to the bottom.

Except Cu and Pb all the other metals were intensified in the bottom portion of the core. Eh value showed increased anoxia in the bottom portion of the core. High sand % revealed a textural independence of metal and showing its source as anthropogenic origin.

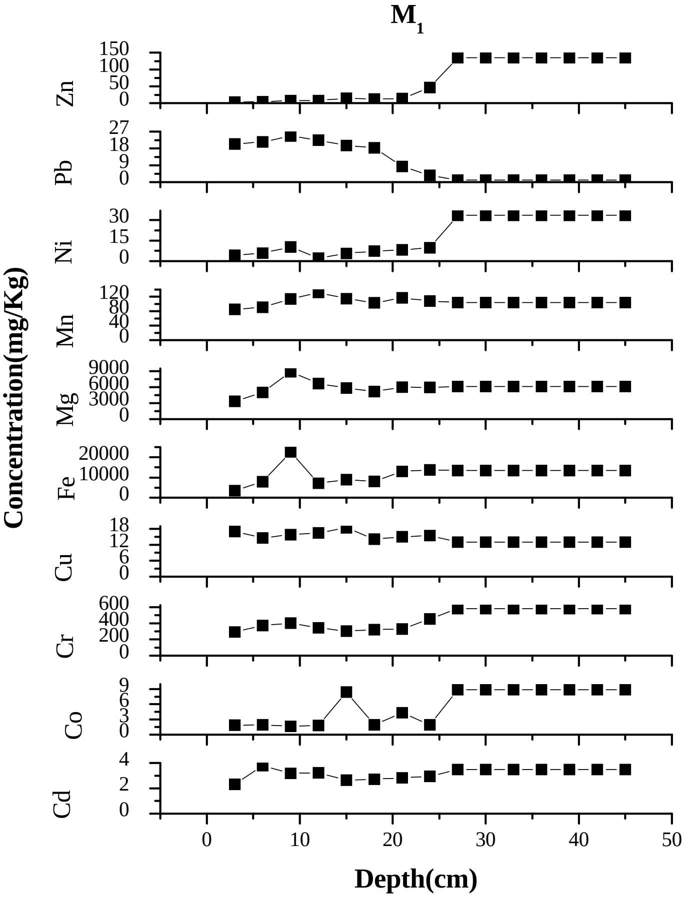


Figure 4.3 Discrepancy of metals in core M_1 (2009)

M_2: Metal distribution was given in Figure 4.4. Cd, Co, Cr, Cu, Fe, Mg, Mn and Ni content was directly related to depth; but for Pb and Zn, concentration was increased towards the middle and decreased wards bottom**.** Except Zn and Pb, all the other metals were intensified in the bottom portion of the core. Eh value showed increased anoxia in the bottom portion of the core. Dominant content of sand revealed, textural independence of metal and clearly outweights its anthropogenic source.

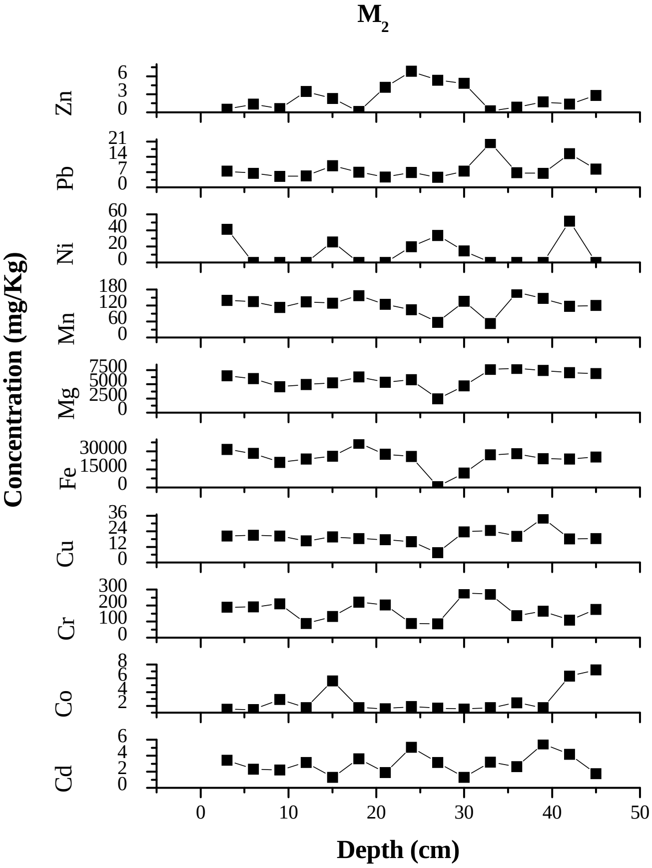


Figure 4.4 Discrepancy of metals in core M_2(2009)

N$_1$: Metal allocation was given in Figure 4.5. Cd and Ni were high along the deeper length of the core. Cr content was improved to the mid portion and diminished to the bottom; concentration of Co, Cu, Fe, Mg, Mn, Pb and Zn were high in the top section of the core and reduced in the remaining sections of the core indicating a reduced metal layer below the bottom portion of the core. The Eh and TOC: TS values also support the increased anoxia along the bottom portion of the core. Most of the metals analyzed revealed increased concentration in the top section of the core which clearly revealed the granulometric dependence as intensified by clay content in the top portion of the core.

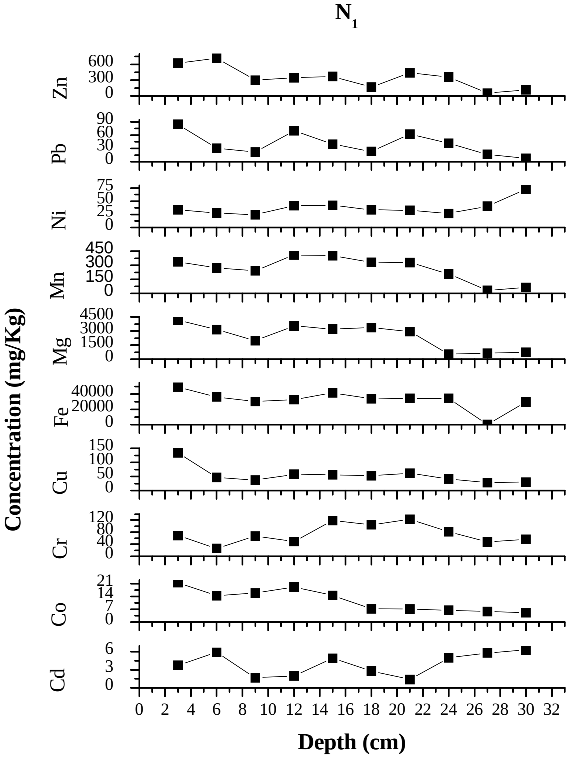


Figure 4.5 Discrepancy of metals in core N$_1$ (2009)

N_2: Distribution of metal was given in Figure 4.6. Fe, Mg and Pb were dominant in the top section of the core; Cd, Ni and Zn were directly related with depth; Co, Cr and Mn content was intensified to the middle and weaken towards the bottom and Cu was decreased to the middle and augmented towards the bottom. This core revealed fluctuated behavior of the different metals and had high concentration in the core due to high clay content and oxic nature of the sediment. Eh and TOC: TS values also support these results.

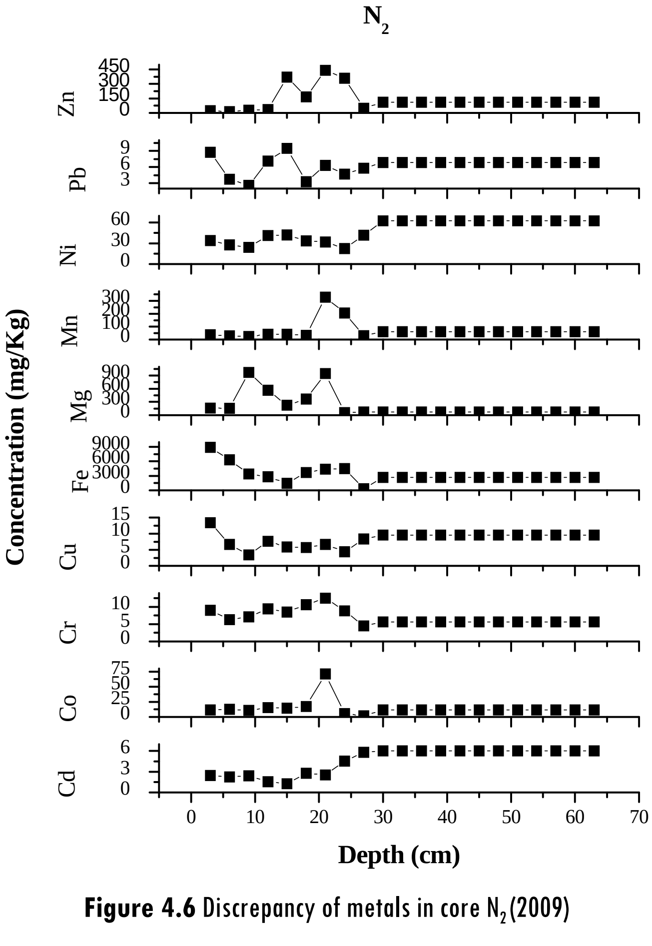


Figure 4.6 Discrepancy of metals in core N_2(2009)

4.2.1. 4 Geochemical Normalisation Methods

1. Antropogenic Factor (AF)

A deviation in anthropogenic metal enrichment in different cores from the study area was observed for AF. In core S_1 showed Cd content anthropogenic enrichment was up to 12 cm depth, towards 18 cm depth it had no enrichment .In the depth 21, 24 and 30 cm had anthropogenic input, whereas at 27 cm depth had no enrichment. Co had anthropogenic pollution at 6, 15, 18, 27 and 30 cm depth. The remaining parts had no anthropogenic input. Up to 12 cm depth, Cr had anthropogenic enrichment; remaining part up to 24 cm has no enhancement. Again towards the bottom, it showed anthropogenic pollution. Cu and Zn revealed severe anthropogenic pollution in the entire core. Fe and Mg had anthropogenic origin only between 12-18 cm depth. Mn had no anthropogenic pollution in the entire core. Ni had exogenic pollution load up to 6 cm and the residual part had no such contamination. Pb generated anthropogenic pollution at 9, 18, 27cm depth and no contamination at the rest. Except Mg and Zn, S_2 are showed for all the metal showed exogenic origin in the entire core. Top to mid section of the core Mg and Zn had wholly different origin. M_1 core had anthropogenic pollution for Cr, Cu and Pb. In M_2 core, most of the metals revealed AF > 1. Zn is excluded from this inference. In core N_1 and $N_{2,}$ all the metals displayed greater anthropogenic factor indicating the exotic origin.

2. Contamination Factor (CF)

Among the metals Cd and Mg had high contamination in core S_1. Core S_2 had high contamination for Cd and Pb than other metals. M_1 core reported contamination for Cd and Cr. In M_2 core, high metal contamination was found for Cd and Cr. Among the metals, Cd, Cu, Pb and Zn had high pollution for core N_1. N_2 core showed high toxicity only for Cd.

3. Enrichment Factor (EF)

In core S_1, Cd content showed significant at 3cm depth, moderate to significant enrichment was found up to 12 cm. Very high enrichment towards 18 cm. At 21cm had moderate enrichment and thereafter up to 27 cm, a significant enrichment was observed. At 30 cm depth, it had moderate enrichment. Co showed minimal enrichment in all the sections of the core. Cr revealed moderate enrichment at 15 -24 cm depth and the rest minimal enrichment. Cu had significant enrichment at 3 cm depth and minimal enrichment in remaining depth. For Pb revealed a minimal enrichment. Mg had moderate enrichment. Mn content had extremely high enrichment at 6-12 cm; in the remaining, it had minimal enrichment. Entire core revealed minimal enrichment for Ni. Zn showed a moderate enrichment at 3cm depth and minimal enrichment in the remaining section. Core S_2 showed Cd as moderate- significant enrichment in the entire core. Mg, Cr and Cu had moderate enrichment. Pb showed extremely high enrichment in this study. Mn showed minimal enrichment. Ni had significant enrichment. For Zn observed of moderate enrichment up to 18 cm, and also moderate up to 21 cm and significant to 30 cm length. In core M1, Cd had extremely high enrichment. Co had minimal enrichment. Cr had maximum enrichment at 3 cm then significant to very high enrichment in the remaining depth. Cu showed moderate to minimal enrichment. Pb had significant up to 18 cm depth and minimal for the rest. Mg showed moderate to minimal enrichment. Mn, Ni and Zn had minimum enrichment. Core M_2 showed Cd as significant, very and extremely high enrichment in the entire core. Co had minimum for the core. Cr had moderate enrichment up to 24 cm then significant enrichment in the remaining depth. Cu and Pb had minimal enrichment. Mg and Mn showed moderate enrichment. Ni showed moderate enrichment. Zn showed minimal enrichment in this core. In core N_1 Cd had extremely high enrichment. Co and Cr showed minimal enrichment. Cu showed moderate to minimal enrichment. Pb showed moderate to extremely enrichment. Mg and Mn showed moderate enrichment. Ni and Zn had minimal to extremely high enrichment. N_2 core revealed Cd as extremely high enrichment. Co showed significant enrichment. Cr had minimum enrichment. Cu showed moderate to low enrichment. Pb showed moderate to maximum enrichment. Mg and Mn showed moderate enrichment. Ni and Zn had minimal to highest enrichment.

4. Geoaccumulation Index (IGEO)

IGEO showed high accumulation rate for Cd in the entire sections of the cores in different zones of the estuary under investigation.

5. Pollution Load Index (PLI)

PLI revealed severe metal contamination for the two cores (N_1, N_2) in the northern region of the estuary.

In core S_1, GCI showed significant anthropogenic and enrichment factors were significant for all the metals. Contamination factor revealed that contamination exists for Cd and Mg. Geoaccumulation index suggests severe accumulation of Cd in the entire core. PLI resulted less contamination in the core.

Except Mg and Zn, all the other metal showed anthropogenic input in the entire section of the core S_2. Mg and Zn revealed anthropogenic origin only at mid section. Contamination factor gave enormous contamination for Cd and Pb. Except Co all the other metals showed enrichment in the study area. Geoaccumulation index suggest severe accumulation of Cd in the entire core. PLI resulted less contamination in the entire core.

Anthropogenic pollution was noted for Cr, Cu and Pb in core M_1. Contamination factor was reported for Cd and Cr. All the metals showed enrichment but Cd showed extreme enrichment, in the study area.

In core M_2, Except Zn most of the metals revealed AF > 1. Contamination factor was found for Cd and Cr. Except Cd all the other metal showed moderate to minimal enrichment. Cd had significant, very and extremely high enrichment in the entire core.

On comparison between the GCI of the cores collected from the north zone showed severe contamination for all the metals.

4.2.1. 5 Statistical Ananlysis

Statistical analysis showed no significant correlation between the components, revealing the anthropogenic input of these metals. Principal component analysis results the reduction of the components to four factors of variance > 8%.

In core S_1, five factors (Table 4.4 annexure) account for total variance 90.43%. The factor 1 corresponds to 31.03% variance revealing the granulometric dependence of the metals, Fe, Mg and Mn. Factor 2 had 23.49% of variance showed anthropogenic origin of Co and Pb and also these metals had strong binding affinity with organic matter. Variance of factor 4, showed as 11.16% which generate exogenic input of Cd.

S_2 generate four factors (Table 4.5 annexure), accounts the total variance as 86.66%. The factor 1 corresponds to 31.03% variance revealing the granulometric dependence of the metals Fe, Mg and Mn. Factor 2 had 23.49% of variance, shows the anthropogenic origin of Co and Pb and also these metals had strong binding character with organic matter. Variance of factor 4 showed as 11.16% which generate exogenic input of Cd.

Four factors (Table 4.6 annexure) account for total variance 86.20 % for core M_1. The factor 1 corresponds to 37.63% variance, revealing the anthropogenic origin of Cd, Co, Cr, Cu, Fe, Mg, Mn and Ni. Factor 2 had 27.62% of variance showed granulometric dependence of Fe, Mg and Mn. Factor 3 and factor 4 demonstrate variance as 11.68% and 8.70 % respectively indicate the exogenic input of Cd.

Core M_2 had four factors (Table 4.7 annexure) which account for total variance 78.69%. The factor 1 corresponds to 56.21% variance, revealing the granulometric and organic matter dependence of anthropogenic origin of Cd, Co, Cr, Cu, Fe, Mg, and Mn. Factor 2 generate 18.90% of variance showed granulometric and organic matter dependence of Zn. Factor 3 had variance of 11.47% organic matter with the control over Cr. Variance of factor 4 showed as 10.69% generate exogenic input of metals.

Core N_1, create three factors (Table 4.8 annexure) which accounts for total variance 81.32 %. The factor 1 corresponds to 37.63% variance revealing the anthropogenic origin of Co, Cu, Fe, Mg, and Mn. Factor 2 and factor 3 generate variance as 14.14% and 18.90% respectively showing exogenic input of Cr and Cd correspondingly.

In core N_2 five factors (Table 4.9 annexure) account for total variance 90.07%.The factor 1 corresponds to 32.99% variance revealing the allothonous input of the metals Co, Cr, Mg and Mn. Factor 2 had 24.19% of variance showed granulometric relation of Cd and Ni and also these metal had strong binding with organic matter. Variance of factor 3 showed as 16.144% which generate exogenic input of Cu and Pb. Factor 4 had variance of 10.342% organic matter with the control over Zn. Variance of factor 5 showed as 8.40% generate exogenic input of Cd.

4.2.2 Part B

This section details the relevant portraits on geochemical characteristics of six sediment cores collected from the specific zones (described same as in the first sampling period, 2009) of CES during November 2011. Most of the earlier published research contributions were based on one-time or seasonal sampling during a year. Present research approach based on the geochemical analysis of sediment cores collected over a considerable time period which could provide a definite change in the environment niche and such studies are limited.

4.2.2.1 General Sedimentary Characteristics

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

S_1: Uniform black colour. 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. Values of Eh ranged from -

101 to +218 mV and it was found highest negative value at 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 slight highest (35% to 49%) percentage of silt was observed at top (0-15 cm) portion of the core. Relative textural distribution was found in the order sand > silt.>clay.

S_2: Greyish brown colour up to 6 cm and uniform black colour up to bottom. Values of pH ranged from 7.4 to 8 and it was found to exhibit an increasing trend with minor fluctuations towards bottom part of the core. Values of Eh ranged from -434 to -323 mV and it was found highest negative value at bottom portion of the core. Sand content dominated in this core, and it was found almost equal (83 % to 98 %) to the entire core. Relative textural distribution was in the order sand >clay > silt.

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

M_2: The whole 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. Values of Eh ranged from -211 to -97 mV and it was found highest negative value at the middle to bottom portion of the core. Sand content was intensified in this 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.

N_1: Black colour up to 21-24 cm section and uniform greyish black colour towards bottom of the core were observed. Values of pH ranged from 6.3 to 7. The highest pH at 9-12 cm depth and lowest at 27-30cm depth. Eh ranged from -86 to +376 mV, and it was found highest positive value at top portion of the core. Clay content varied between 35 % and 94 %. Along the core, as depth increases sand content also intensified. The textural variation was in the order: clay> silt> sand.

N_2: The whole core appeared black in colour. Values of pH ranged from 5.2 to 8.1 and highest a were highest at middle portions of the core. . Eh ranged from +64 to +376 mV and it was found highest positive value at top portion of the core. Top portion of the core was dominated with silt content and showed a variation ranging from 43 % to 89 %. As depth increases, silt fraction was decreased and increased sand content was noted towards the bottom portion of the core. The textural variation was in the order: silt > clay> sand.

4.2.2.2 TOC and CHNS

In 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. In S_2 core, TOC ranged from 0.12 to 0.29 showing the lowest and the highest at a depth of 3-6 cm and 21-24 cm respectively.

Core M_1 showed percentage of TOC as 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. For M_2 core, percentage of TOC ranged from 1.12 to 1.95. The maximum was noted at 24-27 cm depth and minimum at 15-18 cm of the core. TOC values increased towards the bottom of the core. In 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 of the core. In Core N_2 the percentage of TOC ranged from 2.39 to 5.6, showing the lowest at bottom and highest at the middle portions of the core.

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 study region. 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.

The ratio of total organic carbon (TOC) % to total sulfur (TS) percentages (TOC: TS), in the studied core sediments was determined. Their values ranged as: core 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. 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 in the cores (S_2, M_1, M_2). These sites were under the threat of anthropogenic inputs and were associated with dredging, and piling activities. This region endure sulfate reduction below an oxygenated water column exhibiting TOC: TS ratios were in the range 1.5 to 5 and well corroborated earlier by Berner and Raiswell.1983. Sediments in the stations (S_1, $N_{1,}$ N_2) were characterized as under predominantly anoxic stipulation in deeper portion of the core. 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 a significant effect on the degradation of sedimentary pigments.TOC/S ratio > 5 in the top to middle portions of the core N_2 are considered as oxic sediment with oxygenated bottom water.

4.2.2.3 Depth Profile of Metals

S_1: Depth profile of metal was given in Figure 4.7. Cd content showed similar trend in the entire sections of the core. The content was diminished to 15-18 cm depth and increased to the bottom. Co was similar dominance in the whole sections of the core with slight decrease till 27 cm and increased to the bottom. Cr was BDL in the samples. The top section of the core is strengthen with Cu and dwindles slightly from 15 cm to the bottom. Fe revealed to be of great heaps in the mid portion (21-30 cm) of the core. Pb showed to be of heavy load in the top and bottom section of the core. Mg was shrinking towards the bottom segment. Mn revealed larger content in the top section (up to 15 cm) of the core and diminished the bottom. Ni was dominant in the top (15 cm) and bottom (39 cm) section of the core and diminished the mid portion Zn concentration was decreased with depth.

Cd, Co and Pb showed increased content in the bottom layer of the core revealed grain size independence to these metal distributions. But Zn and Mg were intensified to the top layer of the core supported by the grain size distribution in these sections. This was also supported by Eh and pH variation. Cr was spotted to be BDL in the samples.

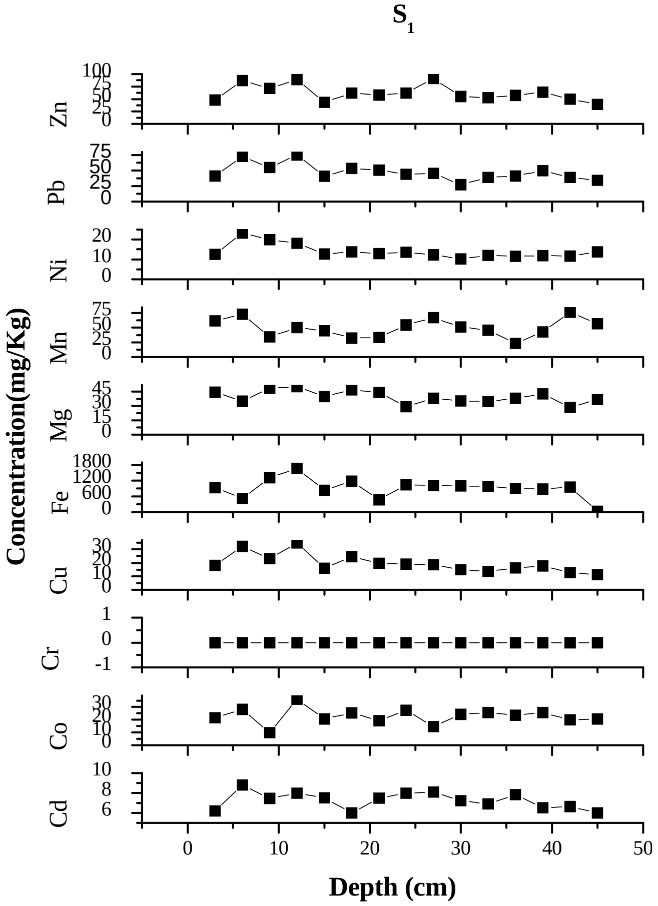


Figure 4.7 Discrepancy of metals in core S_1(2011)

S_2: Depth profile of metal was given in Figure 4.8. Cd content showed similar trend in the entire sections of the core as it prevailing in the top - bottom section and lessen in mid portion. Co revealed that as depth was directly related to metal content. Cr content was BDL. Cu showed a fluctuated metal content variation. Fe and Mg shows same pattern as concentrations diminished with increased depth. Pb content was directly related to metal content and was maximum at 48 cm depth. Mn and Ni had the same trend as depth increased metals were also amplified.Zn content showed trend as metal intensification in the top- mid section.

Co , Cu, Mn , Pb and Ni were intensified in the bottom portion of the core. Cd was high at top and bottom portion of the core. Cr content was BDL. Fe and Mg concentration were intensified at the top portion of the core. Zn had intensification towards the top mid section of the core. The high negative Eh and increased pH values also support these outcomes. Sandy texture of the sediment suggests anthropogenic origin of these metals.

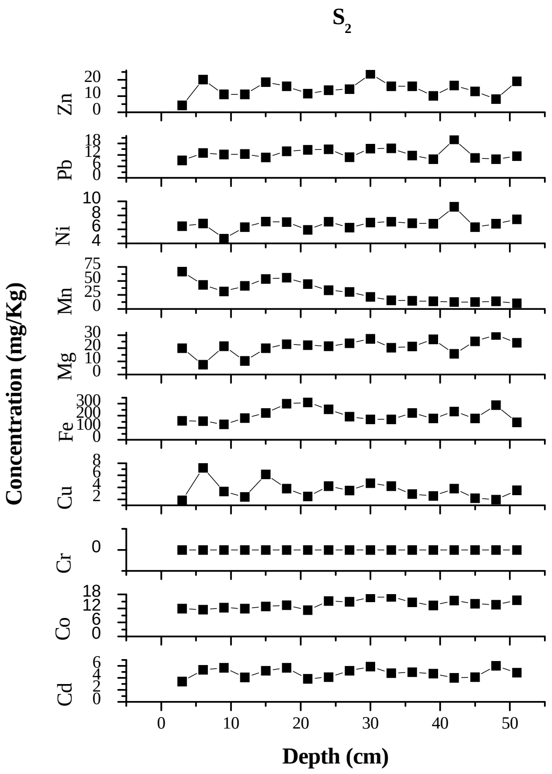


Figure 4.8 Discrepancy of metals in core S_2(2011)

M_1: Depth profile of metal was given in Figure 4.9. Concentration of Cd, Co, Cu, Fe, Mg, Pb and Zn were intensified to the middle and shrink to the bottom section of the core. High negative Eh and increased pH values responsible for this distribution. But content of Cr was BDL where as Mn and Ni augmented with improved depth. Coarse nature of the sediment account for the anthropogenic origin of these metals.

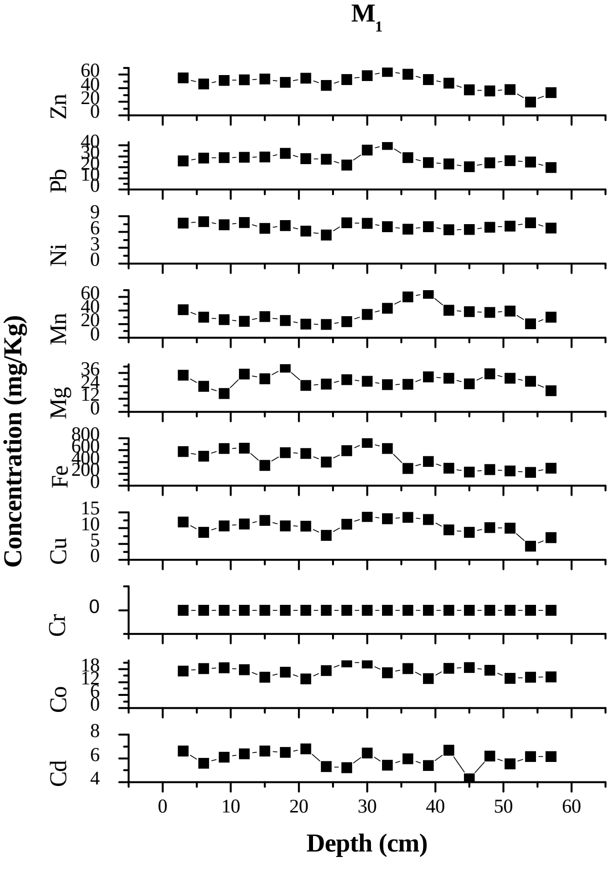


Figure 4.9 Discrepancy of metals in core M_1 (2011)

M_2: Depth profile of metal was given in Figure 4.10. Cd and Mn content were decline to the middle and amplified to the bottom; Co, Fe, Mg, Pb and Ni were enlarged to the mid section then drop off to the bottom and Cu, Zn content enhanced with increase in depth. Co, Fe, Mg, Pb and Ni distribution was influenced by the Eh and pH variation. Textural distributions revealed dominant sand content suggesting the anthropogenic source of this metal.

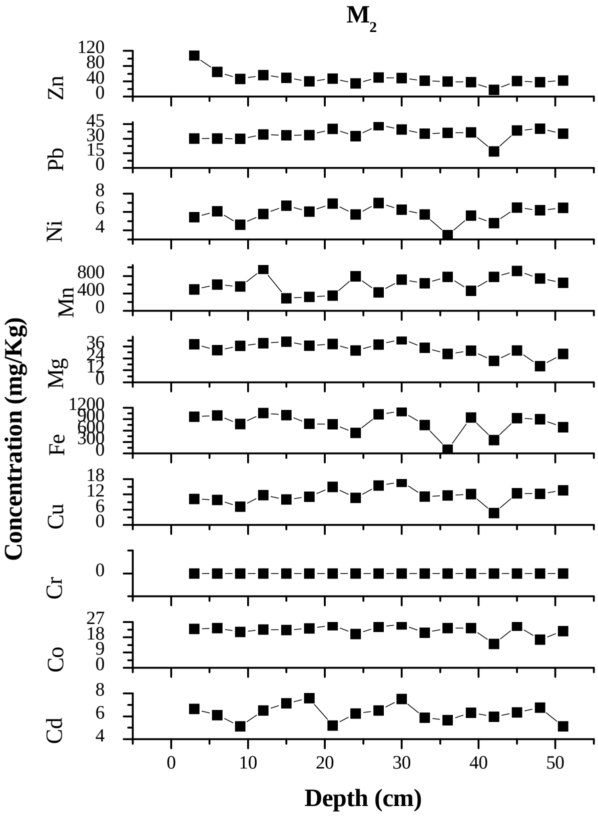


Figure 4.10 Discrepancy of metals in core M_2(2011)

N_1: Depth profile of metal was given in Figure 4.11. Cd, Cr, Cu, Pb, Mn and Zn content were inversely related with depth; Co ,Fe, Mg and Ni were increased to the middle and lessen to the bottom. Highest pH and oxic nature of the sediment (high positive Eh) in the top section responsible for the metal abundance. Textural characteristics revealed the granulometric dependence of these metals.

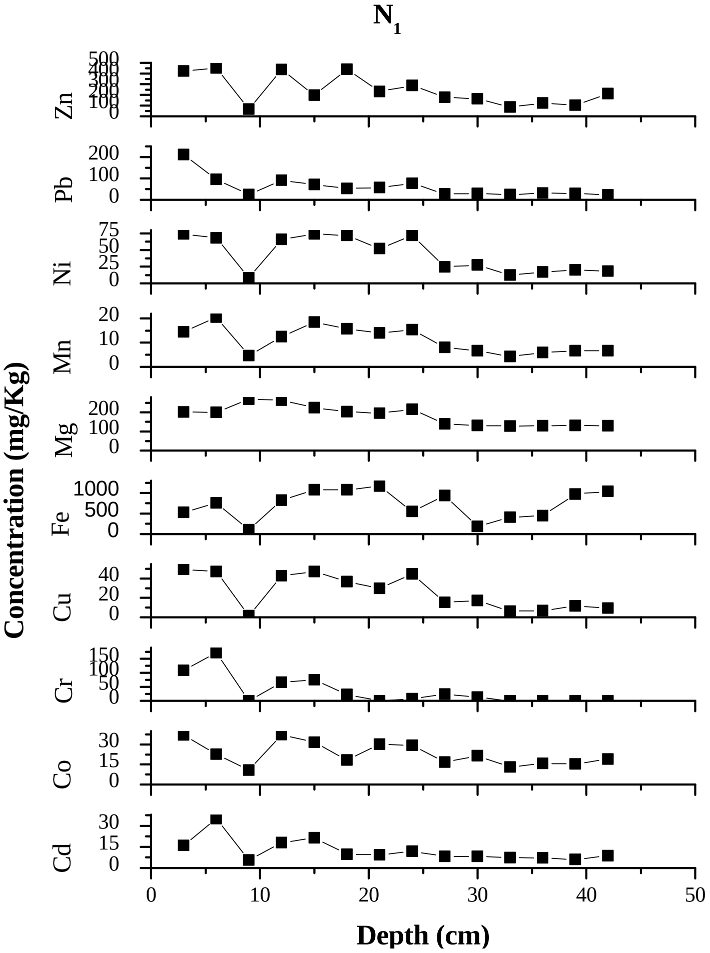


Figure 4.11 Discrepancy of metals in core N_1 (2011)

N_2: Depth profile of metal was given in Figure 4.12. Cd was lessen to the middle and augmented to the bottom; Cr was amplified to the middle and diminished to the bottom; Co, Cu, Fe, Mg, Pb , Ni and Zn were prevailing in the top section and lessened in the bottom section. Mn content was directly related to depth. Highest pH and oxic nature of the sediment (high positive Eh) in the top section responsible for the metal abundance. Textural characteristics revealed the granulometric dependence of Co , Cu , Fe , Mg , Pb , Ni and Zn.

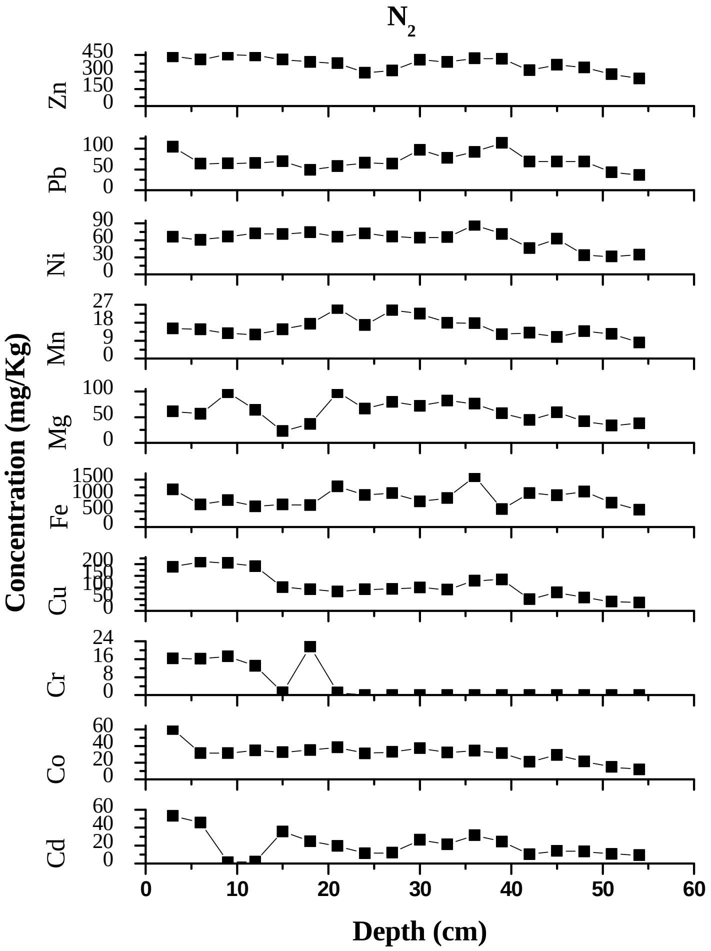


Figure 4.12 Discrepancy of metals in coreN_2(2011)

4.2.2.4 Geochemical Normalisation Methods

1. Antropogenic Factor (AF)

AF revealed vast variation of anthropogenic metal enrichment in different cores from the study area.

The core S_1 revealed AF < 1 for Cr. But Cd, Co, Cu, Ni and Zn had exotic nature in the mid and bottom sections of the core. Fe, Mg and Pb showed extravagant input at the top and bottom sections of the core. Mn had anthropogenic origin only in the bottom section of the core. Core S_2 showed no anthropogenic origin for Cd, Cr, Ni and Zn. Exotic origin was observed at the top section of the core for metals Co, Cu and Fe. The entire section of the core enriched with Mg, Mn and Pb. Excluding Cr all the other metals displayed exotic toxicity for M_1core. In core M_2 most of the metals revealed AF > 1. Cr is the exception for this inference. N_1 and N_2 cores displayed greater anthropogenic factor for all the metals indicating the exotic origin.

2. Contamination Factor (CF)

In core S_1 showed great contamination for Cd, Co and Pb. Among the metals S_2 exposed contagion only for Cd. In M_1 core metal contamination reported for Cd and Pb. Metal toxicity was found for Cd, Co and Pb in core M_2. N_1 core revealed amid the metals immense pollution opened for Cd, Co, Cr, Cu ,Ni , Pb and Zn. Core N_2 had enormous toxicity was revealed for Cd, Co, Cu, Ni, Pb and Zn.

3. Enrichment Factor (EF)

In core S_1, all sections of the core showed extremely high enrichment for Cd. Co showed extremely high enrichment in the entire core. Cr was BDL. Cu at depth 6 cm, 21 cm and 45 cm showed extremely high enrichment and residual part had significant to very high enrichment. Pb generated extremely high enrichment. Mg had minimal enrichment. Mn had minimal enrichment in the entire core. Ni showed extremely high enrichment. Zn was enriched at 6 cm, 21 cm, 27 cm and 45cm depth had extremely high enrichment and the rest very high enrichment. S_2 core Cd showed extremely high enrichment in the entire section. Cr and Cu had at 6 cm depth extremely high enrichment, very high enrichment at 30- 33 cm and the residual section showed significant enrichment. Pb showed extremely high enrichment for the study. Mg showed minimal for the core. Mn showed minimal enrichment. Ni had extremely high enrichment. Zn showed shuffled significant, very high and extremely high enrichment. M_1 core Cd had extremely high enrichment. Co had extremely high enrichment. Cr was BDL. Cu showed significant, very and extremely high enrichment in the entire core. Pb had extremely high enrichment. Mg showed minimal enrichment. Mn had minimal enrichment Ni and Zn had extremely high enrichment. M_2 showed Cd had extremely high enrichment. Co had extremely high enrichment. Concentration of Cr was BDL. Cu and Pb had extremely high enrichment. Mg and Mn showed moderate enrichment. Ni showed extremely high enrichment in the entire core. Zn showed very high enrichment in the entire core. N_1 core Cd had extremely high enrichment. Co and Cr showed extremely high enrichment in the entire core. Cu showed extremely high enrichment in the entire core. Pb showed extremely high enrichment in the entire core. Mg and Mn showed moderate enrichment. Ni and Zn showed extremely high enrichment in the entire core. N_2 core Cd had extremely high enrichment. Co showed extremely high enrichment in the entire core. Cr had extremely high enrichment in the entire core. Cu showed extremely high enrichment in the entire core. Pb showed extremely high enrichment in the entire core. Mg and Mn showed moderate enrichment in the core. Ni and Zn had extremely high enrichment in the entire core.

4. Geoaccumulation Index (IGEO)

IGEO showed Cd had enormous accumulation in the entire sections of the cores in different zones of the estuary studied.

5. Pollution Load Index (PLI)

PLI revealed severe metal contamination for the two cores (N1 and N2) from the biennial collection in the northern region of the estuary.

In core S1, except for Cr all the metals showed anthropogenic origin. Contamination factor revealed contamination for the metals Cd, Co and Pb. Enrichment factor showed extreme enrichment for Cd, Co, Cu, Pb, Mg, Mn, Ni and Zn. Geoaccumulation index suggest severe accumulation of Cd in the entire core. PLI resulted less contamination in the core.

GCI studies for core S_2 revealed no anthropogenic origin for Cd, Cr, Ni and Zn. In the top section of the core showed exotic origin for Co, Cu and Fe. The entire section of the core anthropogenically loaded with Mg, Mn and Pb. Contamination factor result high contamination only for Cd. Enrichment factor showed enrichment for Cd, Cr, Cu, Pb, Mg, Mn, Ni and Zn. Geoaccumulation index suggest severe accumulation of Cd in the entire core.PLI resulted less contamination in the core.

Except Cr all the other metal had high anthropogenic and enrichment factor for core M1. Greater contamination factor was reported for Cd and

Pb. Geoaccumulation index suggests severe accumulation of Cd in the entire core. PLI resulted less contamination in the core.

Except Cr, all the other metal had high anthropogenic and enrichment factor for core M2. Greater contamination factor was reported for Cd, Co and Pb. Geoaccumulation index suggest severe accumulation of Cd in the entire core.PLI resulted less contamination in the core. On comparison between the GCI of the cores the cores collected from the north zone (N1 and N2) showed severe contamination for all the metals except Cr.

4.2.2.5 Statistical Ananlysis

Statistical analysis showed no significant correlation between the components, revealing the anthropogenic input of these metals. Principal component analysis results the reduction of the components to four factors were variance > 7%.

In core $S_{1,}$ four factors (Table 4.10 annexure) account for total variance 82.10%. The factor 1 corresponds to 47.89 % variance revealing the granulometric and organic matter dependence of the metals Cd, Cu, Mn, Ni and Pb. Factor 2 had 15.08 % of variance showed anthropogenic origin of Cd and Mg. Variance of factor 3 and 4 showed as 10.65% and 8.48 % which corresponds to exogenic input of Co.

S_2 generate five factors (Table 4.11 annexure), accounts the total variance as 84.22 %. The factor 1 corresponds to 24.04 % variance revealing the granulometric independence of all the metals. Factor 2 had 21.73% of variance, shows the anthropogenic origin of these metal.

Variance of factor 3 and 4 showed as 16.55 and 12.44% which also generate exogenic input of the metals.

Four factors (Table 4.12 annexure) account for total variance 76.71% for core M_1. The factor 1 corresponds to 36.72% variance, revealing the granulometric and organic matter dependence of Cu, Fe, Ni and Zn. Factor 2 had 16.18% of variance showed granulometric dependence of Pb. Factor 3 and factor 4 demonstrate variance as 13.63% and 9.19 % respectively indicating the exogenic input of all the metals.

Core M_2 had four factors (Table 4.13 annexure) which account for total variance 74.35%. The factor 1, 3 and 4 had variance corresponds to 32.77%, 11.88 % revealing the anthropogenic origin of the metals. Factors 2, generate 21.92% of variance showing the organic matter dependence of Cu, Mn and Ni.

Core N_1 create two factors (Table 4.14 annexure) account for total variance 80.42%. The factor 1 corresponds to 67.11% variance revealing the granulometric relation of Cd, Co, Cu, Mg, Mn, Ni and Zn and also these metal had strong binding behavior with organic matter. Factor 2 generate variance as 13.31% showing exogenic input of all the metals.

In core N_2 four factors (Table 4.15 annexure) account for total variance 83.50%. The factor 1 corresponds to 46.97% variance revealing granulometric relation of Cd, Co, Cu, Mg, Mn, Ni, Pb and Zn also these metal had strong binding with organic matter. The allothonous input of the metals Co, Cr, Mg and Mn. Factor 2 had 17.43% of variance showed granulometric relation of Cu and Cr. Variance of factor 3 showed as 11.77%

generate granulometric dependence of Mg. Factor 4 had variance of 7.33% showed exogenic input of these metals.

The two year gap variation of the depth profile of metals in the CES revealed greater metal content was found in the northern part of the estuary which was due to the high clay content present in the sediment. The sediment textural characteristics in terms of changing hydrography of the CES have been predominantly studied by Nair et al. 1993 revealed large areas of the estuary was covered by clay. Similar trend for textural behavior was observed in most of the sediments cores of the present study. The dependence of metal with organic matter and texture revealed a fluctuation in distribution due to dynamic nature of the estuary. Zonal comparison of the metal in cores gave the order as North Zone > Middle Zone >South Zone. Due to the weak flow and the huge input of industrial effluents, higher levels of metals were found in the northern estuary (Thomson. 2002). On the contrary, consistent with a strong flow, moderate levels of metals were found in the central estuary, which receives both domestic and industrial effluents. Decreasing trends in metal levels, detected towards the central estuary when compared with north may be due to strong rectilinear current, which maintains an effective flushing (Balachandran. 2008). Likewise, in relation with weak flow and minor inputs, lower levels of metals characterized in the southern estuary, which receives agricultural wastes from Kuttanad Paddy fields.

4.2.3 Sediment Quality Guideline Comparison

The major and minor metals in the core sediments from three prominent zones of CES were compared with different world wide used guidelines (Table 2.2 in Chapter 2) .The major and minor metal disparity were given in Table 4.1 and 4.2.

Table 4.1 Biennial major metal disparity

ZONE	CORE CODE	YEAR	MINOR METAL DISPARITY (mg/Kg)				
			Cd	Co	Cr	Cu	Pb
SOUTH	S1	2009	0.67 - 2.98	0.54 -11.62	3.57 - 105.67	20.44 – 134.06	1.22 -22.95
		2011	5.99 - 8.79	9.74 – 35.97	0	11.18 – 34.80	28.65 – 50.19
	S2	2009	3.59 - 8.58	0.99 – 11.70	8.57 - 95.67	9.76 – 18.69	75.61 – 106.10
		2011	3.38 - 6.02	11.27 – 16.9	0	1.81 – 7.27	7.5 – 30.11
MIDDLE	M1	2009	2.31 - 3.78	1.65 – 8.91	293.23 – 582.51	13.05 – 18.35	1.11 – 24.63
		2011	4.29 - 6.81	13.52 -21.32	0	4.28 – 13.67	17.1 – 41.43
	M2	2009	1.31 - 6.21	1.47 – 8.31	52.59 – 391.54	7.59 – 68.03	1.13 – 20.51
		2011	4.29 - 6.81	13.52 -21.32	0	4.28 – 13.67	17.1 – 41.43
NORTH	N1	2009	1.38 - 6.31	5.11 – 21.51	26.33 – 122.51	28.32 – 134.39	7.81- 714.29
		2011	5.65 - 35.2	10.7 – 37.32	0 – 171.34	1.55 – 49.33	22.91 – 211
	N2	2009	1.27 - 6.01	1.68 – 71.14	4.51 – 12.51	3.46 – 13.39	2.59 – 9.47
		2011	1.33 -53.05	11.95 – 60.4	0 – 21.63	35.82 – 210.28	36.53 – 114.66

Cadmium concentration of the core sediments in the south zone ranged as 0.67 - 8.79 mg/Kg, middle zone revealed the array as 1.31 -6.81 mg/Kg and northern zone showed variation as 1.27 - 53.05 mg/Kg. In the study area Cd concentration was found to be maximum (53.05 mg/Kg) in core sampled from the northern region of the estuary and minimum (1.27 mg/Kg) was analyzed for the cores from the southern region. The cadmium concentration recorded in the present study was above the permissible limit (0.6- 10 mg/Kg) given by different SQGs listed in Table 2.2 in Chapter 2.

Co content of the core sediments in the south zone ranged as 0.54 - 35.97 mg/Kg, middle zone showed as 1.47 - 21.32 mg/Kg and northern zone revealed discrepancy as 1.68 - 71.14 mg/Kg. In the study area Co was found to be maximum (71.14 mg/Kg) in core sampled from northern region of the estuary and minimum (1.68 mg/Kg) was noted for the cores obtained from the southern region. The concentration of Cobalt documented in the present study was above the permissible limit (2 mg/Kg).

Cr in the core sediments of the south zone sort as BDL - 105.67 mg/Kg, middle zone showed the range as BDL - 582.51mg/Kg and northern zone exposed divergence as BDL - 171.34 mg/Kg. In the study area Cr was found to be maximum (171.34 mg/Kg) in core sampled from northern region of the estuary and minimum (BDL) was found for the core sections obtained from the southern and middle region. On comparison, with the different SQGs (Table 2.2 in Chapter 2) the content of Cr was above the permissible limit (25-75 mg/Kg).

Concentration of Cu in the core sediments of the south zone arrange as 1.81-134.06 mg/Kg, middle zone ranged as 4.28 - 68.03 mg/Kg and in the northern zone open to the discrepancy as 1.55 - 210.28 mg/Kg. In the study area, Cu was established to be maximum (210.28 mg/Kg) in core obtained from northern region of the estuary and minimum (1.81 mg/Kg) was found for the core sections from the southern region. Copper concentration cited in this study was moderately above the permissible limit (16- 270 mg/Kg) given by different SQGs listed in Table 2.2 in Chapter 2.

Pb in the core sediments of the south zone assembled as 1.22- 106.10 mg/Kg, middle zone ranged as 1.11 - 41.43 mg/Kg and northern zone exposed divergence as 2.59 - 714.29 mg/Kg. In the study area Pb was maximum (714.29 mg/Kg) in the core from northern region of the estuary and minimum (1.11 mg/Kg) was observed for the core sections from the middle region. The Lead concentration cited in this study was above the permissible limit (12.5- 400 mg/Kg) given by different SQGs listed in Table 2.2 in Chapter 2.

Table 4.2 Biennial minor metal disparit

ZONE	CORE CODE	YEAR	MAJOR METAL DISPARITY (mg/Kg)				
			Fe	Mg	Mn	Ni	Zn
SOUTH	S1	2009	14827.59 – 39311.59	26046.8 – 54682.93	66.4 – 63987.8	12.95- 45.53	2.31 – 137.61
		2011	32.08 – 1671.93	23.5 – 72.95	10.26 – 23.18	26.97 – 74.91	39.25 – 91.21
	S2	2009	3574.88 – 3862.19	2646.8 – 4624.26	105.1 – 152.8	15.62 – 56.88	10.85 – 94.26
		2011	129.66 – 312.04	10.2 – 66.88	4.66 - 9.22	9.15 – 20.15	4.31 – 23.81
MIDDLE	M1	2009	3472.91 – 22721.67	3325.12 – 8903.94	85.47 – 131.53	2.24 – 33.63	3.83 -135.47
		2011	226.26 – 728.49	19.69 – 60.3	5.4 – 7.93	19.95 - 40.79	19.46 – 64.72
	M2	2009	783.58 – 45373.13	2425.37 – 13818.41	52.82- 31741.29	0 -53.63	0.12 – 6.81
		2011	100.58 – 1108.86	317.07 – 962.87	3.48 – 6.99	16.94 – 43.87	17.51 -108.14
NORTH	N1	2009	340.53- 48878.74	516.67 – 4161.13	30.56 – 411.47	24.28 – 72.46	49.83- 814.91
		2011	102.97 – 1169.36	130.2 – 268.44	4.27 – 20.49	8.25 -74.27	65.33 – 452.6
	N2	2009	340.53- 8878.74	56.67 – 968.44	24.28 – 206.67	22.67 – 62.46	14.29 - 370.07
		2011	542.69 – 1603.55	22.68 -98.51	8.06 – 25.29	31.58 – 87.50	240.46- 454.4

Iron concentration of the core sediments in the south zone ranged as 32.08-39311.59 mg/Kg, middle zone revealed the array as 100.58 -45373.13 mg/Kg and in the northern zone showed variation as 102.97-48878.74 mg/Kg. In the study area, Fe concentration was found to be maximum (48878.74 mg/Kg) in core sampled from northern region of the estuary and minimum (32.08 mg/Kg) was noted for the cores obtained from the southern region.

Mg content of the core sediments in the south zone ranged as 10.2 -54682.93 mg/Kg, middle zone had the assortment as 19.69 - 13818.41 mg/Kg and northern zone exposed divergence as 22.68 -4161.13 mg/Kg. In the study area, Mg was found to be maximum (54682.93 mg/Kg) and minimum (10.2 mg/Kg) in the cores from the southern region.

Mn in the core sediments of the south zone sort as 4.66 - 63987.8 mg/Kg, middle zone showed the range as 3.48 - 31741.29 mg/Kg and northern zone exposed divergence as 4.27-411.47 mg/Kg. In the study area Mn was found to be maximum (63987.8 mg/Kg) in core obtained from southern region of the estuary and minimum (3.48) was for the core sections sampled from the middle region. The Manganese concentration generated in this study was moderately above the permissible limit (30 - 3000 mg/Kg) as given by different SQGs listed in Table 2.2 in Chapter 2.

Concentration of Ni in the core sediments of the south zone range as 9.15-74.91 mg/Kg, middle zone ranged as BDL - 53. 63 mg/Kg and northern zone observed as 8.25 -87.50 mg/Kg. In the study area Ni was established to be maximum (87.50 mg/Kg) in core from northern region of the estuary and minimum (BDL) was noted for the core sections from the middle region. The Nickel concentration cited in this study was moderately above the permissible limit (16- 315mg/Kg) given by different SQGs listed in Table 2.2 in Chapter 2.

Zn in the core sediments of the south zone assembled as 2.31-137.61 mg/Kg, middle zone ranged as 0.12 - 135.47 mg/Kg and northern zone exposed divergence as 14.29 -814.91 mg/Kg. In the study area Zn was maximum (814.91 mg/Kg) in the core sediment from the northern region of the estuary and minimum (0.12 mg/Kg) was found in the core sections from the middle region. The Zinc concentration cited in this study was moderately above the permissible limit (70-820 mg/Kg) given by different SQGs listed in Table 2.2 in Chapter 2 generate moderate pollution in the study area.

Most of the identified metal in the core revealed pollution load as concentration far higher than the guideline values. This revealed moderate to severe pollution of metals in the study area

4.2.4 Previous Literature Comparison

Metal enrichment was found in the Cochin estuarine sediments, it would be worth to compare the metal concentration values with previously reported within the system and other large urban-coastal settings or recognized polluted areas (Table 4.3). In comparison to the ranges reported worldwide, the maximum values of metals were found in this study and were similar order of magnitude or even higher than those reported for other polluted estuaries, placing the region as one among the impacted estuaries around the world.

Table 4.3 Comparison metal concentration (mg/Kg) within the system and other large urban-coastal settings or recognized polluted areas

Location	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Zn	References
CES	53.05	71.14	582.51	210.28	48878.74	54682.93	63987.8	87.50	714.29	814.91	Present Study
Pearl River Estuary	1.55	23.9	138	105	NA	NA	NA	76.6	88.5	274	Baolin Liu et al. 2011
CES	29.4	NA	NA	1683	NA	NA	15490	72.3	98.9	2246	Harikumar and Nasir. 2010
CES	0.73	NA	NA	49.43	67510	NA	860.97	64.02	54.42	211.39	Harikumar et al. 2009
Manakudy Estuary	3.168	6.052	482.138	45.867	4887.462	5284..064	358.216	28.912	176.877	72.623	Sugirtha P Kumar and Patterson Edward. 2009
CES	16	52	NA	50	NA	NA	NA	118	NA	858	Priju and Narayana. 2007
Gdansk Basin ,Baltic Sea	NA	19	107	71	52000	NA	419	46	83	210	Belzunce Segarra et al. 2007
Manjeshwar and Someshwar	NA	20	NA	36	NA	NA	449	103	43	80	Karbassi and Shankar. 2005
Bilbao,Spain	NA	NA	350	1949	NA	NA	NA	NA	2566	7687	Cundy et al. 2003
Tamki Estuary New Zealand	1.49	NA	NA	60.35	NA	NA	NA	NA	200	365	Abrahim and Parker 2002
Golden Horn , Turkey	6	24.5	390	194	NA	NA	NA	NA	510	890	Tuncer et al. 2001

NA-Not Available

On comparison with the previous reports (Table 4.3) within the CES and other polluted estuaries, Cd concentration was high in the study area. The heavy load of Cd can be justified in the light of local pollution due to dumping of sewage and industrial effluents. Co resulted severe pollution in the estuary and was very high as compared to the earlier reports of the same aquatic system and polluted estuaries. The heavy load of Co can be justified in the light of local pollution due to dumping of sewage and industrial effluents. Cr was found elevated values compared with other estuaries (Table 4.3). Sugirtha and Patterson. 2009 reported a similar concentration (482.138 mg/Kg) than the above trend. Cr establishes to be highly intensified in the study area due to the excess of industrial and municipal effluents. The previous reports (Table 4.3) within the CES and other impacted estuaries, Cu content heavily magnified in the study area. The source of copper includes industrial and municipal effluents. Fe was increased in the study area as compared to the previous reports (Table 4.3), but there are exception, showing heavy concentration of the metal reported earlier by Belzunce Segarra et al. 2007 (52000 mg/Kg) than the present study. On comparison with earlier studies in Table 4.3, Mg showed a greater amount for the present study than the previous report. The heavy load of Mg is due to the disposal of wastes, sewage and industrial effluents. Concentration of Mn was high in this study when compared within the system and the other reports listed in the Table 4.3. The Mn source includes industrial and municipal effluents. Concentration of Ni was very high in this study as compared within the system and the other reports listed in the Table 4.3. But there are exceptions showing heavy concentration of the metals by Karbassi and Shankar 2005. (103mg/Kg) and Priju and Narayana. 2007 (118 mg/Kg) than the present study. Ni ascertains to be highly intensified in the study area. The source of Ni includes industrial and municipal effluents. Content of Pb was high in this study when compared within the system and the other reports listed in the Table 4.3. The effluent from chromium plating industries is one of the major sources of lead. Zn concentration was high in this study when compared within the system and the other reports listed in the Table 4.3. But there are exceptions showing heavy concentration of the metals by Harikumar and Nasir. 2010 (2246mg/Kg) and Cundy et al. 2003 (7687mg/Kg) than the present study. The effluent from industries is one of the major sources.

4.3 Conclusion

The distribution, movement and storage of contaminants in the hydrosphere have a substantial effect on various scientific aspects of ecology, environmental biogeochemistry and proper management of aquatic resources. Therefore, the study compiles the ecological risk of metals in the estuary with reference to biennial spatial and depth profile of core sediment in CES. Investigation on the influence of anthropogenic activities using GCI resulted in moderate to severe pollution for all the metals under investigation and specifically for Cd. The link between geoaccumulation and ecological risk has been examined to gain insight into the processes affecting the representation of pollution magnitude in terms of toxicity of metals. SQG comparison generate severe contamination for Cd , Co, Cr, Pb, Mn, Zn and moderate for Cr and Ni. Except elements Ni and Zn, all the metals showed enrichment in comparison with previous reports placing the region as one among the impacted estuaries around the world. This study generates an authority on metal distribution and their chemical control in the estuarine core sediments. An assessment has been made based on a sequential extraction procedure to understand the binding fractions and mobility of metals to the surrounding environment. These geochemical fractionation of metal in specific core sediment of CES is studied in detail and are given in Chapter 5.

Annexure

Table 4.4 Component matrix of the core sediment S_1 (2009) using principle component analysis

	Component				
	1	2	3	4	5
Cd	-.382	-.385	.194	.675	.085
Co	-.431	.569	-.115	-.467	.468
Cr	-.430	-.266	.400	.073	-.021
Cu	.319	-.771	.391	-.166	.308
Fe	.817	.029	-.418	.318	.091
Mg	.816	.043	-.427	.313	.080
Mn	.855	.319	.256	.078	-.293
Ni	-.444	.027	-.890	-.077	.047
Pb	.068	.602	.127	-.088	.718
Zn	-.107	-.884	.111	-.185	.302
TOC	.246	.544	.415	-.434	-.463
SAND	-.912	.114	-.111	.157	-.297
CLAY	.733	-.464	-.150	-.415	.048
SILT	.138	.616	.423	.466	.368

Table 4.5 Component matrix of the core sediment S_2 (2009) using principle component analysis

	Component			
	1	2	3	4
Cd	.059	.330	.891	-.159
Co	-.910	.109	.225	-.112
Cr	-.141	.563	-.274	.665
Cu	-.132	-.882	.062	.151
Fe	-.168	-.444	.555	-.572
Mg	.846	.089	-.050	-.363
Mn	.586	.248	.533	.444
Ni	-.064	.280	.894	.282
Pb	.845	.098	-.049	.094
Zn	.857	.321	.152	.004
TOC	-.817	.093	.288	.235
SAND	-.347	.866	-.165	-.255
CLAY	.533	-.717	.188	.157
SILT	-.204	-.809	.043	.354

Table 4.6 Component matrix of the core sediment M_1 (2009) using principle component analysis

	Component			
	1	**2**	**3**	**4**
Cd	.441	.308	.523	.527
Co	.449	.295	-.700	.271
Cr	.938	.120	.190	.104
Cu	-.721	-.009	-.288	-.241
Fe	.385	.574	.471	-.333
Mg	.138	.832	.428	-.227
Mn	-.125	.841	-.120	-.290
Ni	.942	.122	-.124	.135
Pb	-.820	.072	.304	.172
Zn	.937	.052	-.223	.130
TOC	.196	-.893	.267	.149
SAND	.507	-.738	.135	-.403
CLAY	-.588	.651	-.082	.447
SILT	.540	.389	-.281	-.319

Table 4.7 Component matrix of the core sediment M_2 (2009) using principle component analysis

	Component			
	1	**2**	**3**	**4**
Cd	.644	.397	-.203	-.363
Co	.589	.333	-.443	-.244
Cr	.536	-.419	.540	.346
Cu	.851	-.209	.373	.052
Fe	.683	-.406	.039	-.318
Mg	.947	-.125	.004	-.080
Mn	.812	-.097	.421	-.067
Ni	.436	.325	-.283	-.049
Pb	-.154	-.282	-.228	.796
Zn	-.433	.703	.356	.023
TOC	.120	.618	.521	.017
Sand	-.685	-.480	.207	-.460
Clay	.115	.820	.203	.250
Silt	.758	.061	-.381	.399

Table 4.8 Component matrix of the core sediment N $_1$(2009) using principle component analysis

	Component		
	1	2	3
Cd	-.533	-.067	.682
Co	.831	-.300	.275
Cr	.178	.752	-.557
Cu	.718	.439	.433
Fe	.779	.247	.144
Mg	.901	.103	.032
Mn	.912	.136	-.258
Ni	-.501	.161	.345
Pb	.772	.323	.162
Zn	.775	-.106	.335
TOC	.774	-.524	.046
Sand	-.976	.090	.079
Clay	.979	.054	-.012
Silt	.371	-.780	-.381

Table 4.9 Component matrix of the core sediment N $_2$(2009) using principle component analysis

	Component				
	1	2	3	4	5
Cd	-.445	.506	-.278	.070	.649
Co	.732	.362	.439	-.222	.011
Cr	.801	-.003	.449	.004	-.083
Cu	-.540	-.150	.643	-.334	.321
Fe	.231	-.712	.313	-.217	.462
Mg	.724	.099	-.096	-.475	-.387
Mn	.725	.345	.308	.135	.392
Ni	-.634	.602	.304	-.267	-.057
Pb	-.348	.064	.879	.085	-.191
Zn	.571	.423	.358	.568	.019
TOC	-.274	.516	.067	.618	-.115
Sand	-.837	-.226	.361	.064	-.243
Clay	.220	.881	-.206	-.320	.084
Silt	.423	-.839	-.053	.319	.100

Table 4.10 Component matrix of the core sediment S_1(2011) using principle component analysis

	Component			
	1	2	3	4
Cd	.543	.606	.095	-.394
Co	.286	.093	.687	.523
Cu	.958	.029	.219	.066
Fe	.429	-.261	.499	-.446
Mg	.017	.671	-.141	.381
Mn	.805	.227	-.131	.090
Ni	.902	.057	.223	.122
Pb	.551	-.777	-.009	-.086
Zn	.765	.308	.271	-.268
TOC	.652	.332	-.386	-.054
Sand	-.877	.208	.346	-.079
Clay	.740	-.390	-.111	.442
Silt	.809	-.087	-.408	-.129

Table 4.11 Component matrix of the core sediment S_2(2011) using principle component analysis

	Component				
	1	2	3	4	5
Cd	.269	-.205	-.156	.688	.522
Co	.727	-.227	.206	.315	-.387
Cu	.478	.022	-.784	.029	.298
Fe	.189	.344	.554	-.304	.588
Mg	-.479	.464	-.389	-.273	.370
Mn	.737	-.040	.064	-.424	-.148
Ni	.706	.205	-.088	-.397	-.132
Pb	-.010	-.462	.680	.391	.192
Zn	.799	-.075	-.438	.194	.150
TOC	.527	.028	.499	-.206	.290
Sand	-.115	-.923	-.120	-.323	.117
Clay	.243	.819	.284	.078	.021
Silt	-.017	.781	-.043	.443	-.201

Table 4.12 Component matrix of the core sediment M $_{1}$(2011) using principle component analysis

	Component			
	1	**2**	**3**	**4**
Cd	.319	.460	-.265	-.417
Co	.407	-.448	-.041	.654
Cu	.780	.006	.542	-.030
Fe	.890	-.056	-.272	.096
Mg	.062	.015	.813	.011
Mn	.343	.204	-.394	.567
Ni	.678	.024	.134	-.156
Pb	.098	.766	.273	.391
Zn	.882	-.126	.379	-.161
TOC	.869	-.109	.181	.041
Sand	-.742	-.180	.443	.157
Clay	.489	-.679	-.365	-.174
Silt	.441	.733	-.218	-.036

Table 4.13 Component matrix of the core sediment M $_{2}$(2011) using principle component analysis

	Component			
	1	**2**	**3**	**4**
Cd	.388	.205	.373	.459
Co	.816	.066	-.385	-.172
Cu	.631	.609	-.325	-.057
Fe	.766	.134	.216	.476
Mg	-.480	.106	-.365	.560
Mn	.577	.577	.349	.022
Ni	.587	.604	-.379	-.105
Pb	.811	-.205	.004	-.120
Zn	.596	-.371	.145	.135
TOC	-.294	.371	.421	.144
Sand	.455	-.822	-.028	.077
Clay	-.446	.570	-.476	.215
Silt	-.210	.623	.531	-.334

Table 4.14 Component matrix of the core sediment N_1(2011) using principle component analysis

	Component	
	1	2
Cd	.820	.000
Co	.777	.271
Cu	.934	.297
Fe	.205	.821
Mg	.650	-.174
Mn	.877	.363
Ni	.900	.360
Pb	.846	-.175
Zn	.843	.210
TOC	.970	-.117
Sand	.908	-.073
Clay	-.834	.516
Silt	.759	-.585
Cr	.860	-.186

Table 4.15 Component matrix of the core sediment N_2(2011) using principle component analysis

	Component			
	1	2	3	4
Cd	.498	-.025	-.746	-.114
Co	.900	-.012	-.234	-.012
Cu	.737	.578	-.016	.101
Fe	.308	-.585	.106	.409
Mg	.620	-.209	.620	.278
Mn	.565	-.657	.243	-.300
Ni	.811	-.025	-.004	.077
Pb	.583	-.144	-.465	.523
Zn	.788	.412	-.129	.258
TOC	.849	-.124	.078	-.240
Sand	-.916	.050	-.095	.267
Clay	.145	.699	.541	.239
Silt	.881	-.244	.202	-.165
Cr	.445	.729	.014	-.330

****

Chapter 5

GEOCHEMICAL METAL FRACTIONATION OF SPECIFIC CORE SEDIMENTS IN THE CES

Contents

5.1 Introduction

Sediments embody the compositional history of the hydrosphere as a whole and especially core sediment would provide as a key for understanding the reconstruction of past environmental conditions of the marine niche. Hence core sediments are used for accessing the pollution history of the aquatic environment (Lopez and Lluch. 2000; Karbassi et al. 2005). Studies on the metal contamination of core sediments often rely on the analysis of total metal content; however information on the total concentrations of metals alone is not sufficient to assess the remobilized potential of metal fraction and the degree of pollution. Therefore, the chemical form of metals in the sediment core is of great significance for updating information on various biological / diagenetic processes prevailing in the ecosystem. Besides, it provides knowledge on the origin, mode of occurrence and both the bioavailability along with the chemical forms of metals residing in the bottom segment (Shiowatana et al. 2001). Furthermore it is necessary to identify and quantify the forms in which a metal is present in the sediments to gain a more precise understanding of the potential and the impacts of elevated concentrations on aquatic life, and to evaluate the processes of downstream transport, deposition and release under changing environmental conditions (Li et al. 2000).

In the present study, ecological risk due to metals in the estuary has been evaluated based on a sequential extraction procedure to understand the binding fractions and mobility of metals to the surrounding environment. Moreover, the study investigates the influence of varying anthropogenic activities on metal binding and their chemical control over the estuarine core sediments. These observations are used to describe the mechanism which controls the solid phase metal distribution and partitioning patterns in different contrasting environments of CES. Fractionations by chemical leaching techniques have great significance in determining the degree of association of metals in the sedimentary column and to what extent they may be remobilized in to the environment (Forstner et al. 1990). The study also provides the pattern of difference with lithogenic origin from those with an anthropogenic origin. In the previous published literature several methods of determining the different forms of metals in sediment were described (Tessier et al. 1979; Kheboian and Bauer. 1987; Marin et al. 1997). Most widely reliable and acceptable methods are based on sequential extraction procedure and there are many such kinds of schemes among which the most widely used is the one proposed by Tessier et al. 1979.

5.2 Geochemical Metal Fractionation

To assess the extent of pollution hazard and to understand the heavy metal dynamics in the entire estuary, the intensities of different chemical fractions in the core sediment have to be looked. In chapter 4, discussed the two year gap variation of the depth profile of metal distribution in the CES and showed that greater metal content was detected in the northern part of the estuary. This was mainly due to the inferred high clay content present in that specific sediment sample. The dependence of metal with organic matter and texture revealed a fluctuation in the distribution. Zonal comparison of the metal in cores provide the order as North Zone > Middle Zone >South Zone. Due to the weak flow and the huge input of industrial effluents, higher levels of metals were found in the northern estuary; moderate levels of metals were found in the central estuary which is consistent with a strong flow, which receives both domestic and industrial effluents and earlier work of Balachandran et al. 2008 supports this outcome. Decreasing trends in metal levels detected towards the central estuary when compared with north zone may be due to strong rectilinear current, which maintains an effective flushing. In relation with weak flow and minor inputs, lower levels of metals were characterized in the southern estuary, which also receives agricultural wastes from nearby paddy fields. The observed Eh and pH fluctuations discussed in Chapter 4 also favour the metal distribution.

This chapter describe and highlights the results of the geochemical distribution of sequentially leached metal fractions (Cd, Cu, Pb, Fe, Mn and Ni) adopting the method of Tessier et al. 1979 in the core sediments sampled from three contrasting zones in the CES. These chemical fractionation of metals are exchangeable (EXC), bound to carbonate (CA), organic matter bound (oxidisable) (OM), Iron and Manganese bound (reducible) (FMO) and residual (RES) fraction. EXC fraction of heavy metals can be easily released back to the water column which may cause secondary pollution and subsequent health risk to the exposed population. The amount of metals in this phase indicated the environmental conditions of the overlying water bodies. Metals in this fraction are the most mobile and readily available form for biological uptake in the environment (Singh et al. 2005; Zakir et al. 2008). In this study, the northern zone of the estuary was enriched with this fraction for most of the metal studied. CA fraction is initially present as metal salts in sediment and readily available following a slight lowering of pH (Turner and Olsen. 2000). Association of metals with this fraction is probably the best example of human-induced influence in the sediments of the study area. An intensification of metal was found for southern and northern part of the estuary which accounts the increased agricultural and industrial runoff in the study area. Metal adsorbed in sediments are found in the FMO fraction. It includes the metal oxides and hydroxide that can be released into the system with a pH decrease or if sediments change from oxic to anoxic condition (Turki. 2007). These oxides become unstable by reduction or acidic transformation of sediments. Among the metal analysed Pb, Mn and Fe are found to be high value for FMO in this study. Fe and Mn oxides fraction was reported to be the main carriers of Fe and Mn (Li et al. 2001) as they easily undergo adsorption phenomena. Further the higher association of Pb was observed in FMO fraction may be due to the higher stability constant of Pb oxides (Fan et al. 2002). Generally the affinity of metals for organic substances and their decomposition products are of great importance for the release of the metals into the aquatic phase. Metal bound to OM fraction is in chelated form and assumed to reflect strong association with sediment organic material and can be immobilized in both oxidizing and reducing condition. It represents the amount of metals bound to the OM that would be released in to the environment if condition becomes oxidative. Cu, Fe, Pb, Mn are dominant in this fraction for both period of study under investigation. The metal present in the residual fraction exists in the form of metal precipitates which can be used as a baseline data for the assessment of the degree of contamination of the system. The association between metals and the residual fraction of uncontaminated sediments are so strong that metal association with non-residual fraction has been used as an indicator of anthropogenic enrichment (Sutherland et al. 2000; Zakir et al. 2008). Residual fraction is an inert phase of metal that cannot be mobilized. Fe and Ni are intensified in this fraction of the study area indicating the lithogenic origin supported by earlier similar studies carried out in the Pearl River estuary and East China Sea (Yuvan et al. 2004).

Each metal in its fractionation profile had its own variation pattern and described separately. The geochemistry of metal (2009 and 2011) fractionation including the depth profile variation of metals was carried out in two year gap sampling period and discussed separately in sections as Part A and Part B.

5.2.1 Part A

This section details the salient portrayal on geochemical characteristics of six sediment cores collected from specific zones of CES during November 2009.

5.2.1.1 Cadmium

a. ***S_1:***

Fractionation profile was given in Figure 5.1. Exchangeable and bound to carbonate fraction, the concentration increased slightly in the direction of the bottom section of the core. Fe and Mn oxide fraction were abundant in the top section of the core and diminished faintly towards the bottom. Fractions bound to organic matter and residual form were intensified weakly in the mid section of the core and diminished towards greater depth.

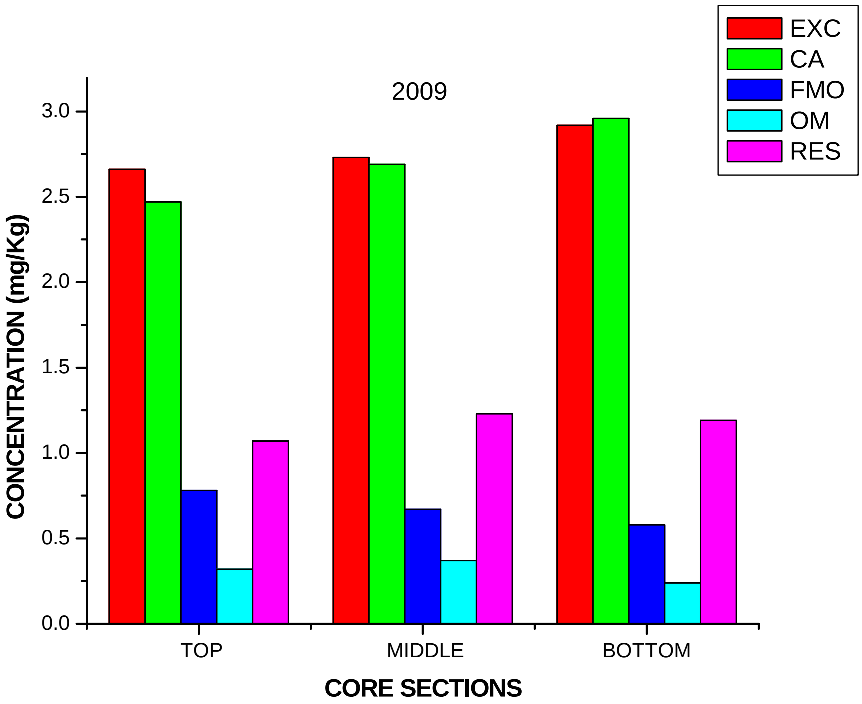


Figure 5.1 Fractionation profile of Cd in the core sediment S_1 (2009)

b. ***S_2:***

Fractionation profile was given in Figure 5.2. Exchangeable fraction was slightly lower to the mid section of the core and inflates weakly as depth increases. The remaining fractions amplified toward the beneath segment of the core.

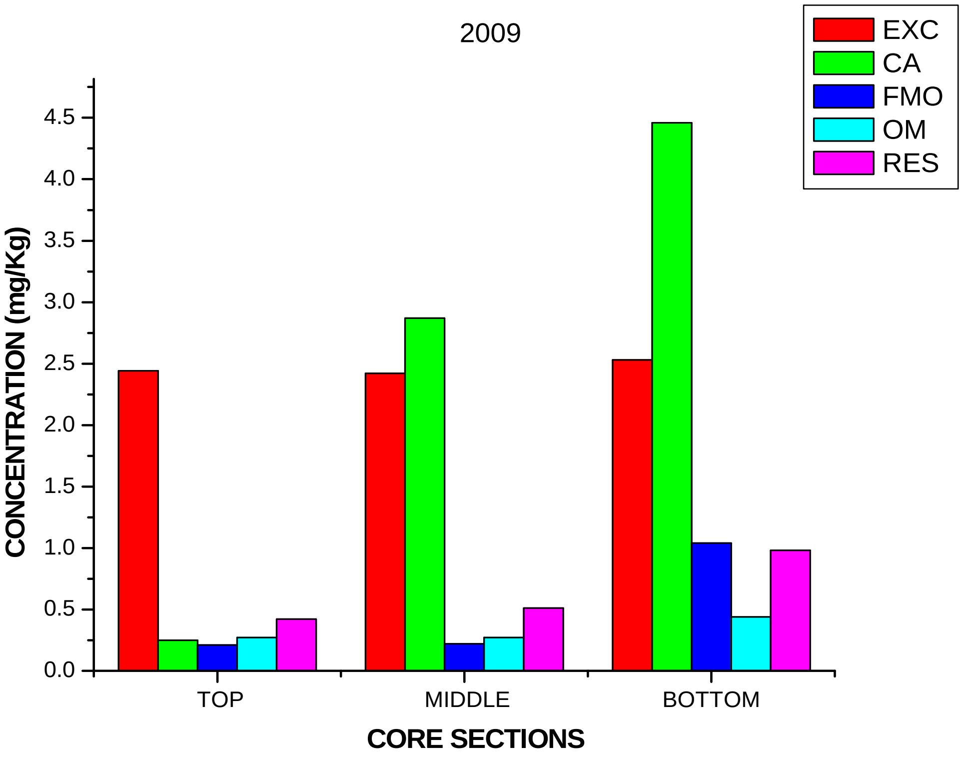


Figure 5.2 Fractionation profile of Cd in the core sediment S_2(2009)

c. M_1:

Fractionation profile was given in Figure 5.3. Exchangeable and bound to organic matter fraction, the concentration increased slightly toward the bottom section of the core. Bound to carbonate fraction abundant in the top section of the core and reduce towards the bottom. Fe - Mn oxide and residual fractions diminished to the mid section of the core and intensified faintly towards deeper section.

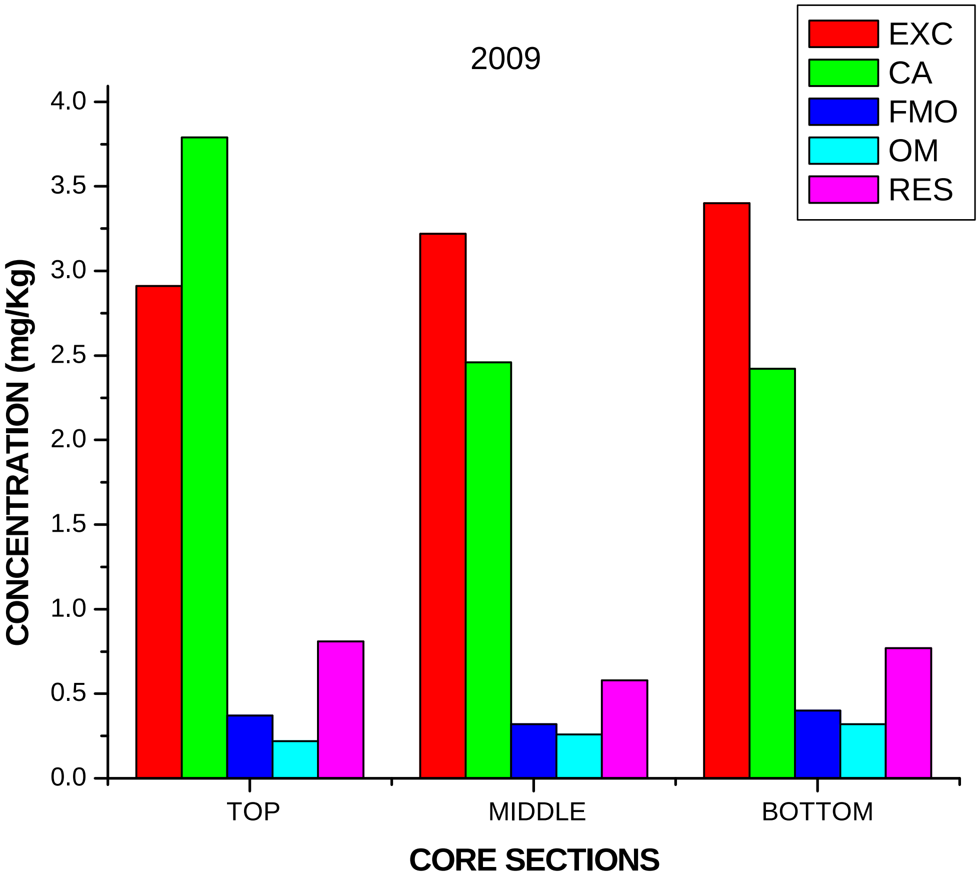


Figure 5.3 Fractionation profile of Cd in the core sediment M_1 (2009)

d. ***M_2:***

Fractionation profile was given in Figure 5.4. Exchangeable, bound to carbonate and Fe - Mn oxide fraction were diminished to the mid section of the core and greater slightly to the bottom part. Bound to organic matter fraction, the concentration faintly increased towards the bottom section of the core. Residual fraction was high to the mid section of the core and lower weakly towards greater depth.

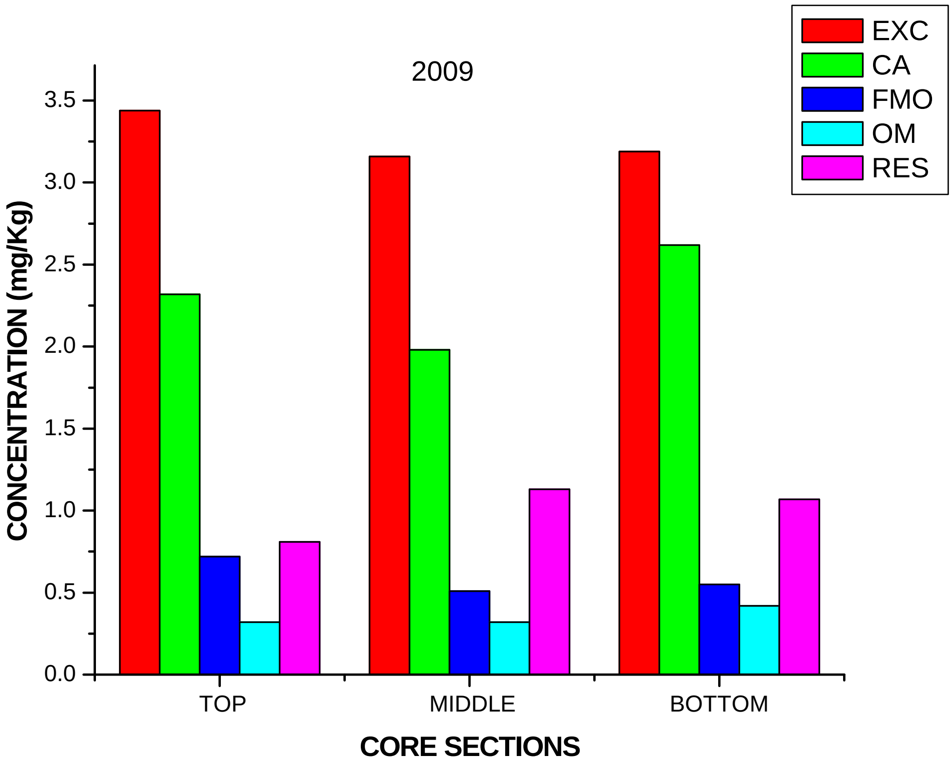


Figure 5.4 Fractionation profile of core sediment M_2(2009)

e. ***N_1**:*

Fractionation profile was given in Figure 5.5. Exchangeable and bound to carbonate fraction were increased faintly toward the lower component of the core. Fe - Mn oxide fraction was abundant in the top section of the core and slightly lower towards the bottom. Bound to organic matter and residual fraction was weakly greater to the mid section of the core and less to the deeper layer of the core.

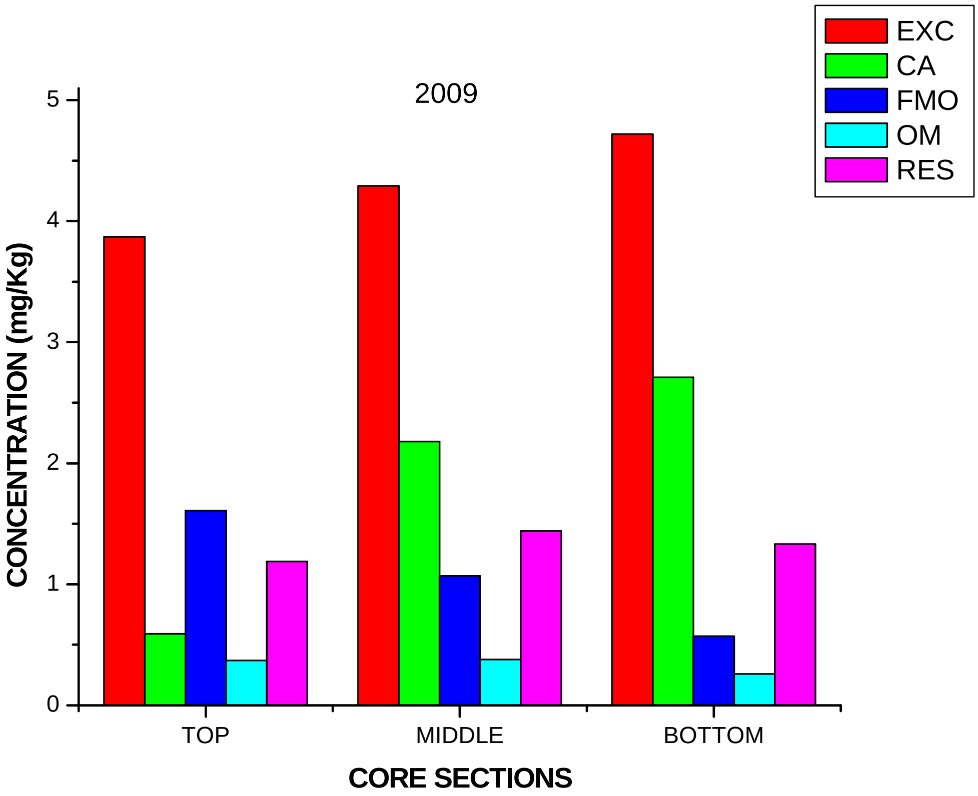


Figure 5.5 Fractionation profile of Cd in the core sediment N_1 (2009)

f. ***N_2*:**

Fractionation profile was given in Figure 5.6. Exchangeable and bound to carbonate concentration were decreased in the direction of the bottom section of the core. Fe - Mn oxide fraction, bound to organic matter and residual fraction were increased slightly to the mid section of the core and low towards bottom segment.

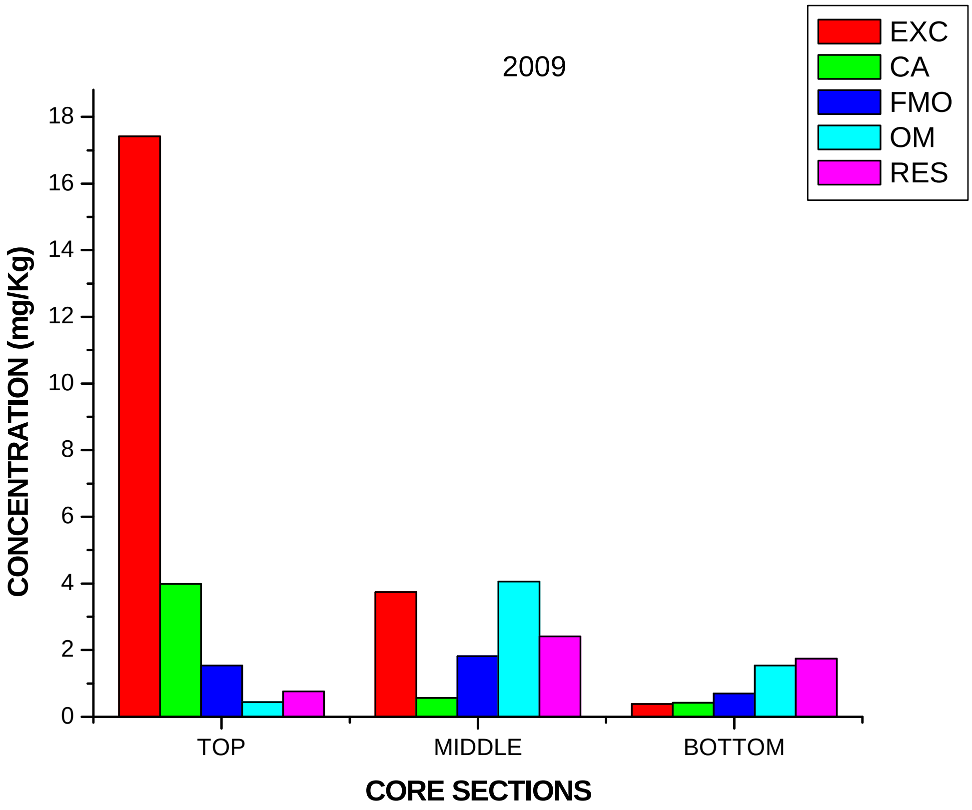


Figure 5.6 Fractionation profile of Cd in the core sediment N_2(2009)

5.2.1.2 Copper

a. S_1:

Fractionation profile was given in Figure 5.7. Exchangeable fraction was the major contributor in the top and mid section of the core and minor towards bottom section. Bound to carbonate fraction was slightly diminished to the mid section of the core and weakly intensified towards the deeper layer. Fe- Mn oxide and residual fraction were faintly greater towards the bottom section of the core. Bound to organic matter was lesser towards the foot section of the core.

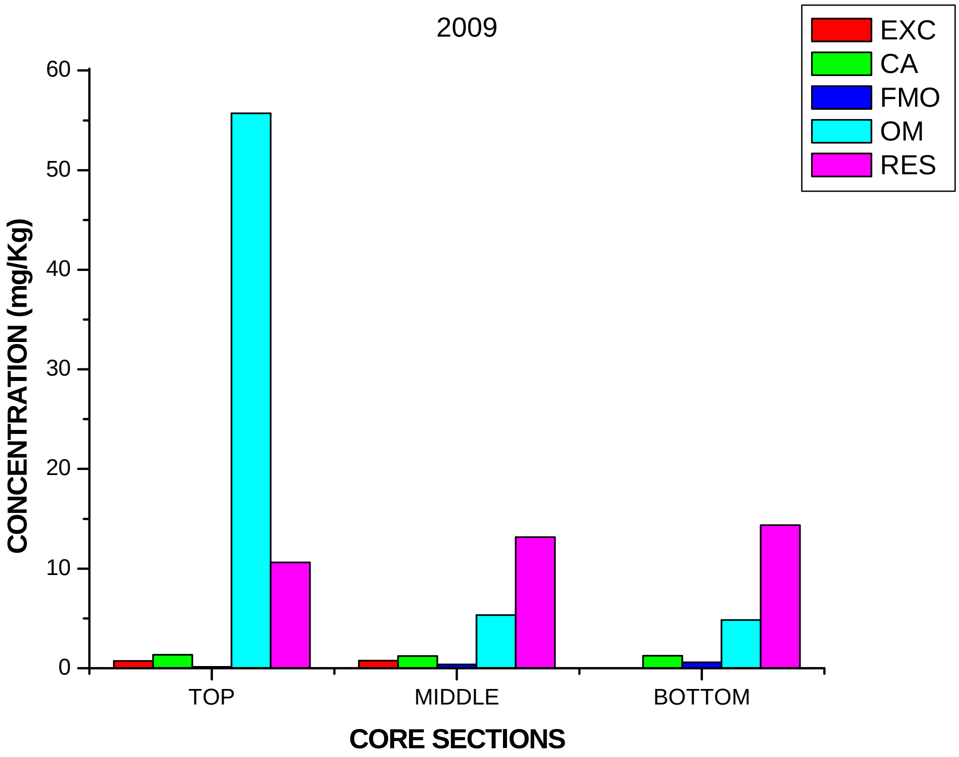


Figure 5.7 Fractionation profile of Cu in the core sediment S_1 (2009)

b. S_2:

Fractionation profile was given in Figure 5.8. Exchangeable fraction was slightly major in the mid section of the core and minor to the bottom layer. Bound to carbonate fraction was diminished weakly to the mid section of the core and intensified to the heavier depth. Fe- Mn oxide, bound to organic matter and residual fraction were high towards the bottom section of the core.

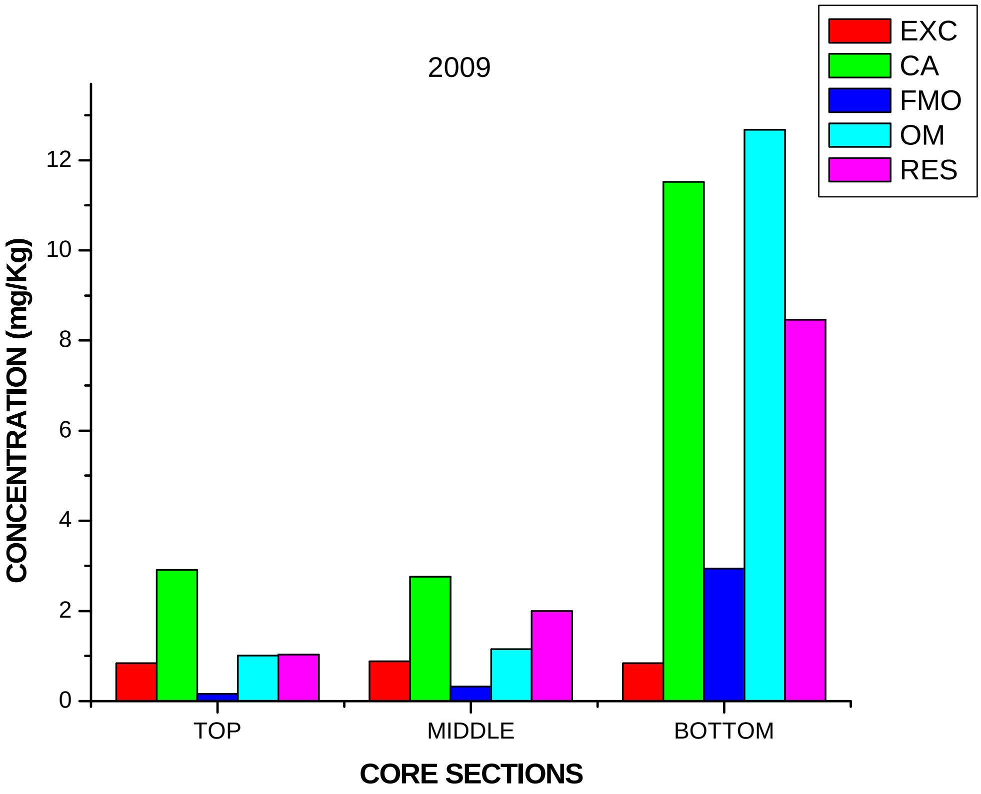


Figure 5.8 Fractionation profile of Cu in the core sediment S_2 (2009)

c. *M_1:*

Fractionation profile was given in Figure 5.9. Exchangeable, bound to carbonate, Fe and Mn oxide, bound to organic matter and residual fraction were minimized to the mid section and improved towards the underneath segment of the core.

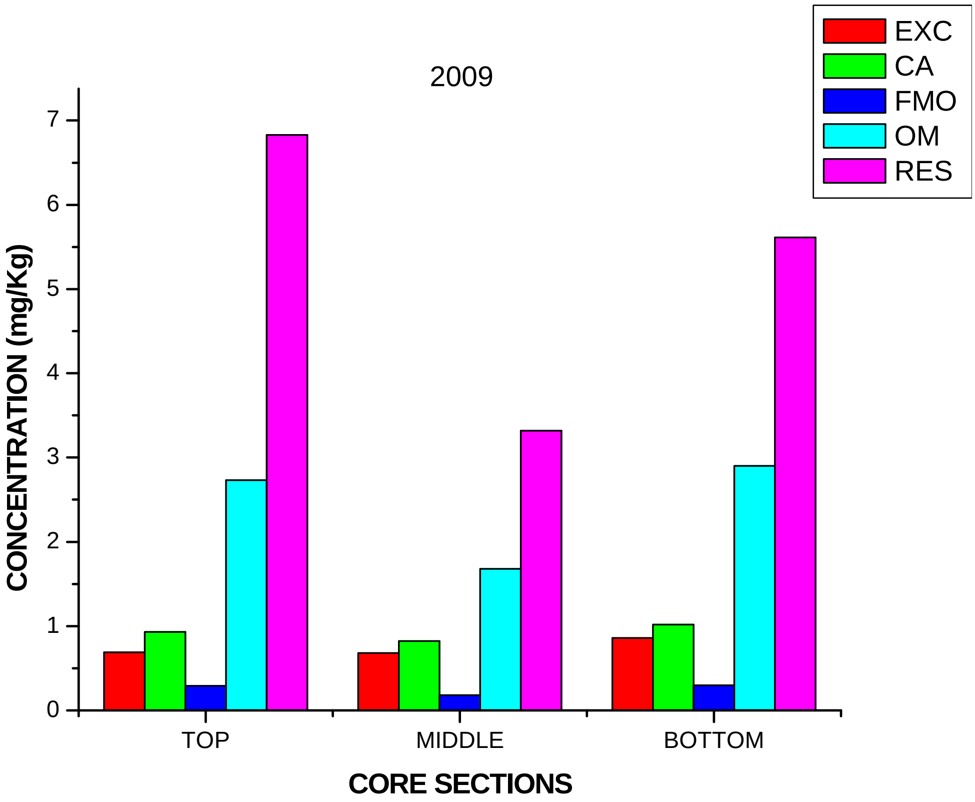


Figure 5.9 Fractionation profile of Cu in the core sediment M_1 (2009)

d. M_2:

Fractionation profile was given in Figure 5.10. Exchangeable and Fe - Mn oxide fractions were increased to the top section of the core and slightly less towards the bottom. Bound to carbonate was slightly greater to the mid section of the core and less to the deeper section. Bound to organic matter was high towards the middle component of the core. Residual fraction was increased at the mid section and less toward the underneath section of the core.

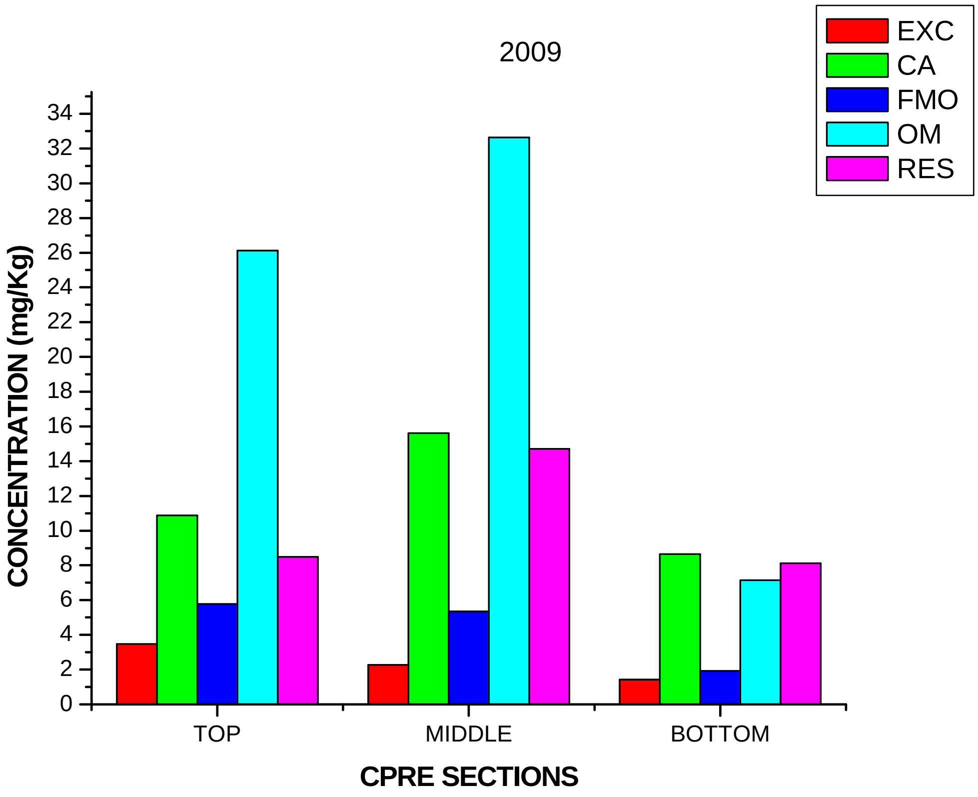


Figure 5.10 Fractionation profile of Cu in the core sediment M_2(2009)

e. N_1:

Fractionation profile was given in Figure 5.11. Exchangeable fraction and bound to carbonate were increased towards the lower component of the core. Fe - Mn oxide fraction slightly increased in the mid section of the core and lesser towards deeper layers. Bound to organic matter and residual fraction were greater weakly to the mid section of the core and less to the bottom.

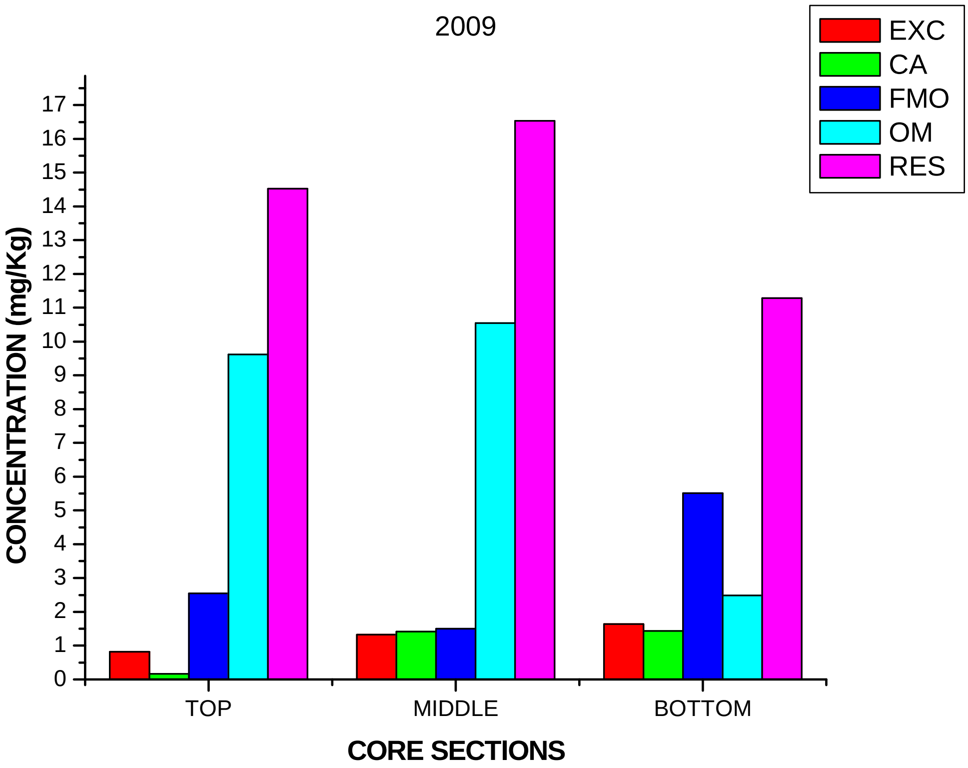


Figure 5.11 Fractionation profile of Cu in the core sediment N_1 (2009)

f. N_2:

Fractionation profile was given in Figure 5.12. Exchangeable and bound to Fe- Mn oxide fraction slightly augmented at top division of the core and decrease towards the bottom. Bound to carbonate, bound to organic matter fraction and residual fractions were greater in the mid section of the core and less towards the increase of depth.

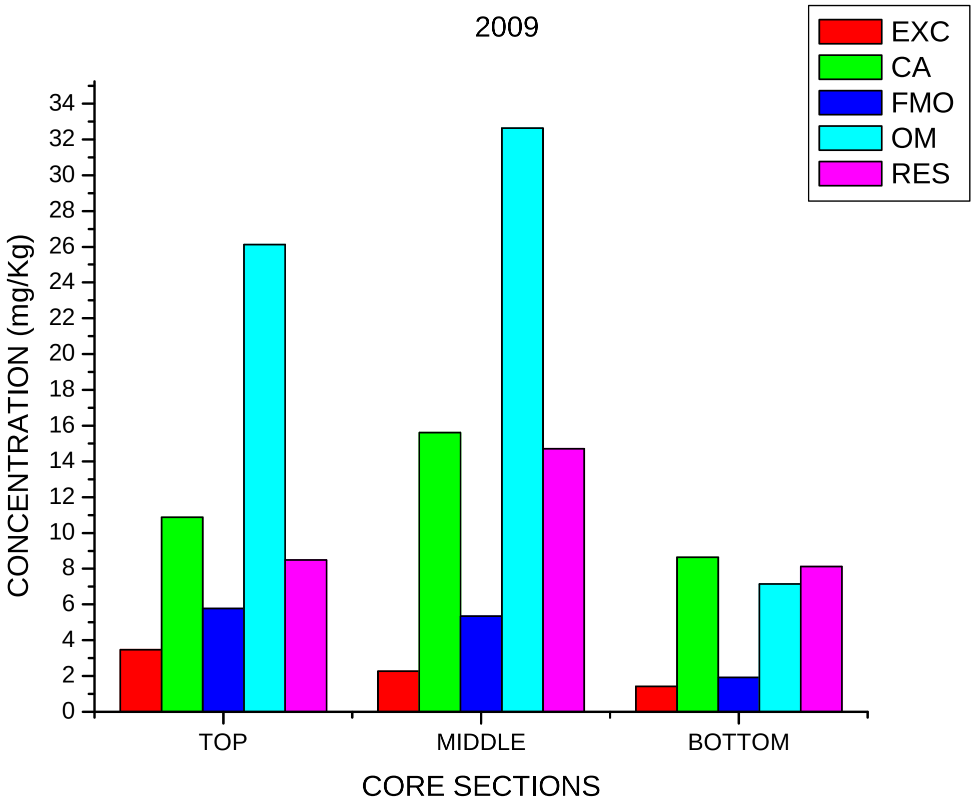


Figure 5.12 Fractionation profile of Cu in the core sediment N_1 (2009)

5.2.1.3 Lead

a. S_1:

Fractionation profile was given in Figure 5.13. Exchangeable fraction was increased to the top section of the core and lessens towards the bottom. Bound to carbonate fraction and Fe- Mn oxide fraction were high towards the bottom section of the core. Bound to organic matter and residual fraction were diminished to the mid section of the core and intensified to the deeper section.

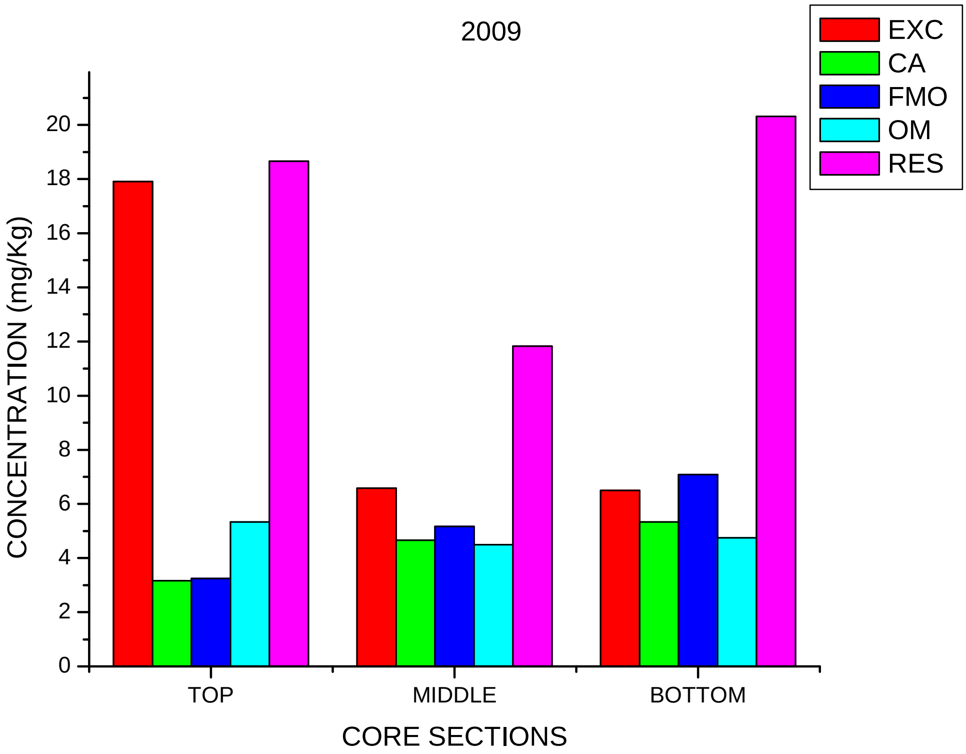


Figure 5.13 Fractionation profile of Pb in the core sediment S_1 (2009)

b. S_2:

Fractionation profile was given in Figure 5.14.Exchangeable fraction, bound to organic matter and residual fraction were slightly high towards the top section and minor to the bottom of the core.Bound to carbonate was diminished faintly to the mid section of the core and weakly intensified to the deeper layer. Fe- Mn oxide fraction was intensified to the deeper layer of the core.

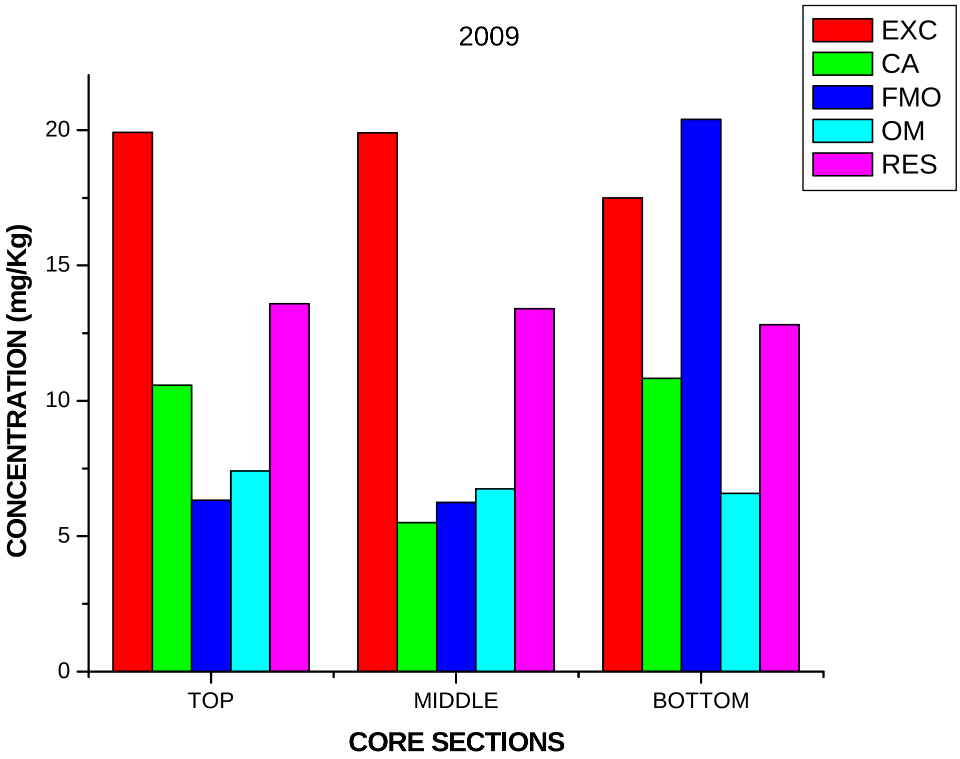


Figure 5.14 Fractionation profile of Pb in the core sediment S_2(2009)

c. M_1:

Fractionation profile was given in Figure 5.15. Exchangeable and residual fraction were weakly minimized to the mid section and enhanced towards the underneath section of the core. Bound to carbonate was increased slightly towards the lower component of the core. Bound to Fe and Mn oxide and bound to organic matter were weakly greater to the mid section of the core and faintly lesser towards the deeper layer.

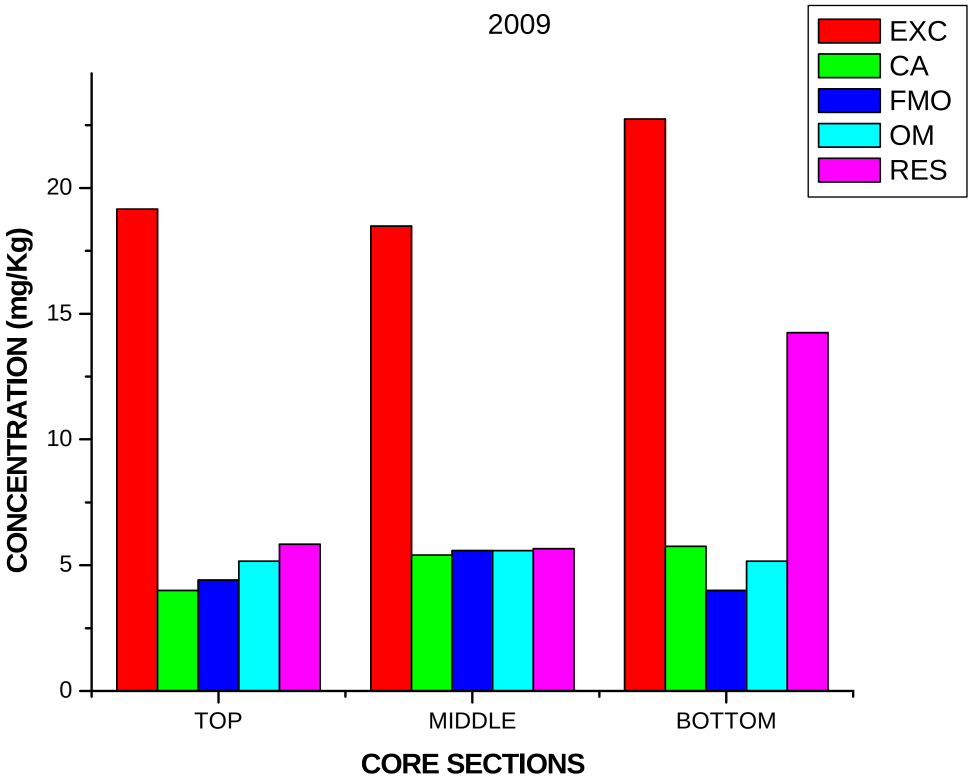


Figure 5.15 Fractionation profile of Pb in the core sediment M_1 (2009)

d. M_2:

Fractionation profile was given in Figure 5.16. Bound to carbonate and bound to organic matter were less to the mid section of the core and weakly high concentrated to the bottom layer. The remaining fractions were high towards the under slice of the core.

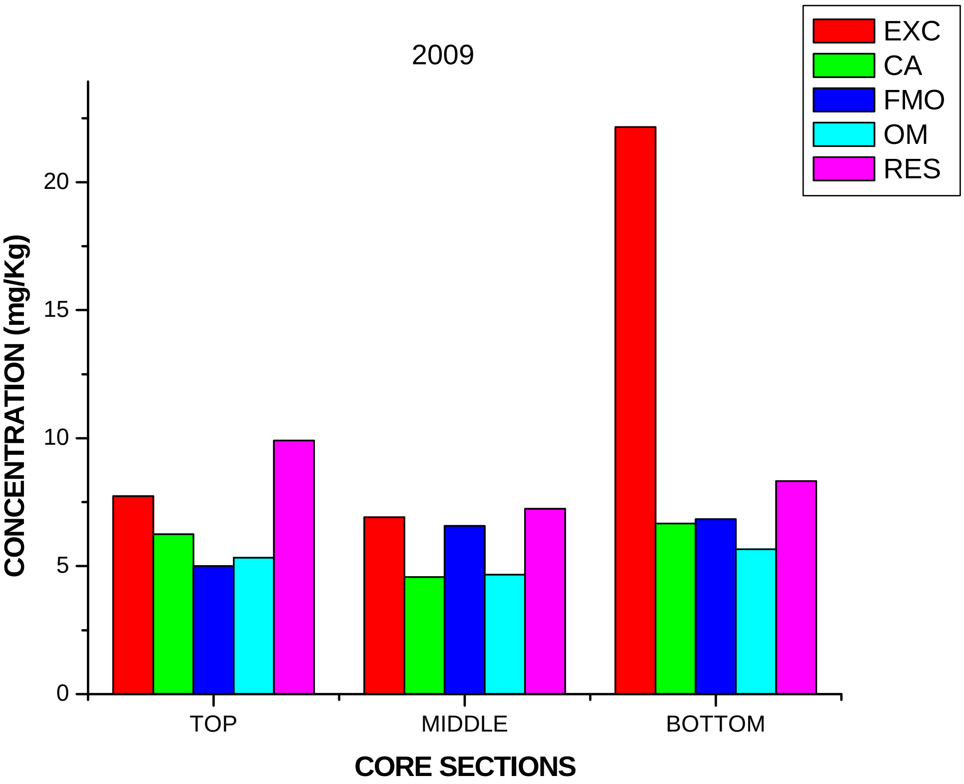


Figure 5.16 Fractionation profile of Pb in the core sediment M_1 (2009)

e. N_1:

Fractionation profile was given in Figure 5.17. Exchangeable fraction, Fe and Mn oxide, bound to organic matter and residual fraction were slightly high toward mid section of the core and diminish to the bottom section. Bound to carbonate less on top portion of the core and augmented weakly towards the bottom.

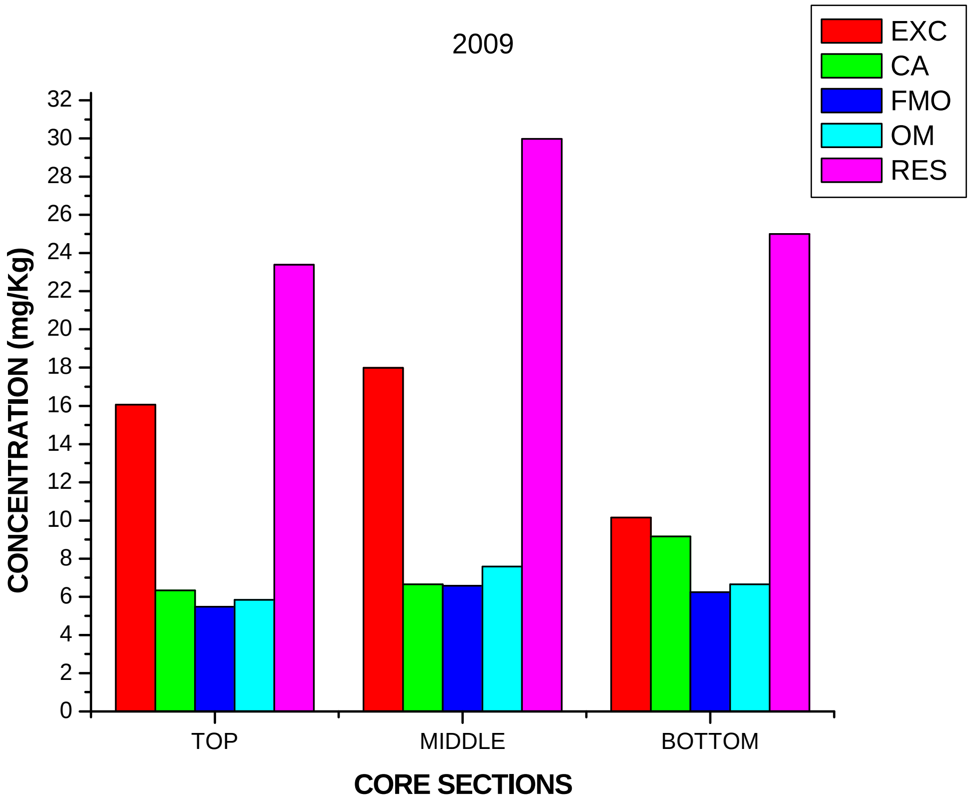


Figure 5.17 Fractionation profile of Pb in the core sediment N_1 (2009)

f. N_2:

Fractionation profile was given in Figure 5.18. Exchangeable, bound to Fe- Mn oxide and bound to organic matter fraction were greater to the mid section of the core and less towards the greater depth. Bound to carbonate and residual fractions were lesser on top division of the core and increase towards bottom.

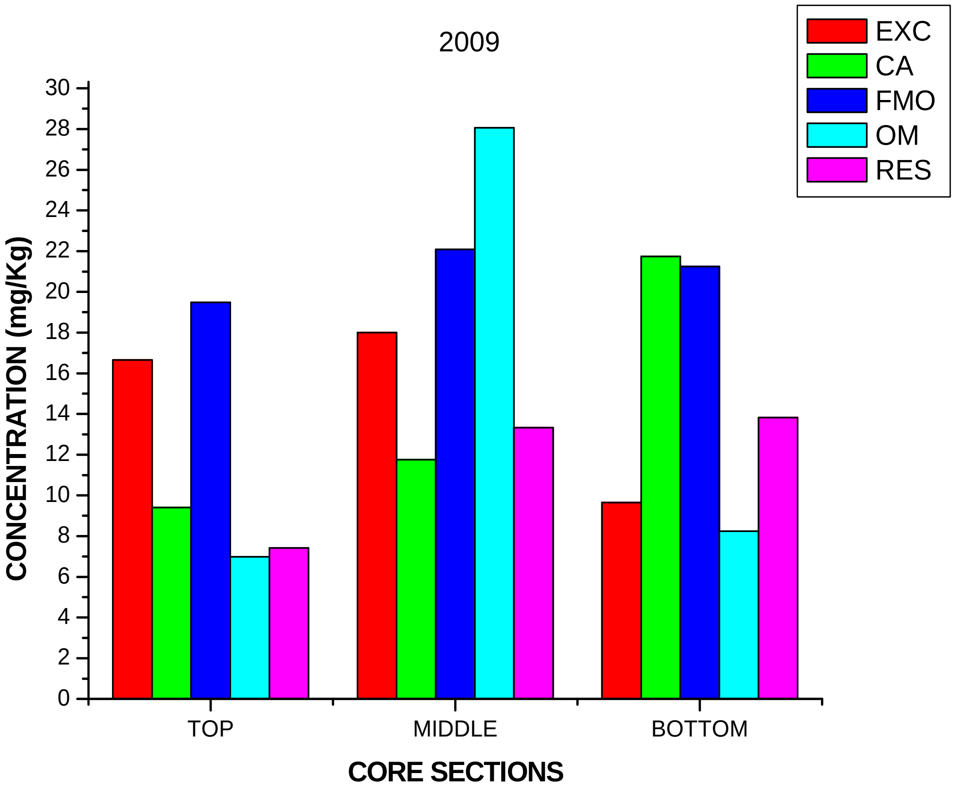


Figure 5.18 Fractionation profile of Pb in the core sediment N_2(2009)

5.2.1.4 Iron

a. S_1:

Fractionation profile was given in Figure 5.19. Exchangeable fraction was increased to the top section of the core and lessens towards the bottom. Bound to carbonate fraction and Fe- Mn oxide fraction were slightly major in the mid section of the core and weakly minor towards the bottom layer. Bound to organic matter decreases faintly towards the bottom section of the core. Residual fraction were diminished faintly to the mid section of the core and intensified weakly to the deeper section.

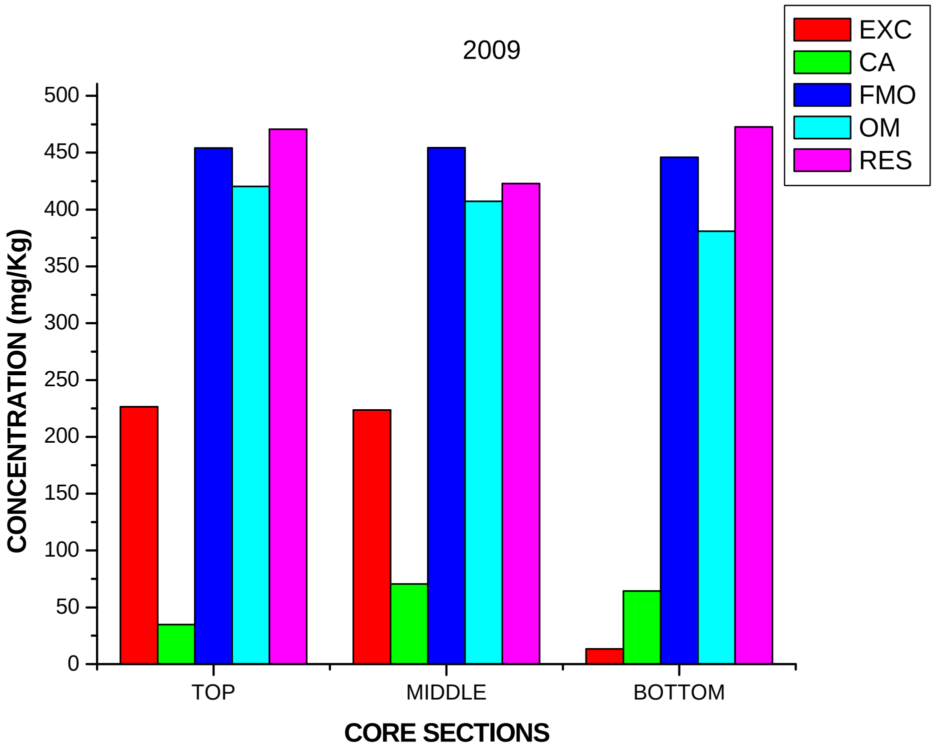


Figure 5.19 Fractionation profile of Fe in the core sediment S_1 (2009)

b. S_2:

Fractionation profile was given in Figure 5.20. Exchangeable fraction, bound to carbonate, Fe- Mn oxide fraction and residual fraction were slightly diminished to the mid section of the core and intensified weakly towards the bottom layer. Bound to organic matter was decreased towards the top section and slightly high towards the bottom part of the core.

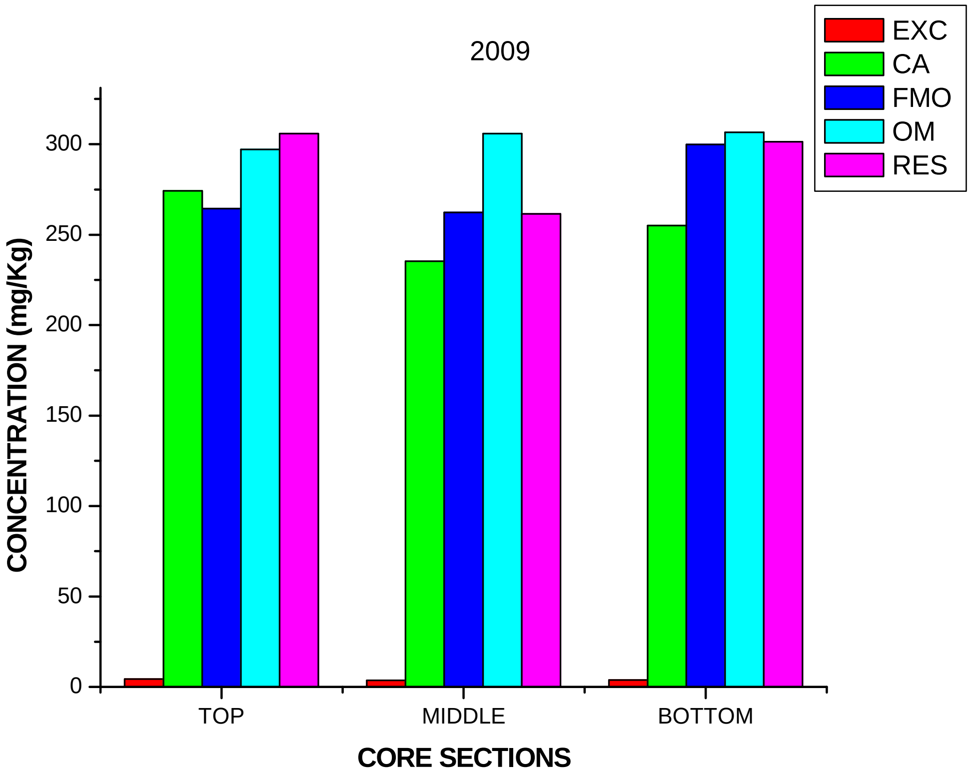


Figure 5.20 Fractionation profile of Fe in the core sediment S_2 (2009)

c. M_1:

Fractionation profile was given in Figure 5.21. Exchangeable, bound to Fe and Mn oxide and bound to organic matter were slightly minimized to the mid section and enhanced towards the underneath section of the core. Bound to carbonate and residual fraction were faintly diminishing towards the lower component of the core.

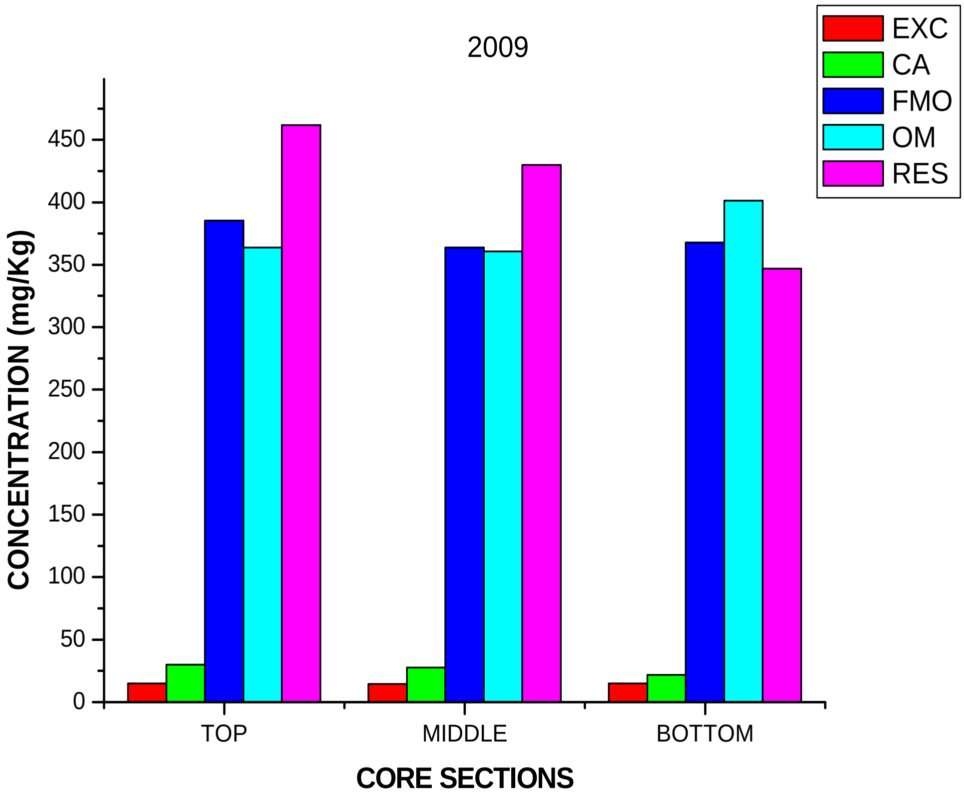


Figure 5.21 Fractionation profile of Fe in the core sediment M_1 (2009)

d. M_2:

Fractionation profile was given in Figure 5.22.Exchangeable and bound to organic matter were slightly high to the mid section of the core and smaller towards increased depth. Bound to carbonate, Fe and Mn oxide and residual fraction were greater towards the top portion of the core.

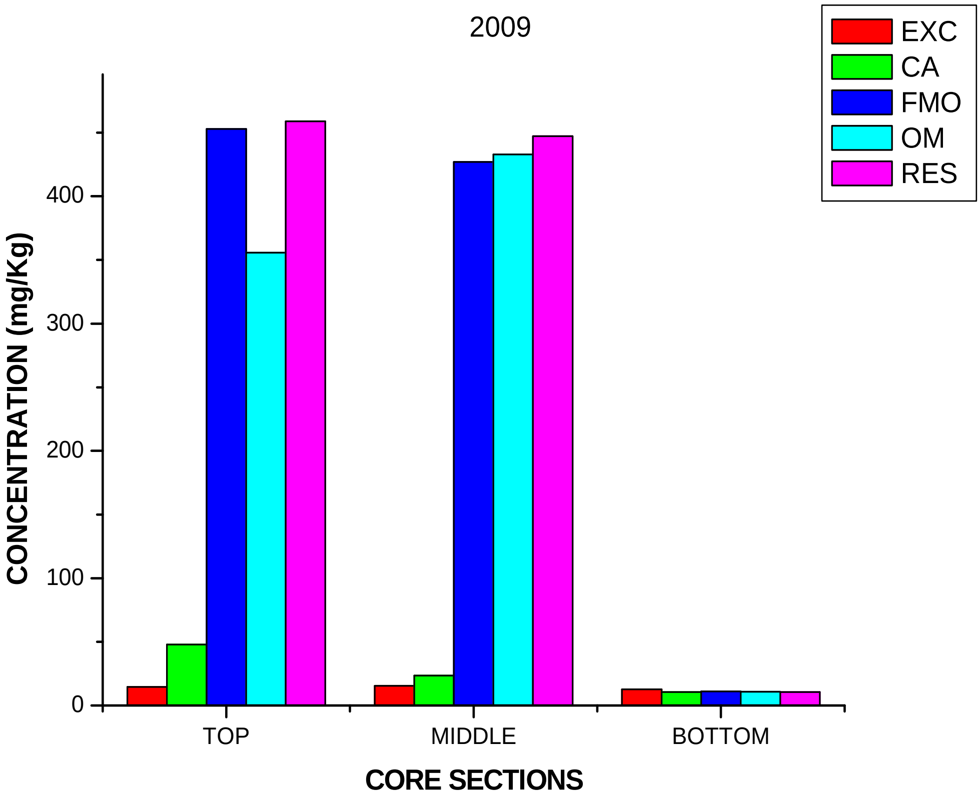


Figure 5.22 Fractionation profile of Fe in the core sediment M_2(2009)

e. N_1:

Fractionation profile was given in Figure 5.23. All the fractions showed somewhat similar concentration in the entire section of the core. Exchangeable fraction was minimum to mid layer of the core and greater when depth increased. Bound to carbonate and bound to organic matter were greater to the mid section of the core and less to the bottom. Fe and Mn oxide low on top partition of the core and weakly augmented towards the bottom section. Residual fraction was slightly increases to the top section of the core and reduces to the deeper section.

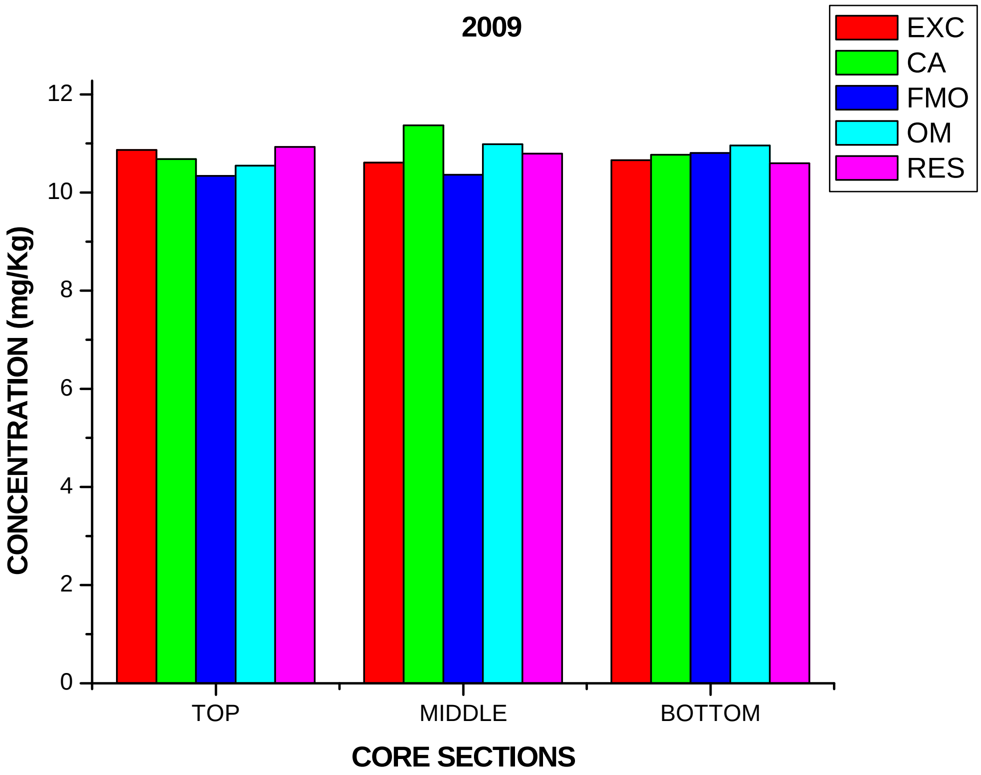


Figure 5.23 Fractionation profile of Fe in the core sediment N_1 (2009)

f. N_2:

Fractionation profile was given in Figure 5.24. Exchangeable fraction was slightly less to the mid layer of the core and faintly greater to the increased depth. Bound to carbonate and bound to Fe- Mn oxide were greater faintly to the mid section of the core and slightly less to the bottom layer. Bound to organic matter and residual fractions were greater on top layers of the core and slightly less towards the bottom.

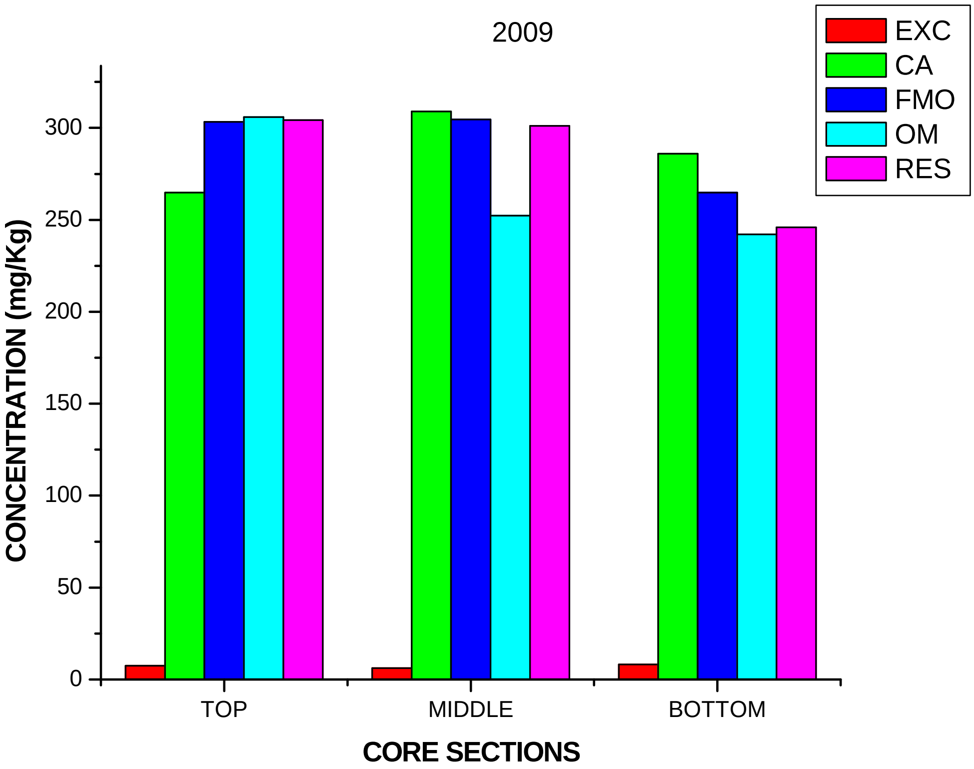


Figure 5.24 Fractionation profile of Fe in the core sediment N_2(2009)

5.2.1.5 Manganese

a. S1:

Fractionation profile was given in Figure 5.25. Exchangeable fraction, Fe- Mn oxide fraction, bound to organic matter and residual fraction were diminished to the mid section of the core and intensified slightly towards the deeper layer. Bound to carbonate was decreased towards the top section and high towards the greater depth of the core. Fe- Mn oxide fractions were found major part in the bottom section of the core and minor to the mid section. Bound to organic matter weakly increases towards the bottom section of the core. Residual fraction were slightly diminished to the mid section of the core and intensified faintly towards the bottom layer.

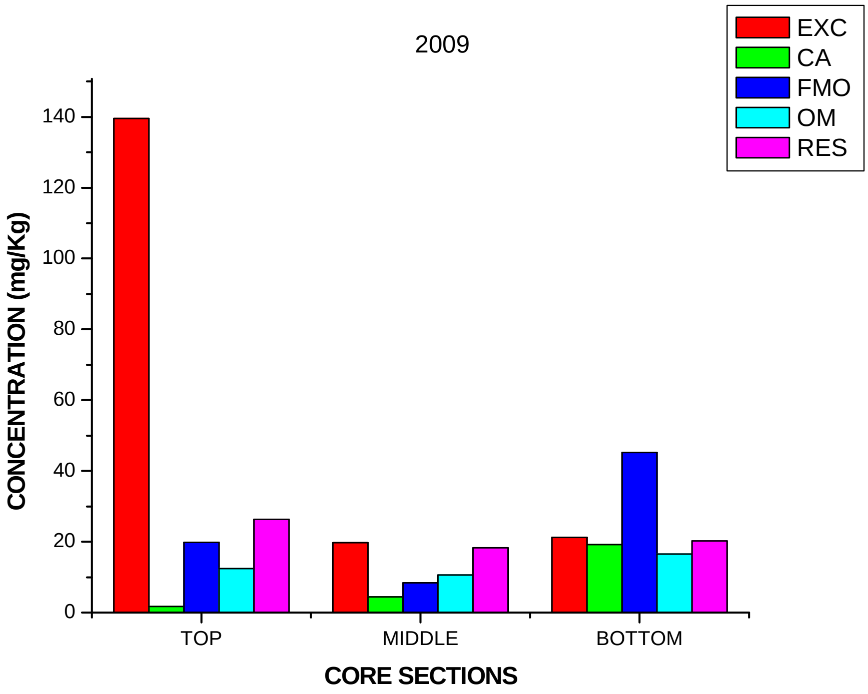


Figure 5.25 Fractionation profile of Mn in the core sediment S_1 (2009)

b. S_2:

Fractionation profile was given in Figure 5.26. Exchangeable fractions were found less to the top section of the core and increases towards the bottom. Bound to carbonate, bound to organic matter and residual fraction were diminished to the mid section of the core and intensified towards bottom part of the core. Fe- Mn oxide fractions were decreased towards greater depth of the core.

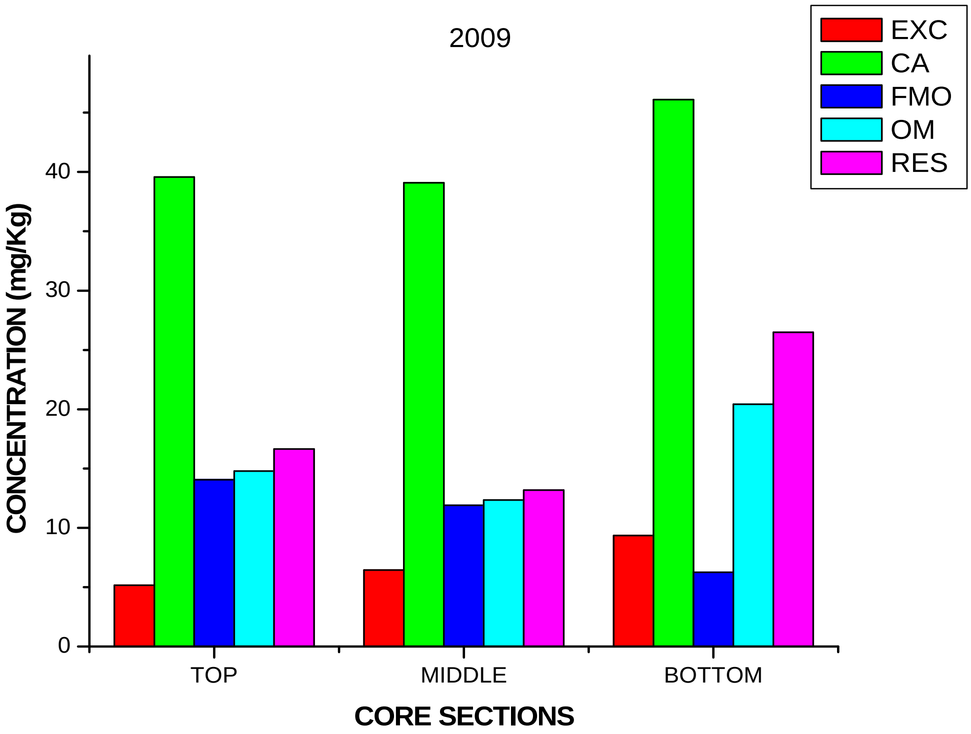


Figure 5.26 Fractionation profile of Mn in the core sediment S_2(2009)

c. M_1:

Fractionation profile was given in Figure 5.27. Exchangeable and bound to organic matter were slightly less in the mid section of the core and high when depth increases. Bound to carbonate, bound to Fe and Mn oxide fraction was increased towards the bottom of the core. Residual fractions were slightly less towards the lower component of the core.

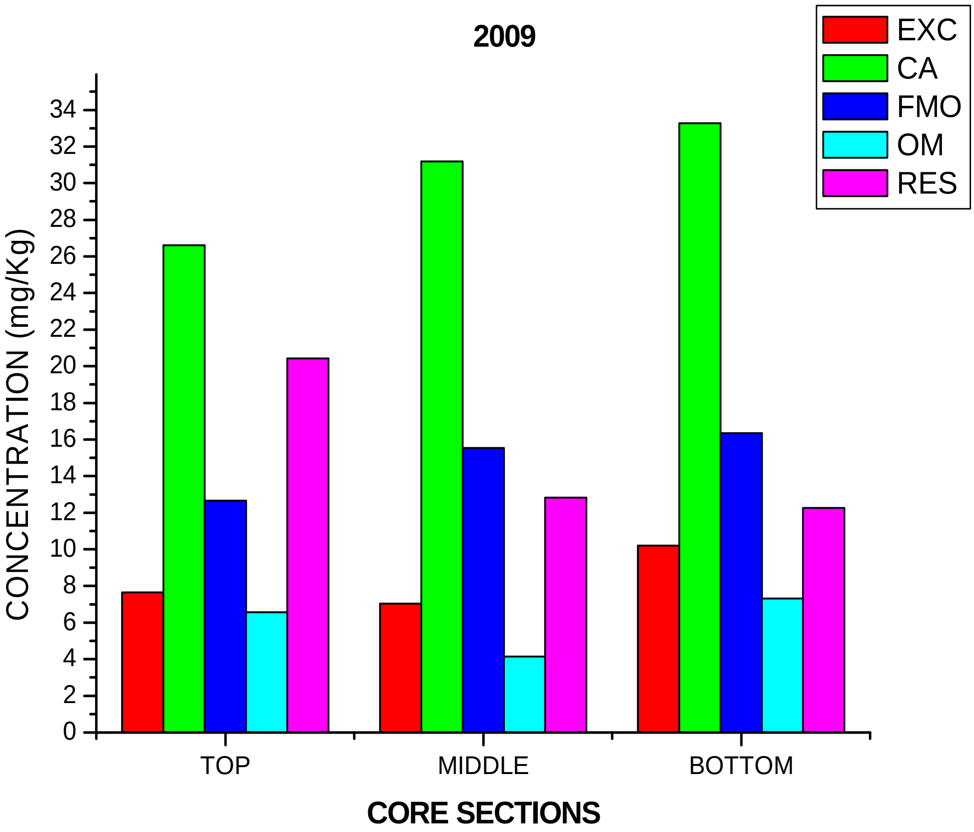


Figure 5.27 Fractionation profile of Mn in the core sediment M_1 (2009)

d. M_2:

Fractionation profile was given in Figure 5.28. Exchangeable fraction was high towards the bottom portion of the core. Bound to carbonate was decreased toward the deeper depth of the core. Fe- Mn oxide fraction and bound to organic matter were intensified to the mid section of the core and slightly diminished when depth increases. Residual fraction were diminished towards the mid portion and intensified to the bottom of the core.

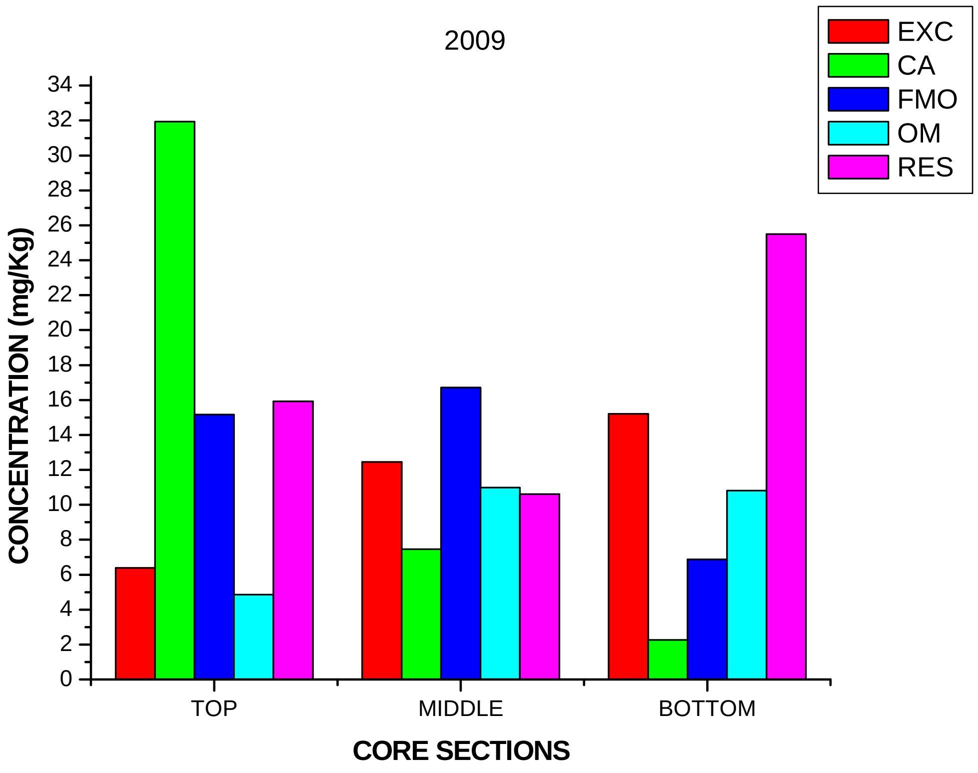


Figure 5.28 Fractionation profile of Mn in the core sediment M_2(2009)

e. N_1:

Fractionation profile was given in Figure 5.29. Exchangeable, Fe - Mn oxide fractions and bound to organic matter were high to the mid stratum of the core and decreased towards the deeper layer of the core. Bound to carbonate and residual fraction were less on top partition of the core and slightly increased towards the bottom.

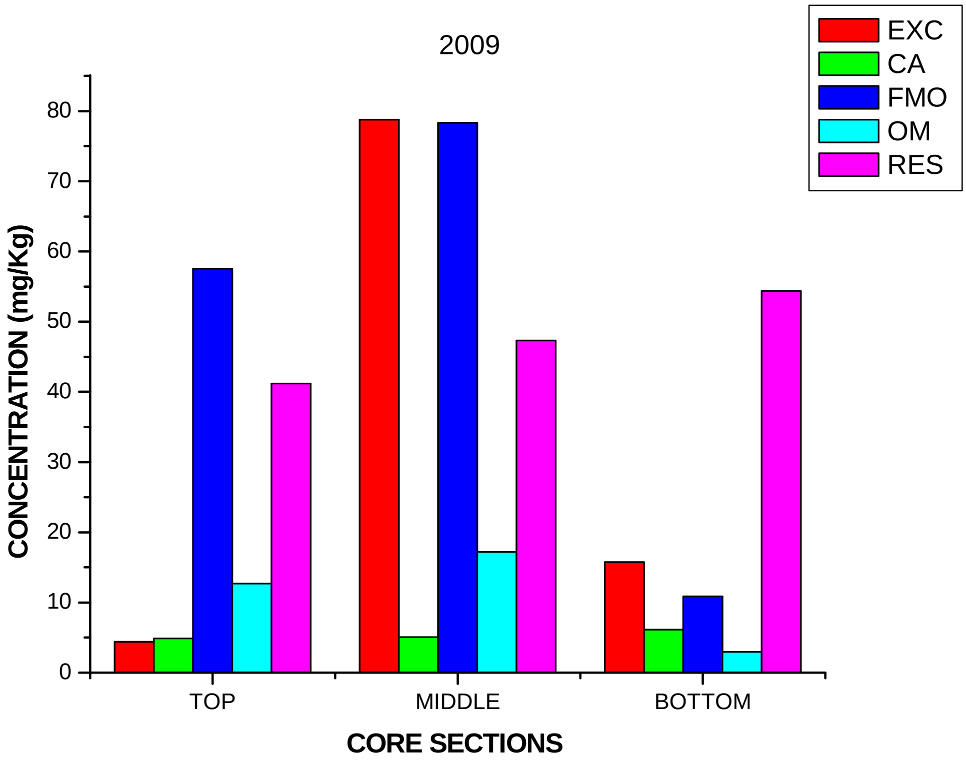


Figure 5.29 Fractionation profile of Mn in the core sediment N_1 (2009)

f. N_2:

Fractionation profile was given in Figure 5.30. Exchangeable and bound to organic matter fraction were greater to the mid section of the core and slightly less to the heavier depth. Bound to carbonate and bound to Fe-Mn oxide were weakly greater on top division of the core and less towards the bottom. Residual fraction was less on top partition of the core and increased towards the bottom.

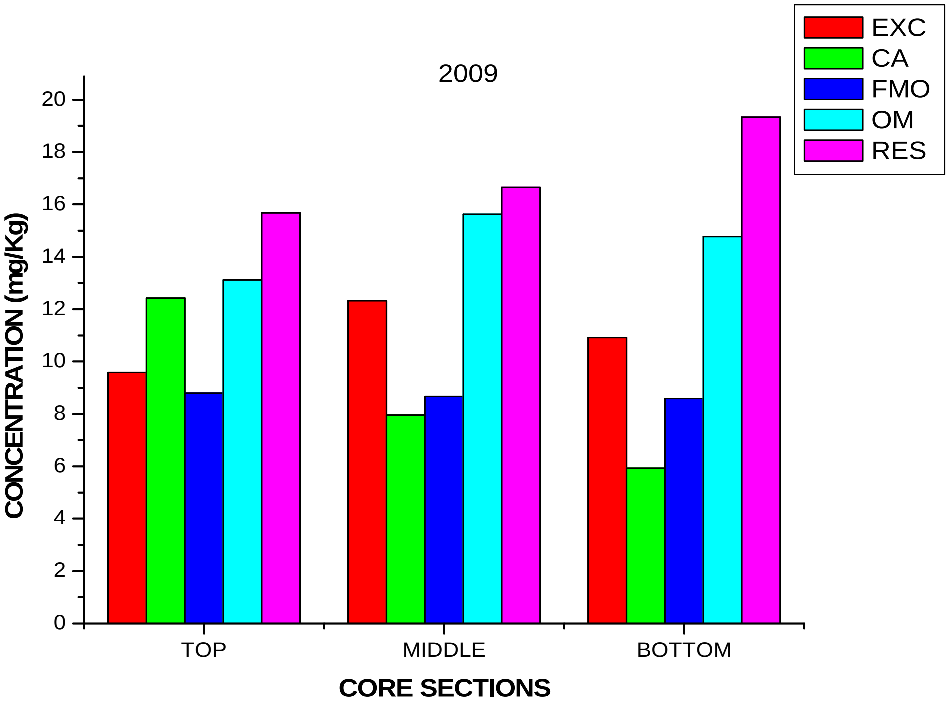


Figure 5.30 Fractionation profile of Mn in the core sediment N_2(2009)

5.2.1.6 Nickel

a. S_1:

Fractionation profile was given in Figure 5.31.Exchangeable fraction was less on top portion of the core and increased towards the bottom. Bound to carbonate was slightly greater to the mid section of the core and less towards deeper layers. Fe- Mn oxide fraction was diminished weakly to the mid section of the core and intensified along the depth. Bound to organic matter fraction was lesser to the top section of the core and greater to the heavier depth. Residual fraction was faintly high to the top section of the core.

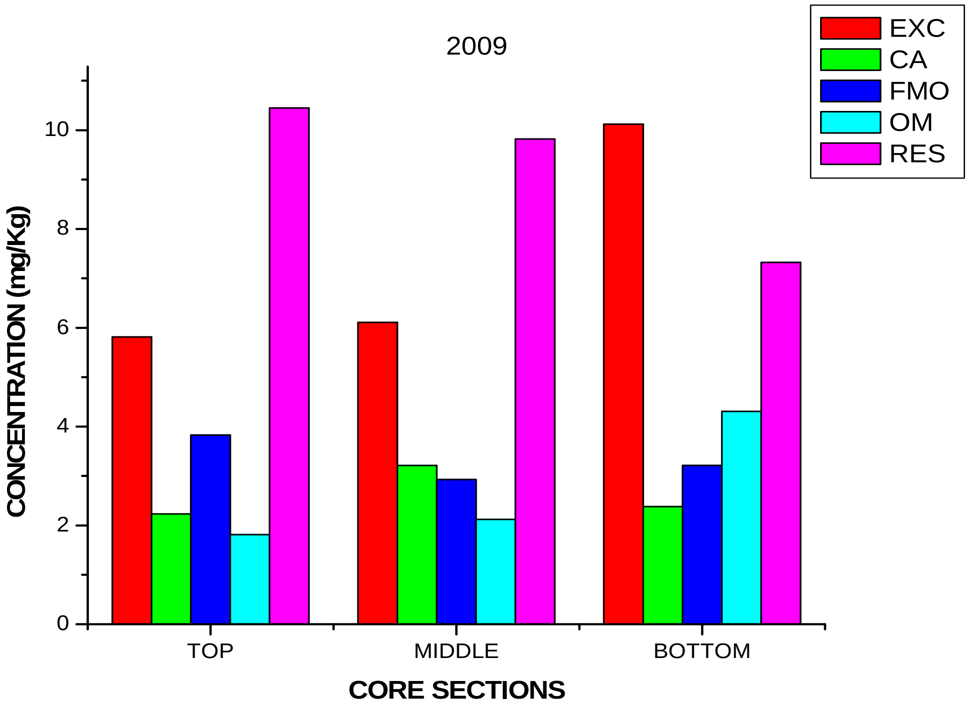


Figure 5.31 Fractionation profile of Ni in the core sediment S_1 (2009)

b. S_2:

Fractionation profile was given in Figure 5.32. Exchangeable, bound to carbonate, Fe and Mn oxide fractions and residual fraction were high towards the bottom sector of the core and was less towards the top. Bound to organic matter fractions showed slight increase in the mid section of the core and fades towards to the bottom.

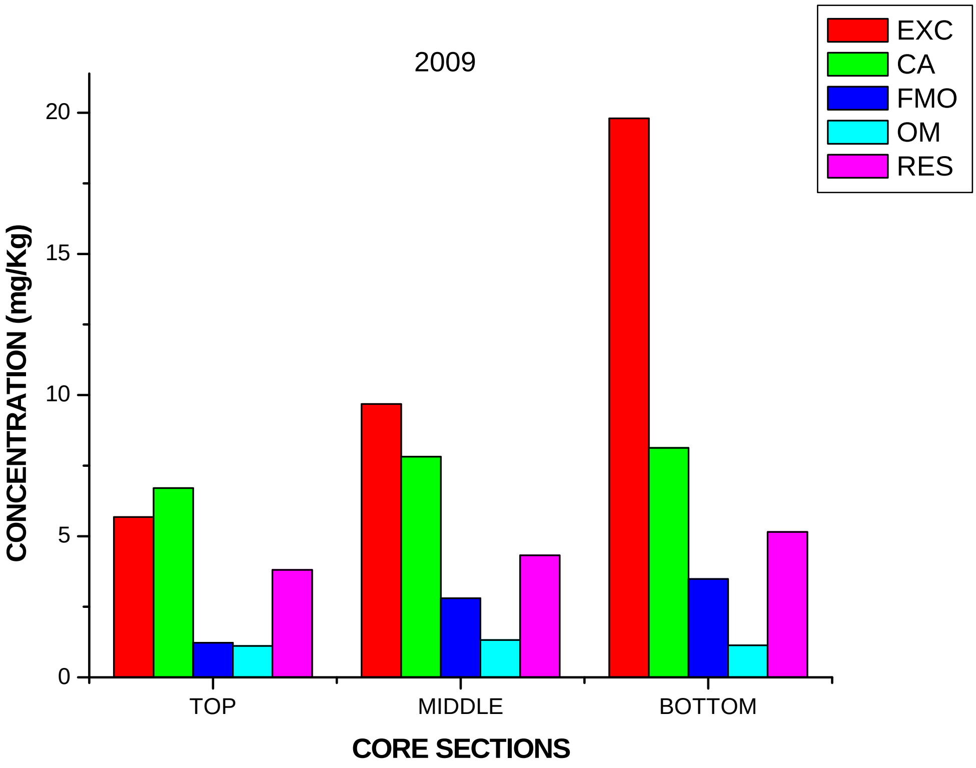


Figure 5.32 Fractionation profile of Ni in the core sediment S_2(2009)

c. M₁:

Fractionation profile was given in Figure 5.33. Exchangeable fraction was less on top portion of the core and increased towards the bottom. The remaining fractions were greater to the deeper section of the core.

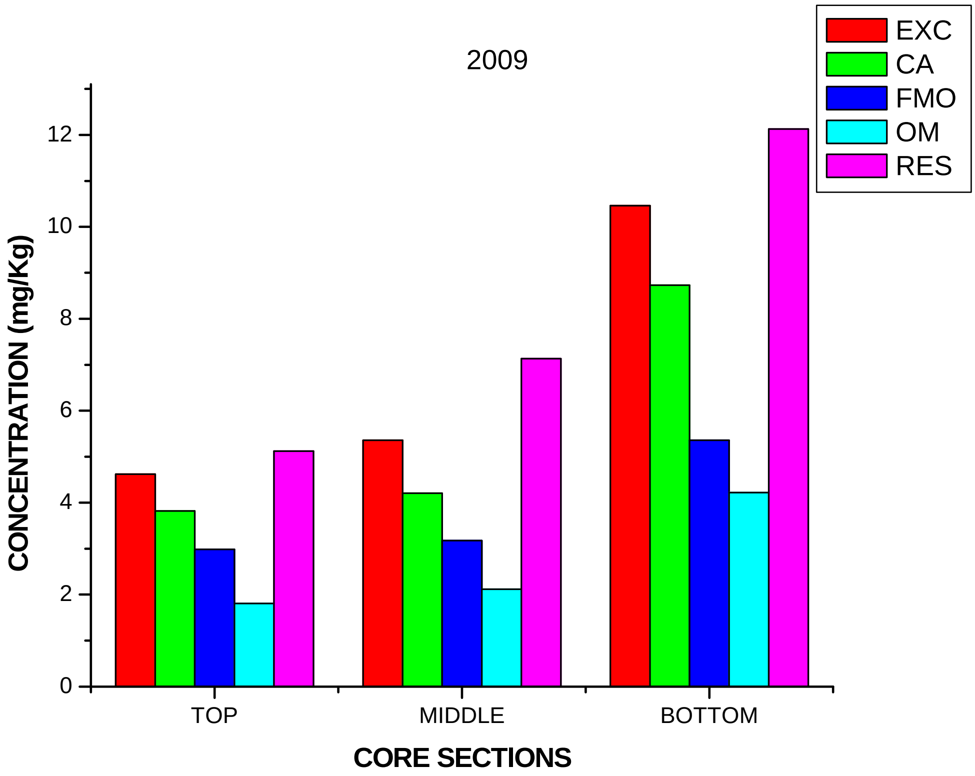


Figure 5.33 Fractionation profile of Ni in the core sediment M_1 (2009)

d. M_2:

Fractionation profile was given in Figure 5.34. Exchangeable fraction was decreased toward the bottom portion of the core. Bound to carbonate, Fe and Mn oxide fraction, and bound to organic matter were slightly intensified towards the mid portion and diminished to the bottom of the core. Residual fraction was decreased to the mid section and increased toward bottom portion of the core.

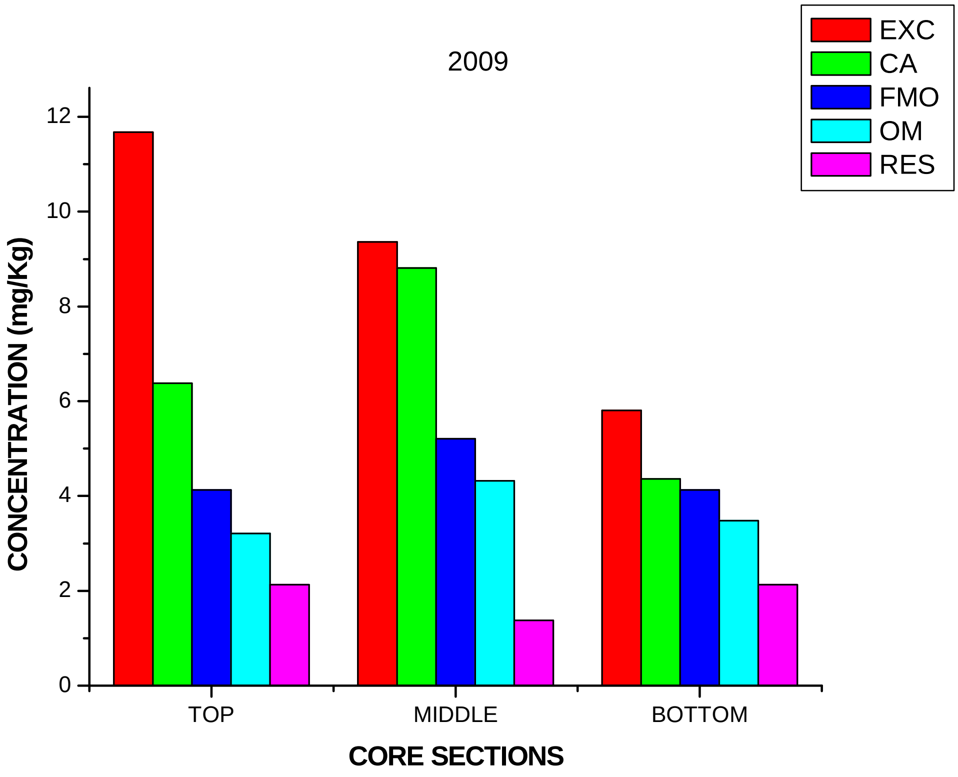


Figure 5.34 Fractionation profile of Ni in the core sediment M_2(2009)

e. N_1:

Fractionation profile was given in Figure 5.35. Exchangeable, bound to carbonate and residual fraction were less on top portion of the core and augmented towards the bottom. Fe - Mn oxide fractions and bound to organic matter were slightly decreased to the mid section of the core and high to the bottom layer.

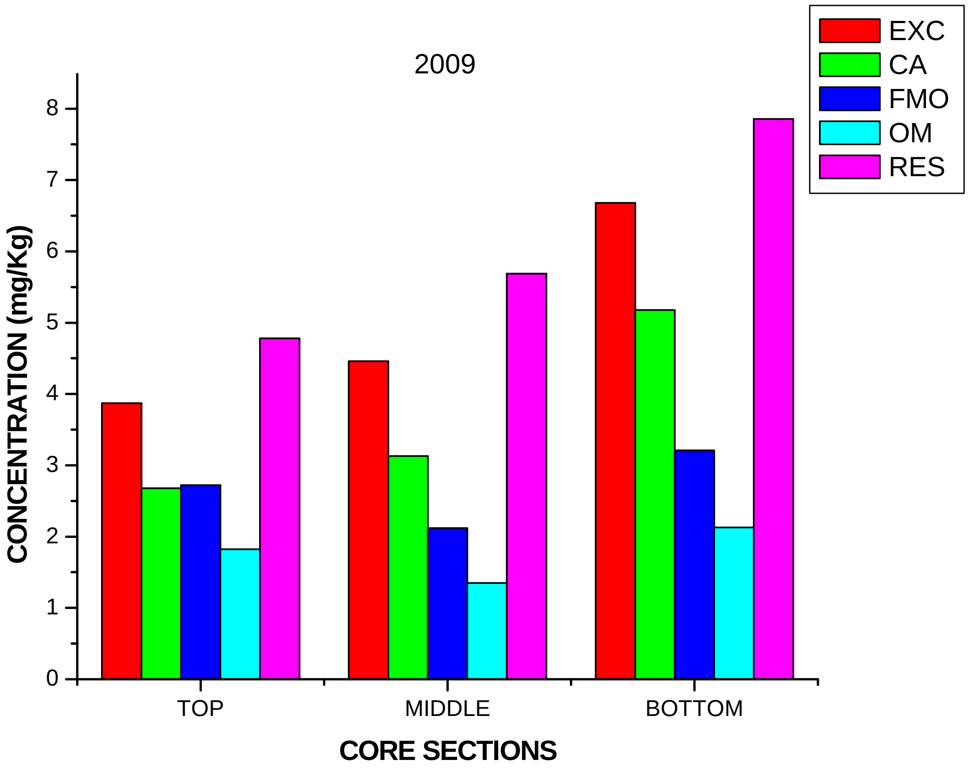


Figure 5.35 Fractionation profile of Ni in the core sediment N_1 (2009)

f. N_2:

Fractionation profile was given in Figure 5.36. Exchangeable, bound to carbonate, bound to Fe- Mn oxide and bound to organic matter fraction were greater on top division of the core and less towards the bottom. Residual fraction was slightly less to the mid section of the core and greater when depth intensified.

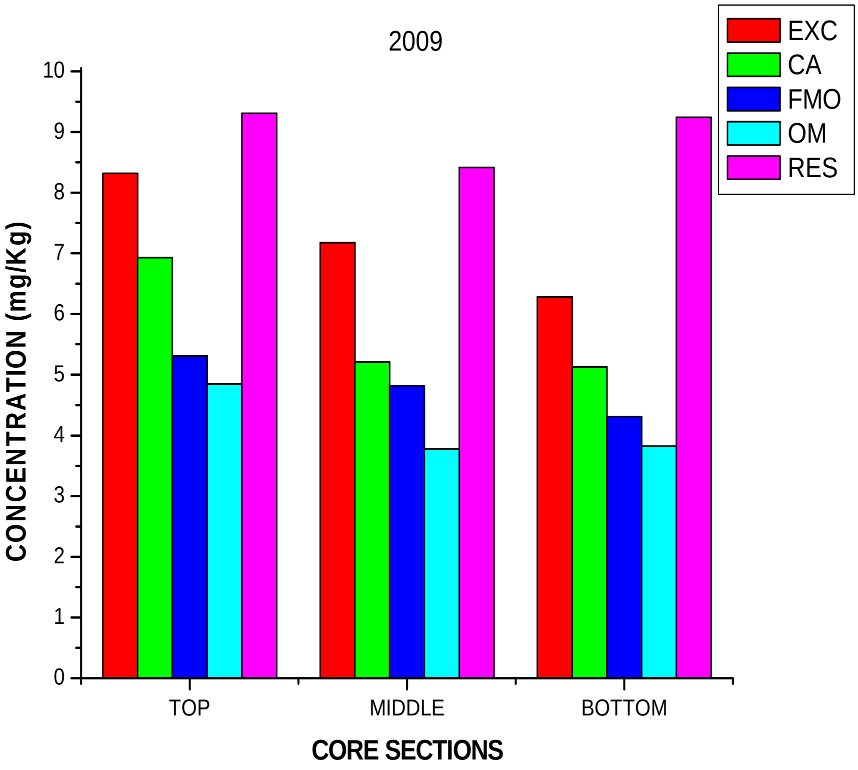


Figure 5.36 Fractionation profile of Ni in the core sediment N_2(2009)

5.2.2 Part B

This section details the relevant sketch on 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. Present research approach based on the fractionation analysis of sediment cores collected over a considerable time period can provide a change occurred within the two-year period in the environment and such studies are limited.

5.2.2.1 Cadmium

a. S_1:

Fractionation profile was given in Figure 5.37. Exchangeable, bound to carbonate fraction and bound to organic matter were profuse slightly in the top section of the core and less towards the bottom. Fe and Mn oxide fraction weakly increased towards the foot section of the core. Residual fraction was fading to the mid section of the core and slightly amplified to the bottom layer.

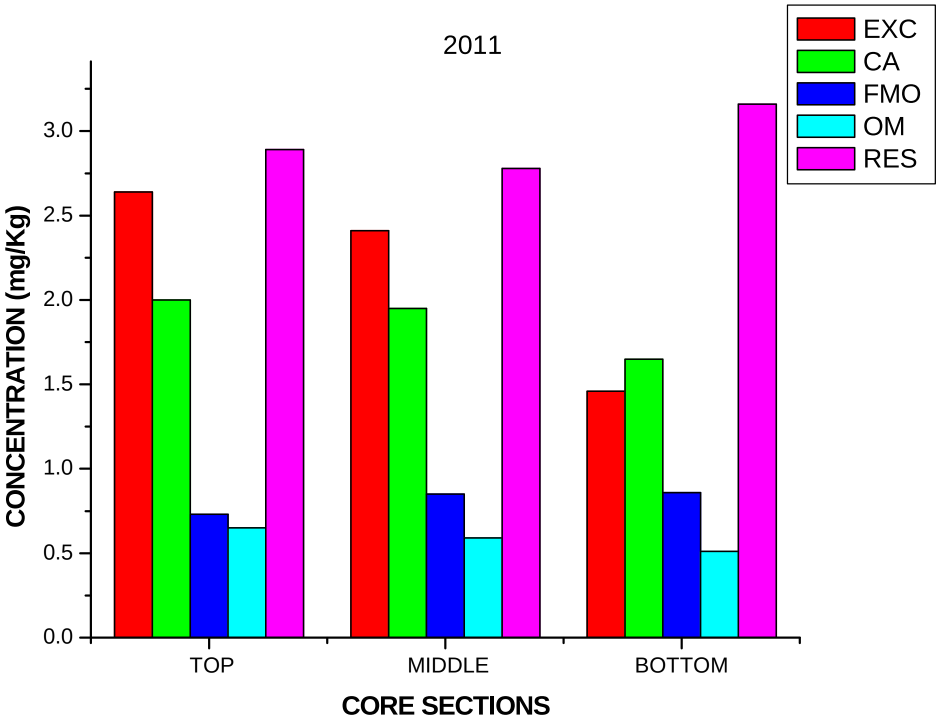


Figure 5.37 Fractionation profile of Cd in the core sediment S_1 (2011)

b. S_2:

Fractionation profile was given in Figure 5.38. Exchangeable and bound to carbonate fraction was slightly raised to the mid section of the core and fades to the bottom section. Fe and Mn oxide fraction lower to mid section of the core and slightly increases deep section of the core. The left over fractions were lower toward the underneath segment of the core.

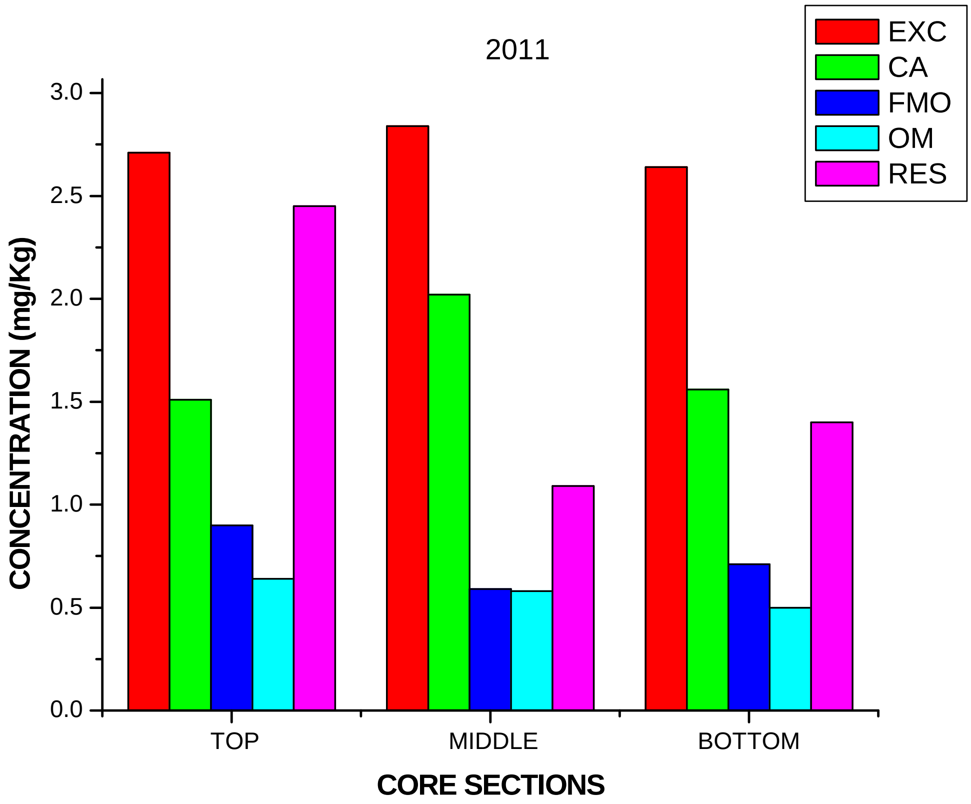


Figure 5.38 Fractionation profile of Cd in the core sediment S_2(2011)

c. M₁:

Fractionation profile was given in Figure 5.39. Exchangeable fraction was less in the top section of the core and increase towards the bottom. Bound to carbonate and bound to organic matter fraction were lift to the mid section of the core and less to the deeper section. Fe - Mn oxide and residual fraction was diminishing to the mid section of the core and increased weakly to the bottom layer of the core.

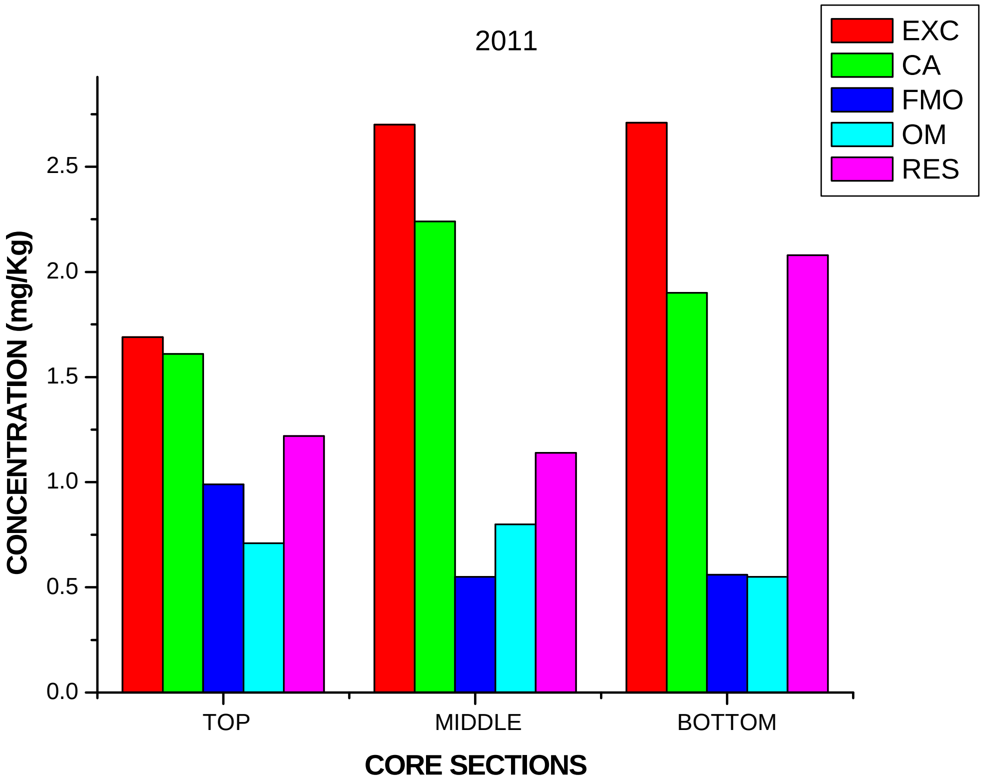


Figure 5.39 Fractionation profile of Cd in the core sediment M_1 (2011)

d. M_2:

Fractionation profile was given in Figure 5.40. Exchangeable was slightly raised to the mid section of the core and fades to the deeper section. Fe- Mn oxide and residual fraction was lower to mid section of the core and embellish weakly to the bottom section. The left two fractions increased towards the lower part of the core.

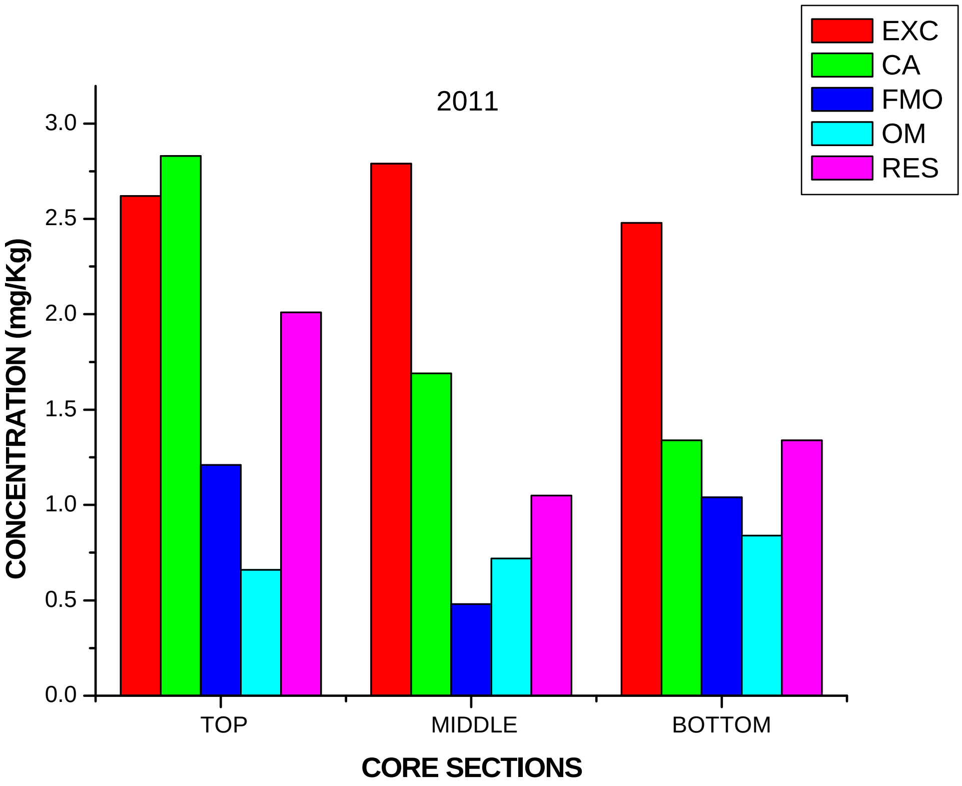


Figure 5.40 Fractionation profile of Cd in the core sediment M_2(2011)

e. N_1:

Fractionation profile was given in Figure 5.41. Residual fraction was less in the top portion of the core and slightly increased towards the bottom. The remaining four fractions augmented on top division of the core.

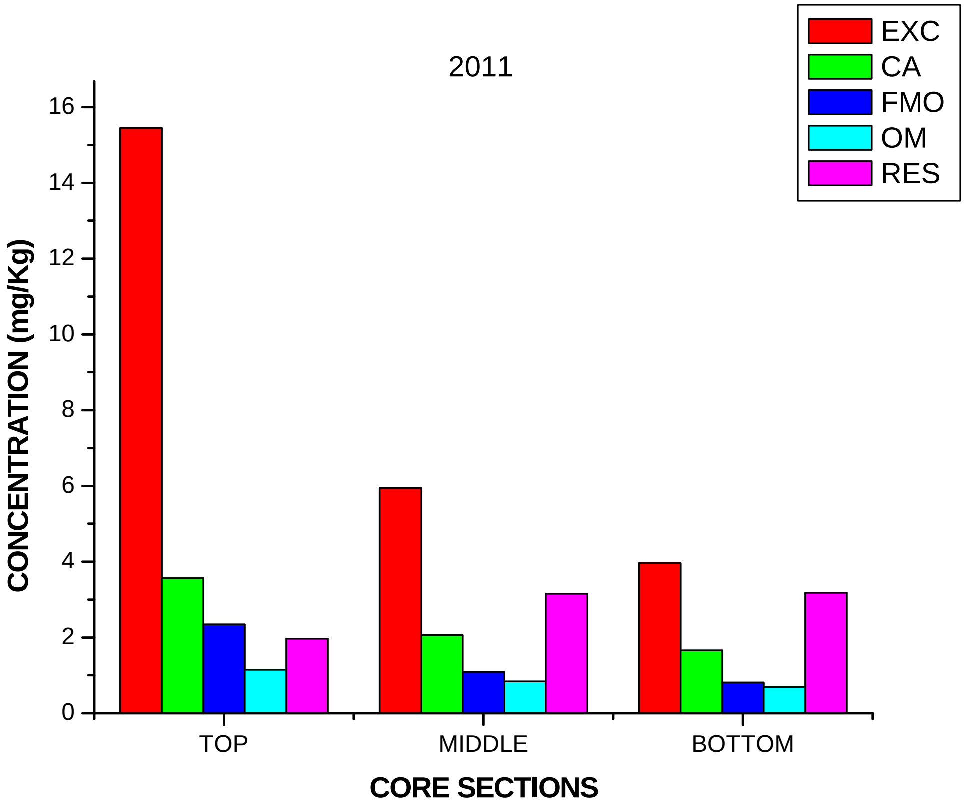


Figure 5.41 Fractionation profile of Cd in the core sediment N_1 (2011)

f. *N2:*

Fractionation profile was given in Figure 5.42. Exchangeable and bound to organic matter fraction were abundant in the top section of the core and less towards the bottom. Bound to carbonate and residual fraction were found low to the mid section of the core and slightly increases towards greater depth. Fe- Mn oxide fraction intensified to the top component of the core.

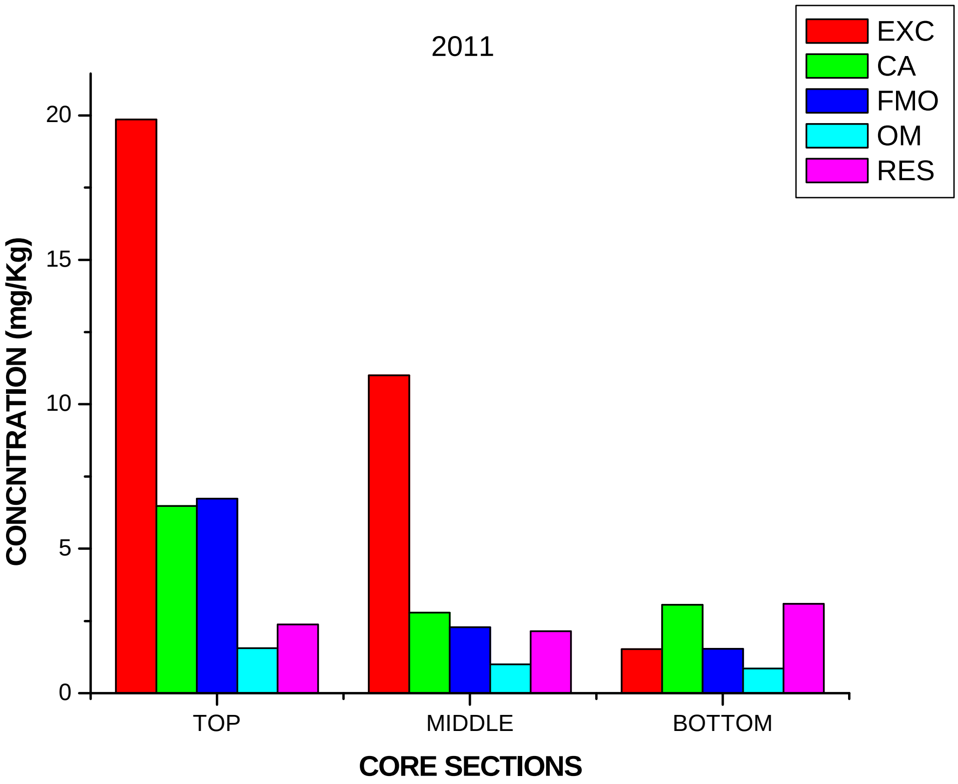


Figure 5.42 Fractionation profile of Cd in the core sediment N_2(2011)

5.2.2.2 Copper

a. S_1:

Fractionation profile was given in Figure 5.43. Exchangeable fraction was slightly major in the mid section of the core and minor to the bottom layer. Bound to carbonate fraction, Fe- Mn oxide fraction, bound to organic matter and residual fraction were decreased along the depth of the core.

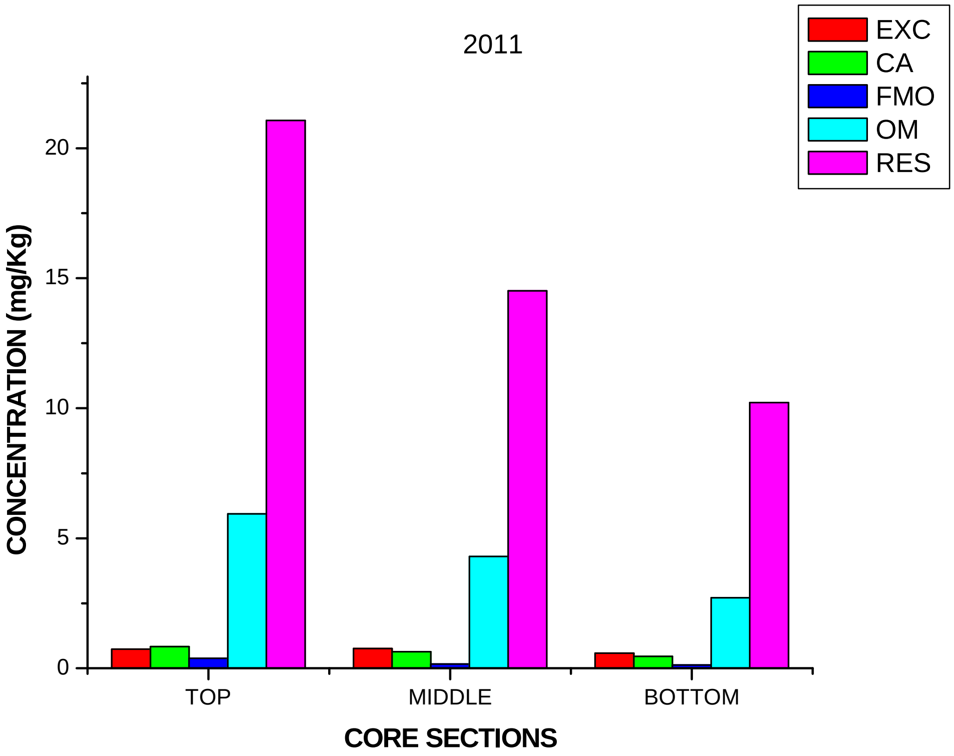


Figure 5.43 Fractionation profile of Cu in the core sediment S_1 (2011)

b. S_2:

Fractionation profile was given in Figure 5.44. Bound to carbonate fraction was slightly major in the mid section of the core and minor to the deeper section. Exchangeable fraction, Fe- Mn oxide fraction, bound to organic matter and residual fraction were found feeble to the greater depth of the core.

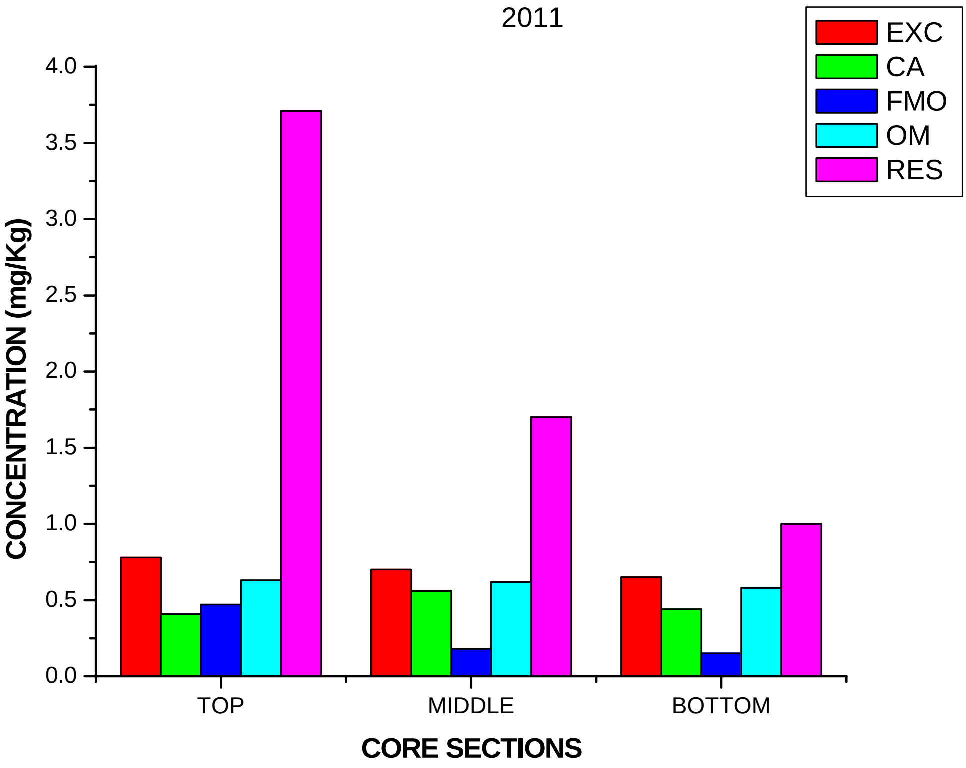


Figure 5.44 Fractionation profile of Cu in the core sediment S_2(2011)

c. M_1:

Fractionation profile was given in Figure 5.45. Exchangeable, bound to organic matter and residual fraction were greater to the mid section of the core and less to the deeper layer. Bound to carbonate was weakly enlarged towards the lower component of the core. Fe and Mn oxide fraction was increased at the top segment and minimize slightly toward the underneath segment of the core.

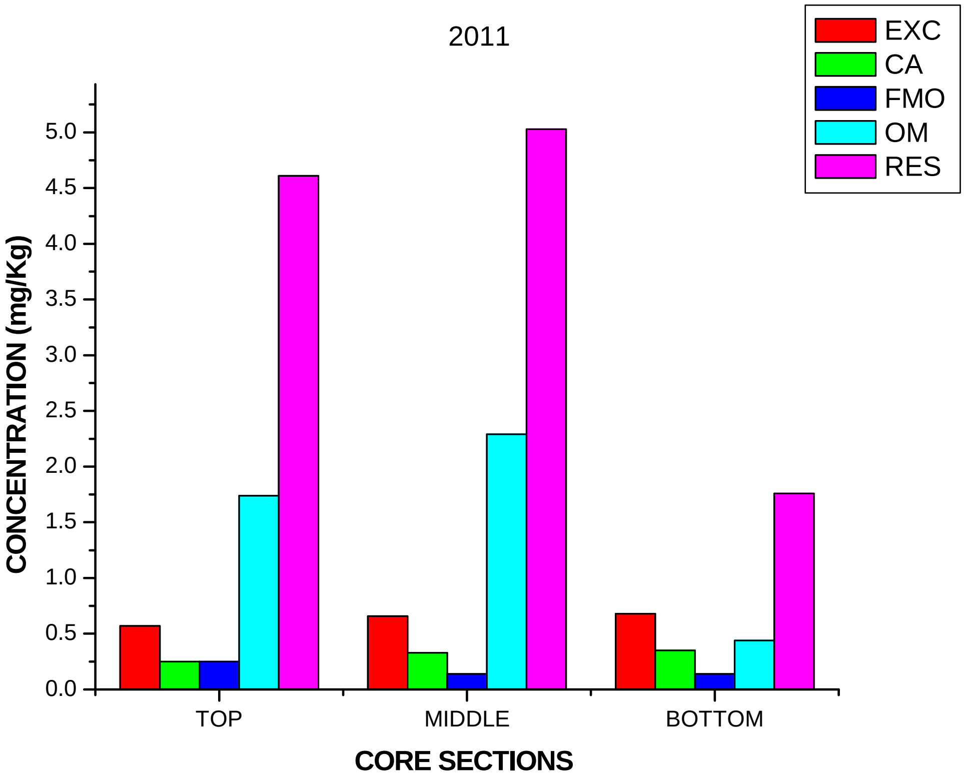


Figure 5.45 Fractionation profile of Cu in the core sediment M_1 (2011)

d. M_2:

Fractionation profile was given in Figure 5.46. Exchangeable , bound to organic matter and Fe and Mn oxide fraction were abundant in the top section of the core and less towards the bottom. Bound to carbonate and residual fraction were increased slightly to the mid section of the core and and diminish towards the bottom section of the core.

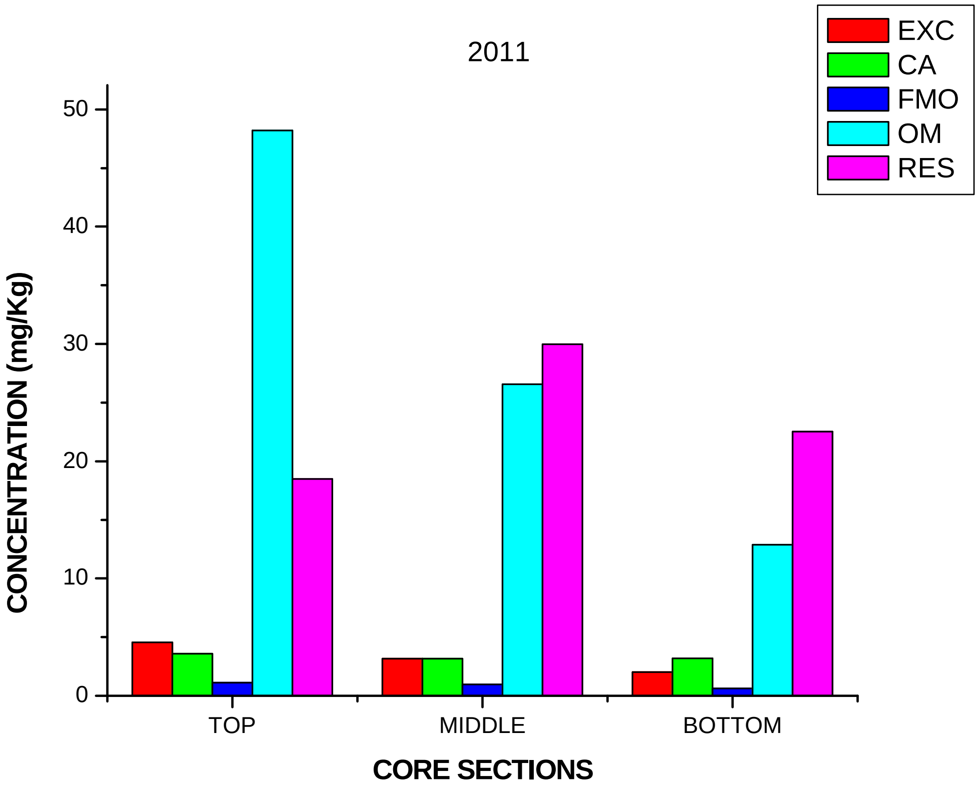


Figure 5.46 Fractionation profile of Cu in the core sediment M_2(2011)

e. N_1:

Fractionation profile was given in Figure 5.47. All the fractions (exchangeable, bound to carbonate, Fe and Mn oxide fractions, bound to organic matter fractions and residual fraction) were high on top section of the core and was limited towards the bottom.

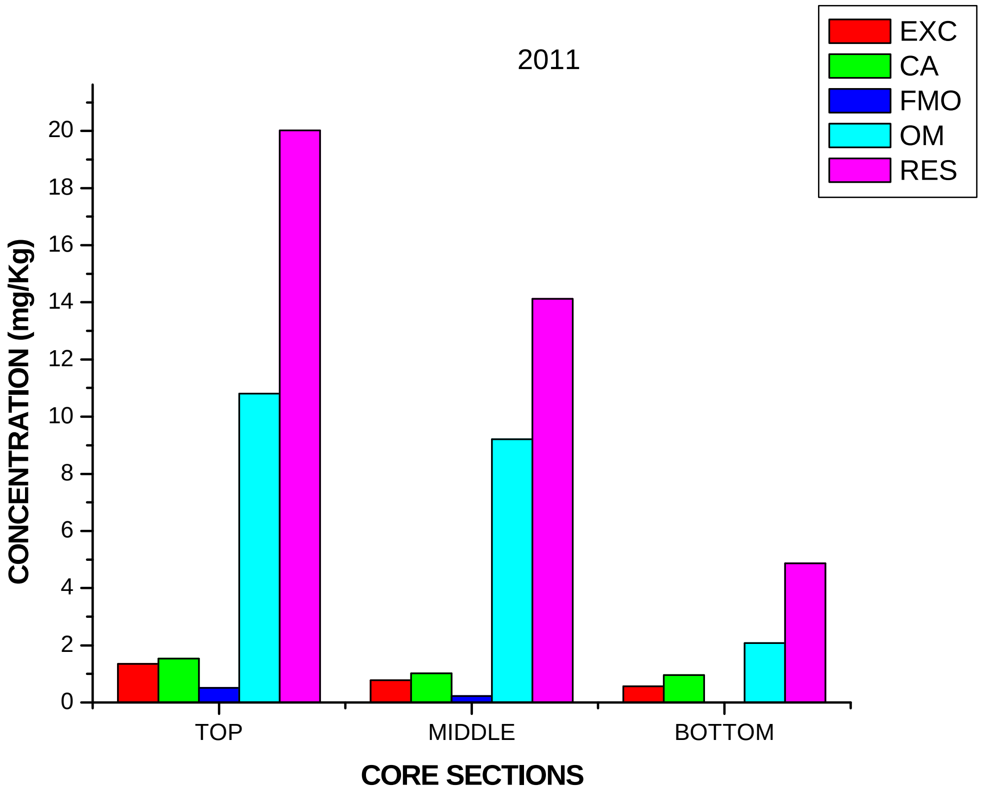


Figure 5.47 Fractionation profile of Cu in the core sediment N_1 (2011)

f. N_2:

Fractionation profile was given in Figure 5.48. Exchangeable and bound to Fe- Mn oxide fraction and bound to organic matter were high on top portion of the core and lower towards the bottom. Bound to carbonate fraction slightly lesser to mid section of the core and intensified to the bottom section. Residual fractions were superior weakly to the mid section of the core and minor to the greater depth.

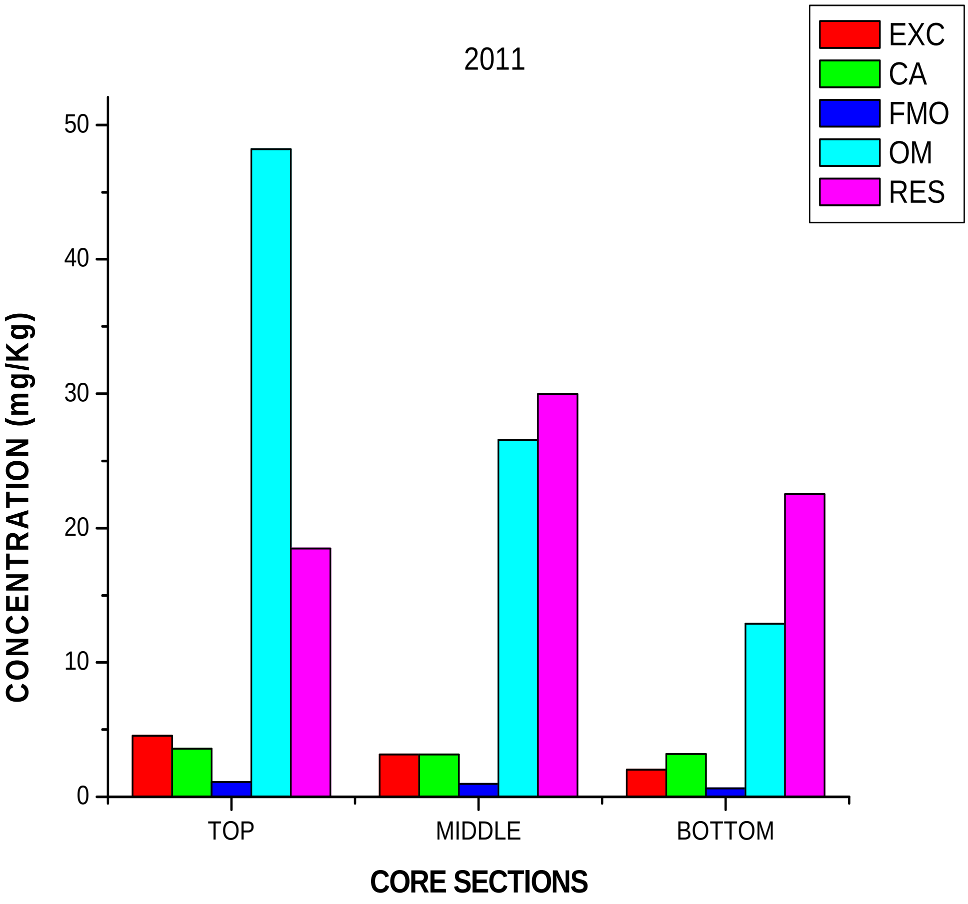


Figure 5.48 Fractionation profile of Cu in the core sediment N_2(2011)

5.2.2.3 Lead

a. S_1:

Fractionation profile was given in Figure 5.49. Exchangeable fraction and bound to organic matter were slightly high in the mid section of the core and minor to the bottom. Bound to carbonate fraction, Fe- Mn oxide bound and residual fraction were fades to the mid section of the core and slightly intensified towards deeper section.

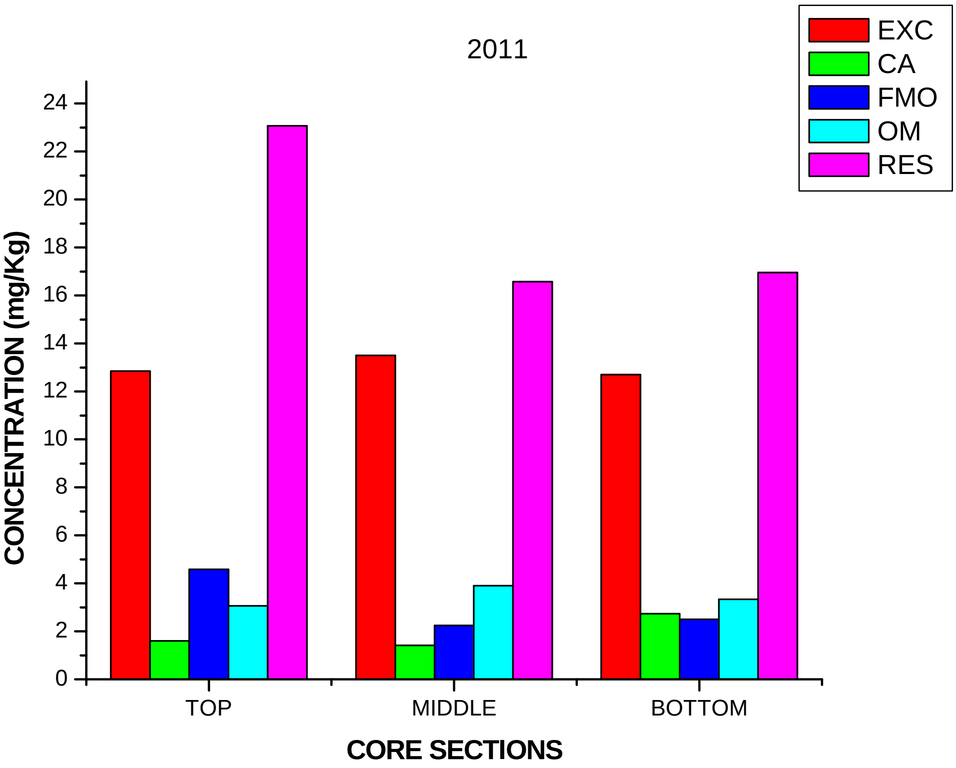


Figure 5.49 Fractionation profile of Pb in the core sediment S_1 (2011)

b. S_2:

Fractionation profile was given in Figure 5.50. Exchangeable and Fe-Mn oxide fractions were slightly major in the mid section of the core and minor towards the bottom. Bound to carbonate, bound to organic matter and residual fraction were decreased to the mid section of the core and increased to the greater depth.

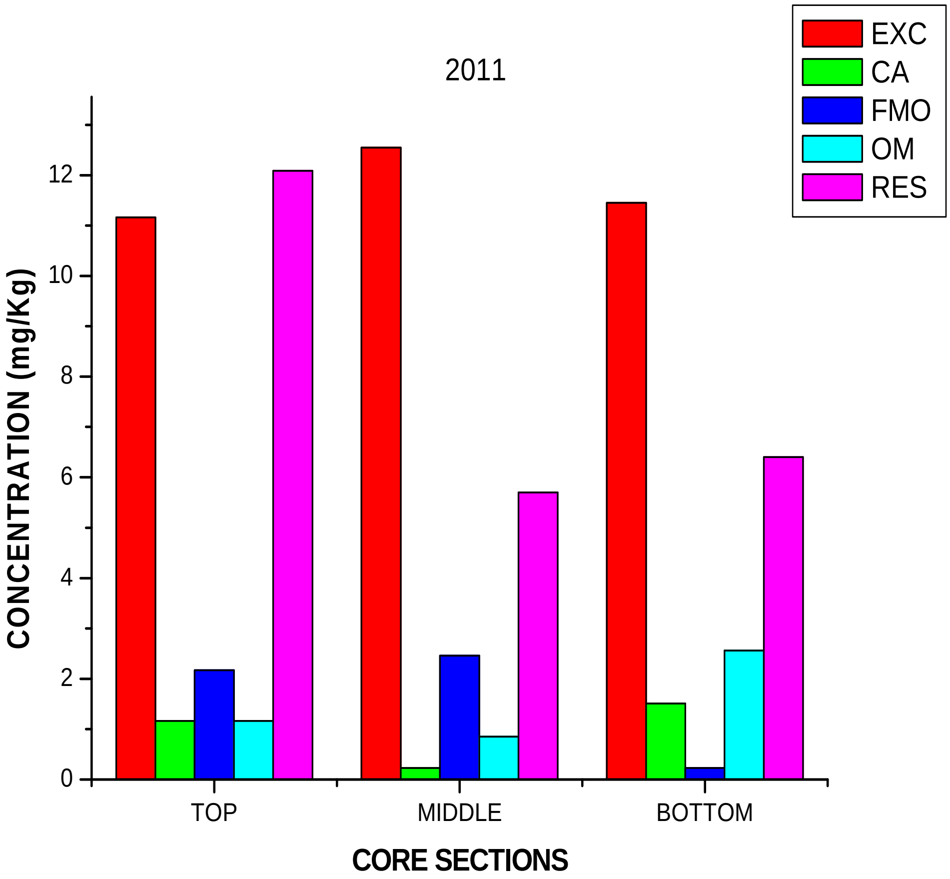


Figure 5.50 Fractionation profile of Pb in the core sediment S_2(2011)

c. M_1:

Fractionation profile was given in Figure 5.51. Exchangeable, bound to carbonate and residual fraction were greater to the mid section of the core and less towards heavier depth. Fe and Mn oxide fraction and bound to organic matter were lower to the mid section of the core and slightly greater to the deeper portion of the core.

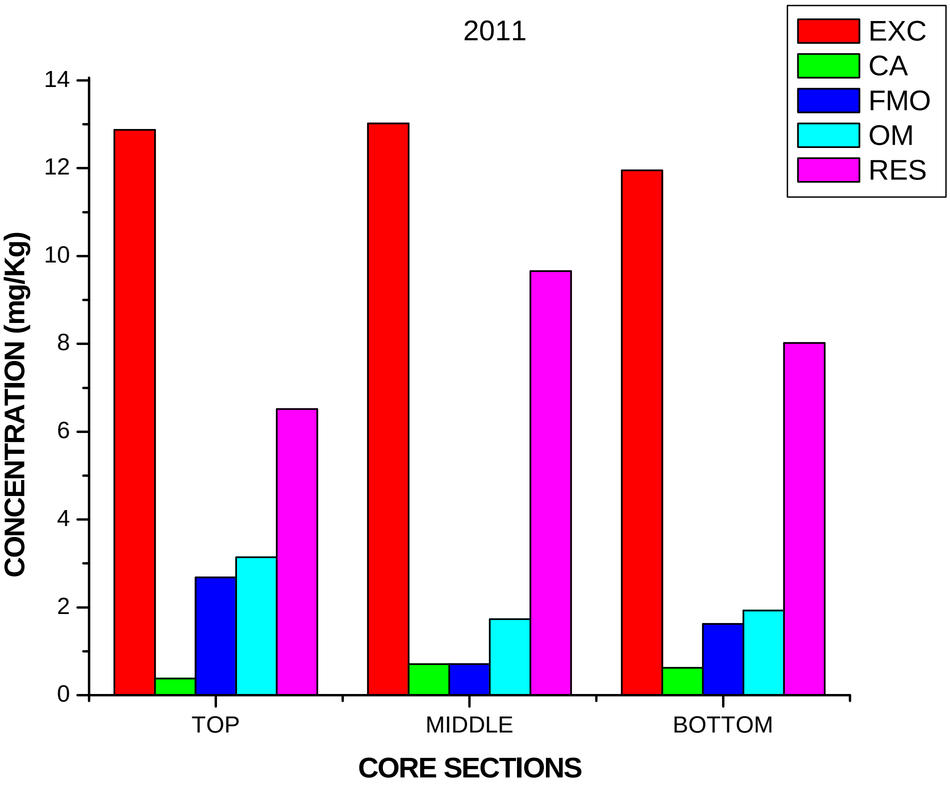


Figure 5.51 Fractionation profile of Pb in the core sediment M_1 (2011)

d. M_2:

Fractionation profile was given in Figure 5.52 .Exchangeable and residual fractions were found enhanced to the mid section of the core and lesser to the bottom. Bound to carbonate, Fe and Mn oxide and bound to organic matter were less to mid section of the core and increased towards the bottom.

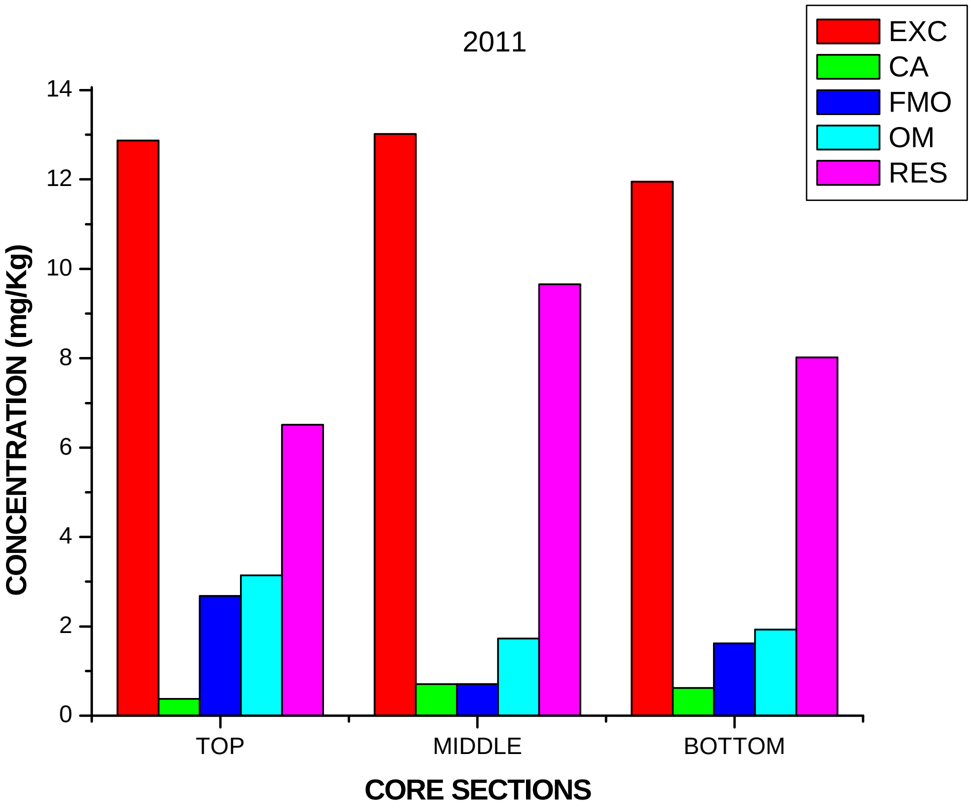


Figure 5.52 Fractionation profile of Pb in the core sediment M_2(2011)

e. N_1:

Fractionation profile was given in Figure 5.53. Exchangeable, Fe and Mn oxide fractions, bound to organic matter fractions and residual fraction were increased on top section of the core and was found limited towards the foot. Bound to carbonate were less to the mid section of the core and greater towards the bottom.

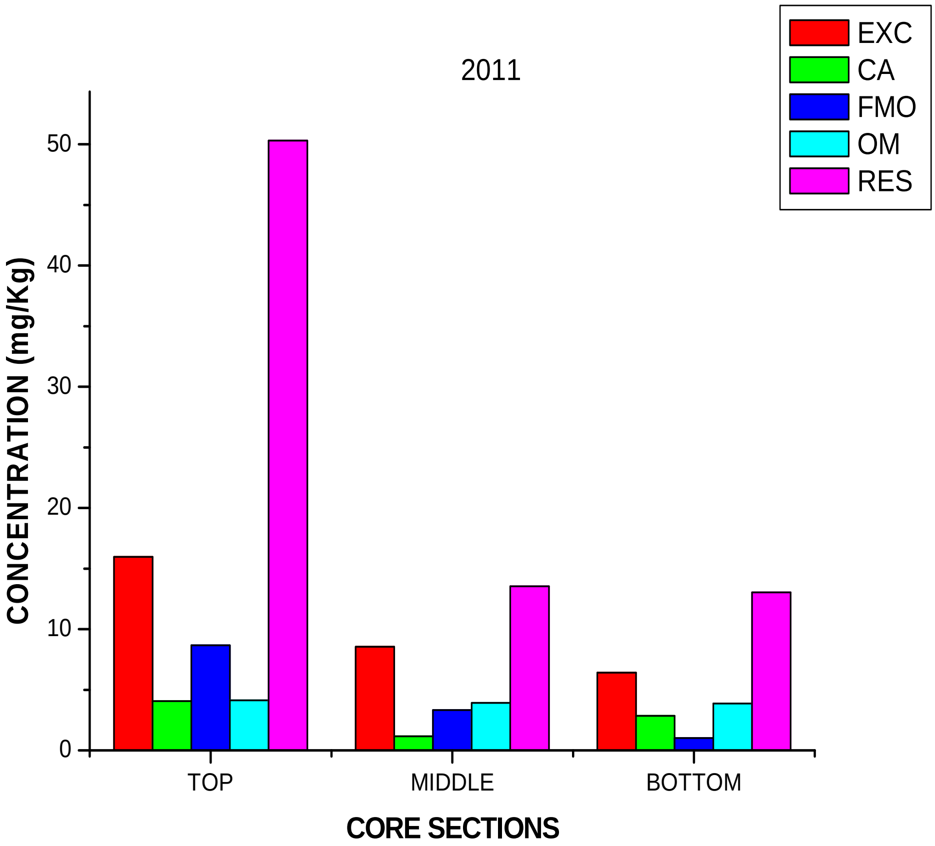


Figure 5.53 Fractionation profile of Pb in the core sediment N_1 (2011)

f. N_2:

Fractionation profile was given in Figure 5.54. Exchangeable and bound to Fe- Mn oxide fraction were increased on top portion of the core and weakly lower towards the bottom. Bound to carbonate and residual fractions were greater slightly to mid section of the core and reduce along the bottom part. Bound to organic matter fraction was superior faintly to the greater depth of the core and minor to the top section.

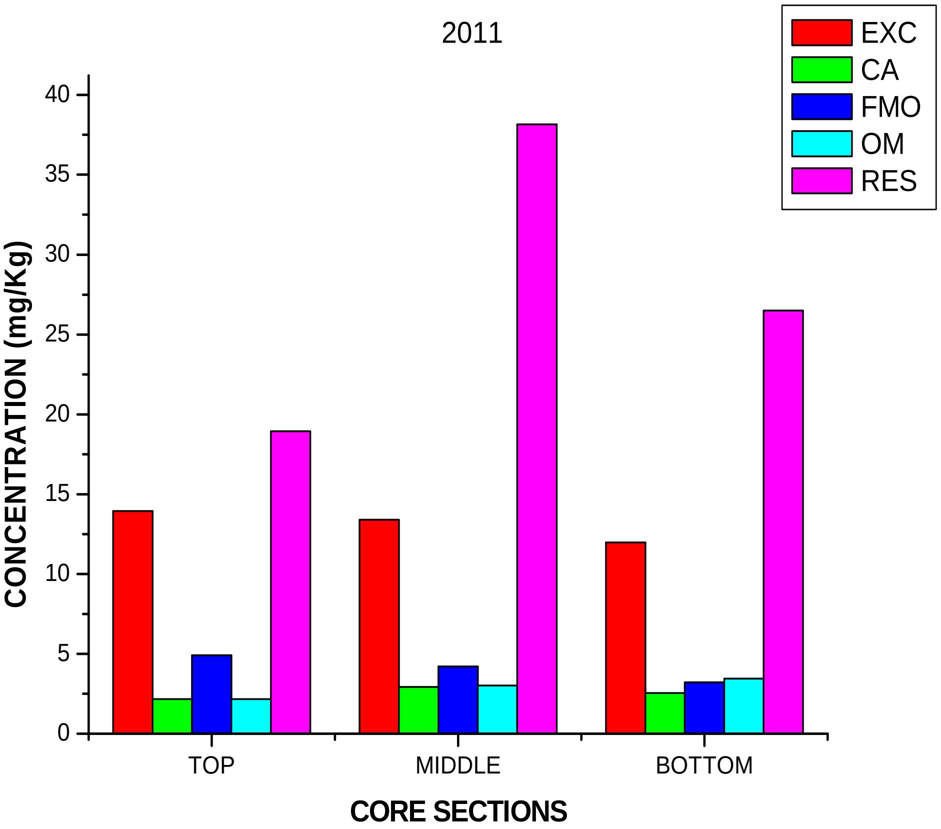


Figure 5.54 Fractionation profile of Pb in the core sediment N_2(2011)

5.2.2.4 Iron

a. S_1:

Fractionation profile was given in Figure 5.55. Exchangeable fraction was slightly high in the mid section of the core and less along the increased depth. Bound to carbonate fraction, Fe- Mn oxide bound and bound to organic matter were weakly greater towards the top section and minor to the bottom part of the core. Residual fraction were faintly diminished to the mid section of the core and intensified towards depth.

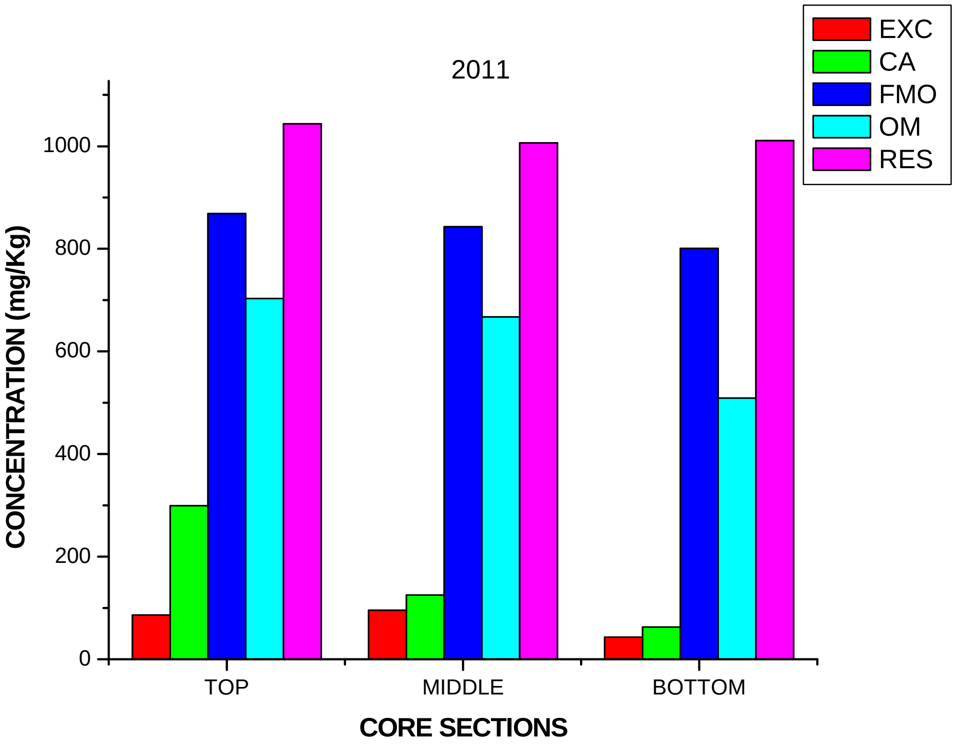


Figure 5.55 Fractionation profile of Pb in the core sediment S_1 (2011)

b. S_2:

Fractionation profile was given in Figure 5.56. Exchangeable and bound to organic matter were less on top partition of the core and weakly amplified towards the bottom. Bound to carbonate, Fe- Mn oxide fraction and residual fraction were slightly major in the mid section of the core and minor to the heavier depth.

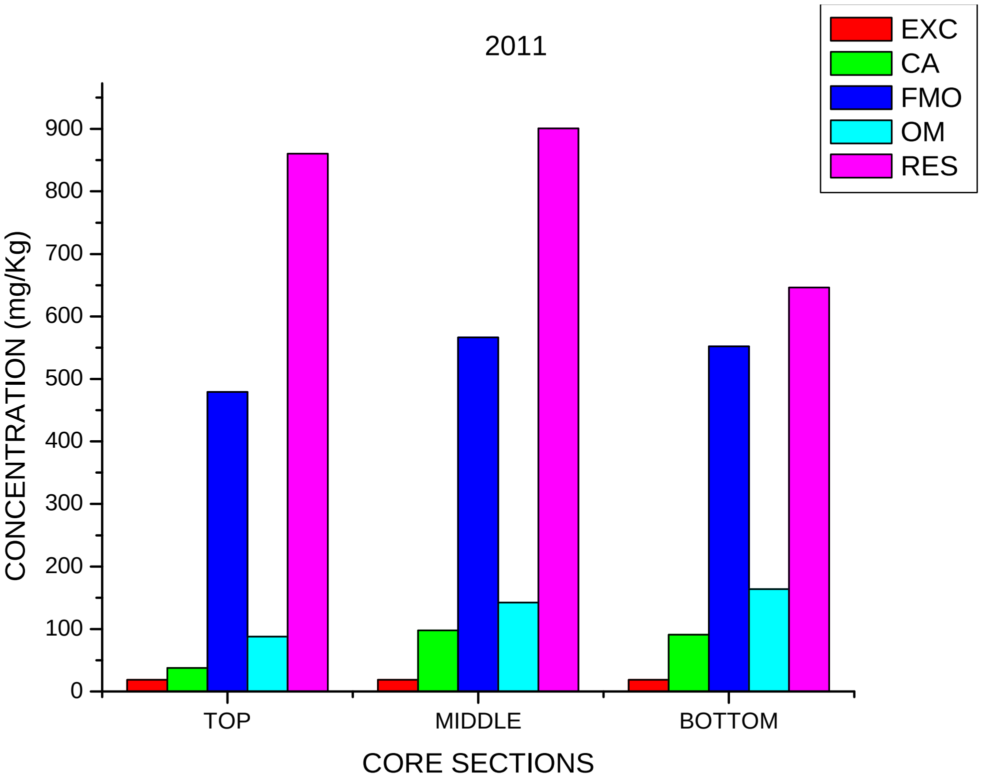


Figure 5.56 Fractionation profile of Pb in the core sediment S_2(2011)

c. M_1:

Fractionation profile was given in Figure 5.57. Exchangeable fraction was weakly superior to the top of the core and minor to the bottom section. Bound to carbonate fraction was slightly high towards the underside slice of the core. Bound to organic matter and residual fraction were greater to the mid section of the core and lesser when depth increases.

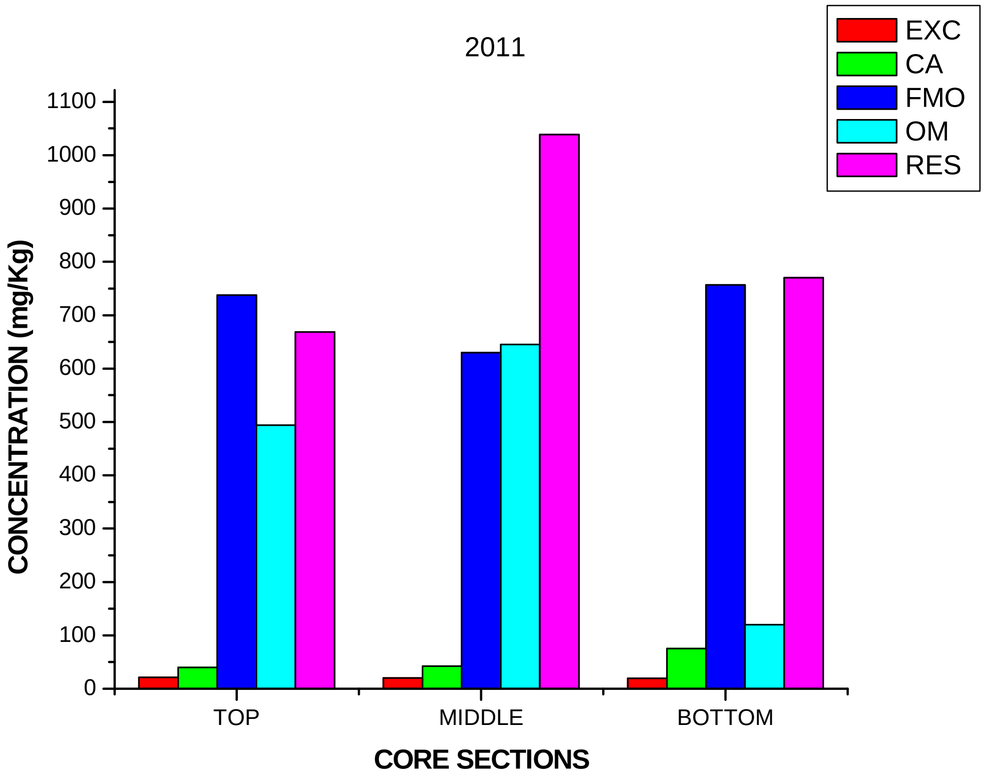


Figure 5.57 Fractionation profile of Pb in the core sediment M_1 (2011)

d. M_2:

Fractionation profile was given in Figure 5.58. Exchangeable and bound to organic matter were intense to the mid section of the core and less extent towards the bottom. Bound to carbonate, Fe and Mn oxide, and residual fraction were minimum in the mid layer of the core and weakly increases towards the bottom layer.

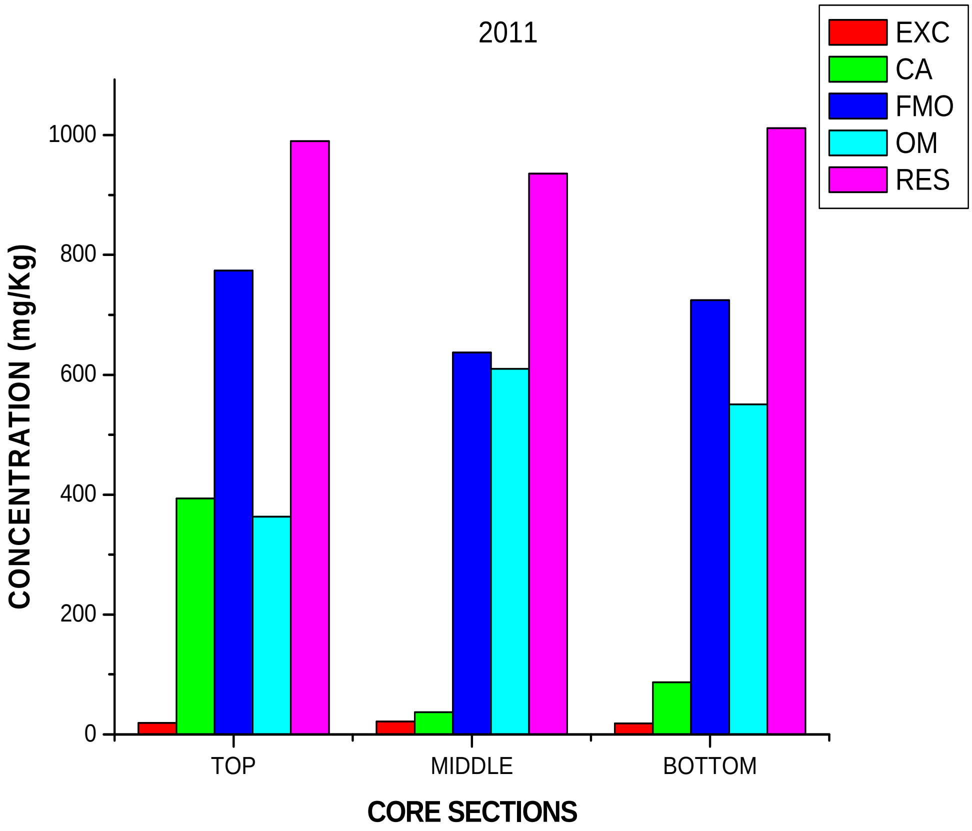


Figure 5.58 Fractionation profile of Pb in the core sediment M_2 (2011)

e. N_1:

Fractionation profile was given in Figure 5.59. Exchangeable and Fe and Mn oxide fractions were slightly greater on top section of the core and were found lesser towards the bottom. Bound to carbonate, bound to organic matter and residual fraction were weakly high in the mid section of the core and small towards the bottom.

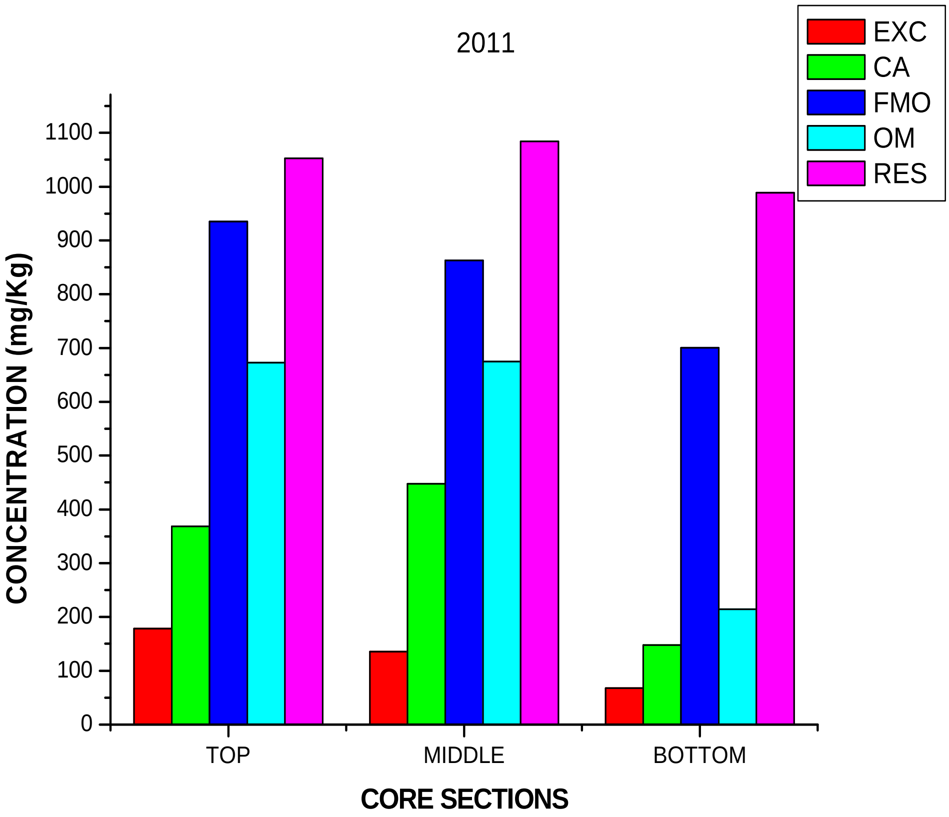


Figure 5.59 Fractionation profile of Pb in the core sediment N_1 (2011)

f. N_2:

Fractionation profile was given in Figure 5.60. Exchangeable, bound to Fe- Mn oxide fraction and bound to organic matter fraction were high on top portion of the core and lower towards the bottom. Bound to carbonate was weakly small to mid section of the core and high towards the bottom. Residual fractions were greater to mid section of the core and reduce to the bottom layer. Bound to organic matter fraction was slightly high at top section of the core and less to the greater depth.

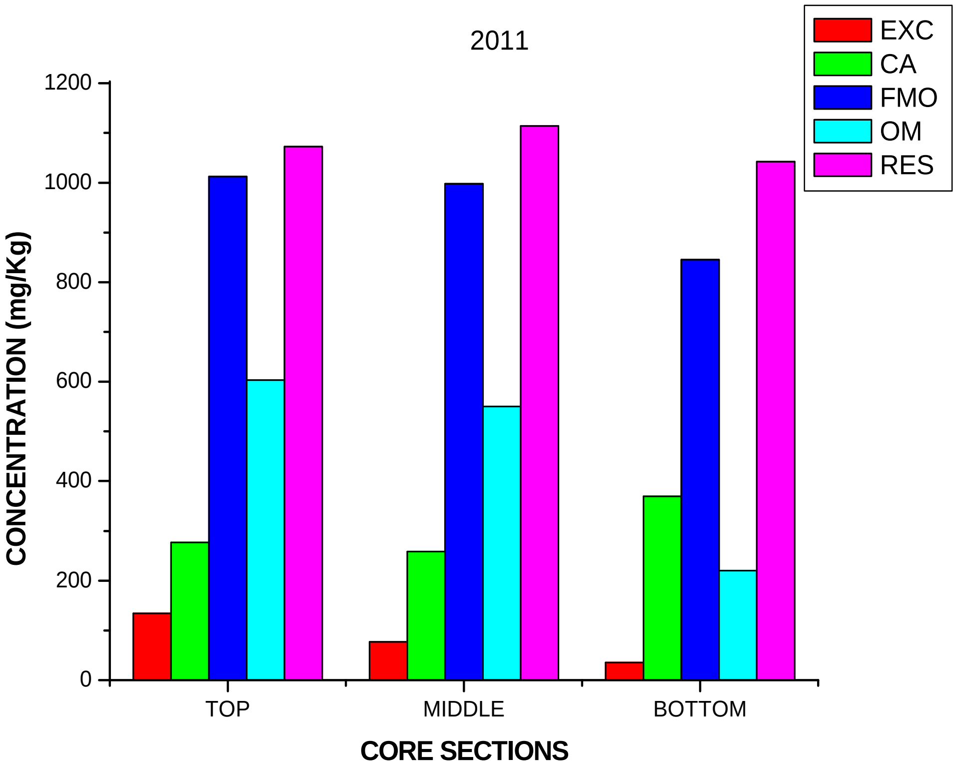


Figure 5.60 Fractionation profile of Pb in the core sediment N_2(2011)

5.2.2.5. Manganese

a. S_1:

Fractionation profile was given in Figure 5.61. Exchangeable fraction and bound to carbonate fraction were increased towards the top section of the core and less towards the bottom. Fe- Mn oxide bound and residual fraction were intensified to the mid section and diminished to the bottom of the core. Bound to organic matter was diminished to the mid section of the core and intensified towards deeper section of the core.

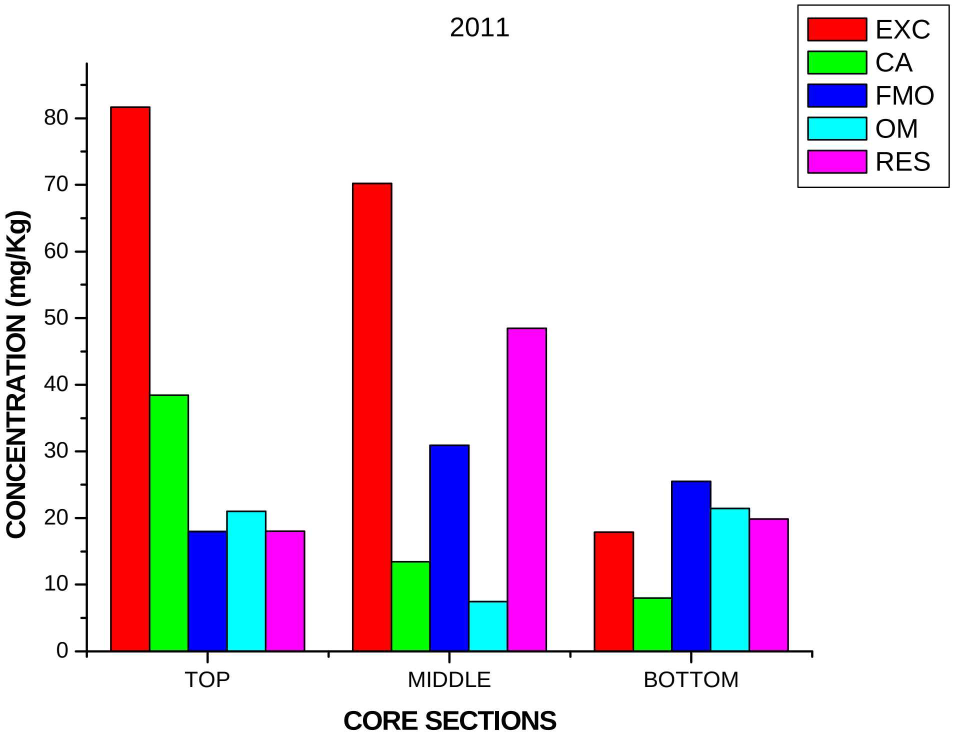


Figure 5.61 Fractionation profile of Mn in the core sediment S_1(2011)

b. S_2:

Fractionation profile was given in Figure 5.62. Exchangeable fraction was slightly greater at top and bottom portion of the core. Bound to organic matter was less on top portion of the core and slightly augmented towards the bottom. Bound to carbonate was major in the mid section of the core and minor towards the bottom. Fe- Mn oxide and residual fraction were decreased slightly towards the bottom part of the core.

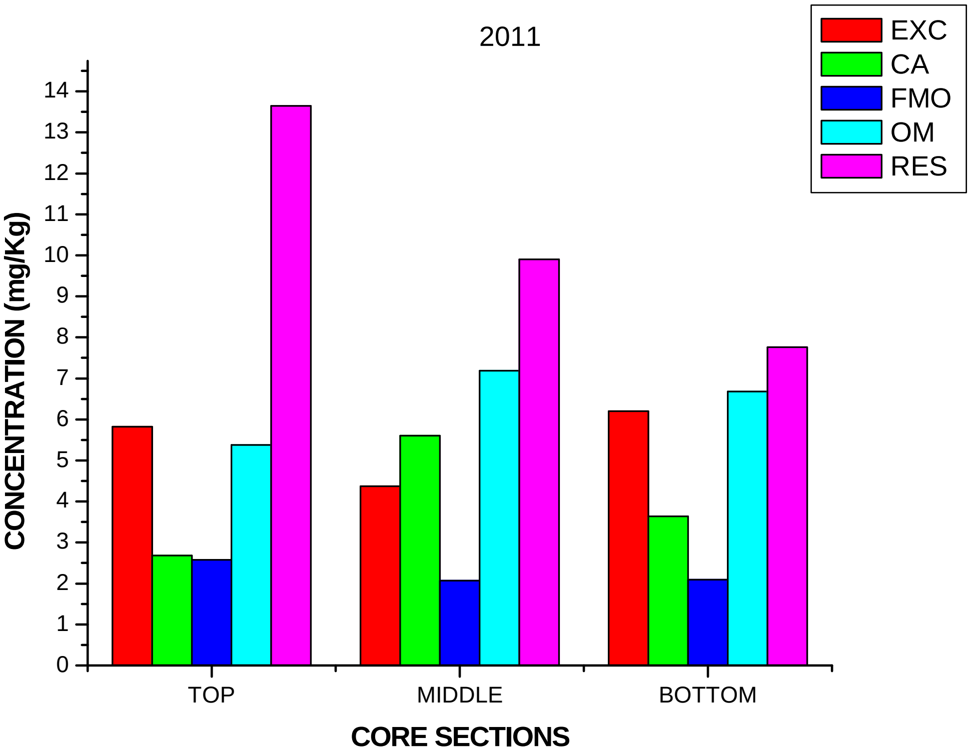


Figure 5.62 Fractionation profile of Mn in the core sediment S_2(2011)

c. M_1:

Fractionation profile was given in Figure 5.63. Exchangeable fraction was increased to the top section of the core and lessens towards the bottom. Bound to carbonate, Fe and Mn oxide and residual fraction were slightly greater to the mid section of the core and smaller to the bottom. Bound to organic matter were minor in the mid section of the core and major to the bottom layer.

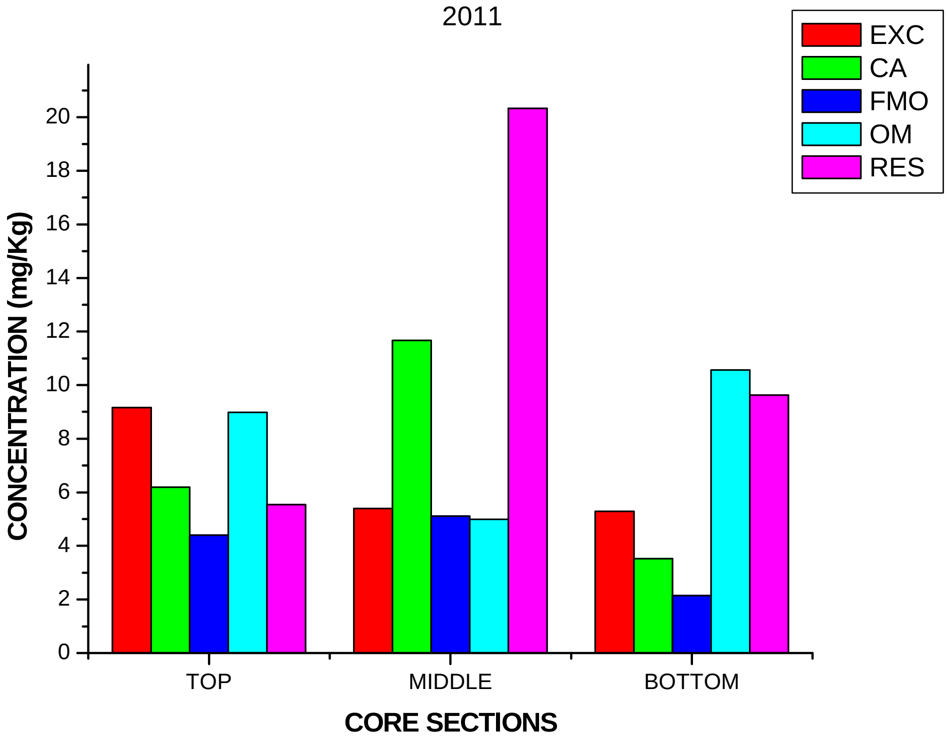


Figure 5.63 Fractionation profile of Mn in the core sediment M_1 (2011)

d. M_2:

Fractionation profile was given in Figure 5.64. Exchangeable and bound to organic matter were weakly smaller to the mid section of the core and increased to depth increases. Bound to carbonate and residual fraction were diminished to the bottom of the core. Fe and Mn oxide was increased to mid layer of the core and minimum to the greater depth.

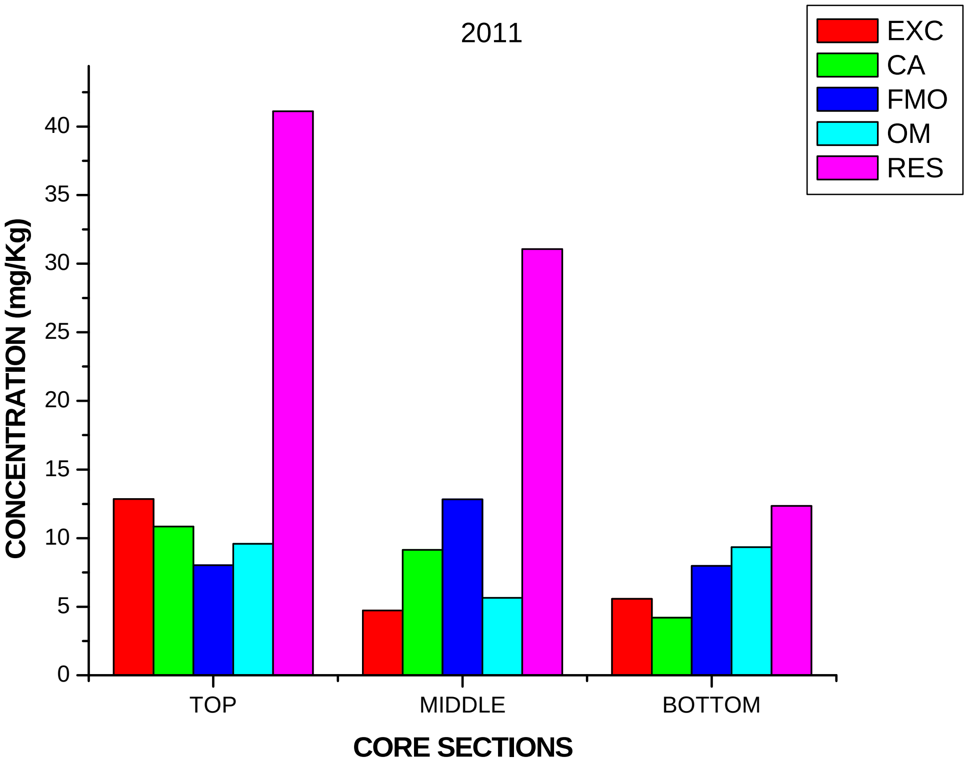


Figure 5.64 Fractionation profile of Mn in the core sediment M_2(2011)

e. N_1:

Fractionation profile was given in Figure 5.65. Exchangeable fraction was less on top portion of the core and augmented towards the bottom. Bound to carbonate and bound to organic matter were high to the mid stratum of the core and decreased towards the bottom. Fe - Mn oxide fractions and residual fraction were high on top segment of the core and was decreased towards the bottom section of the core.

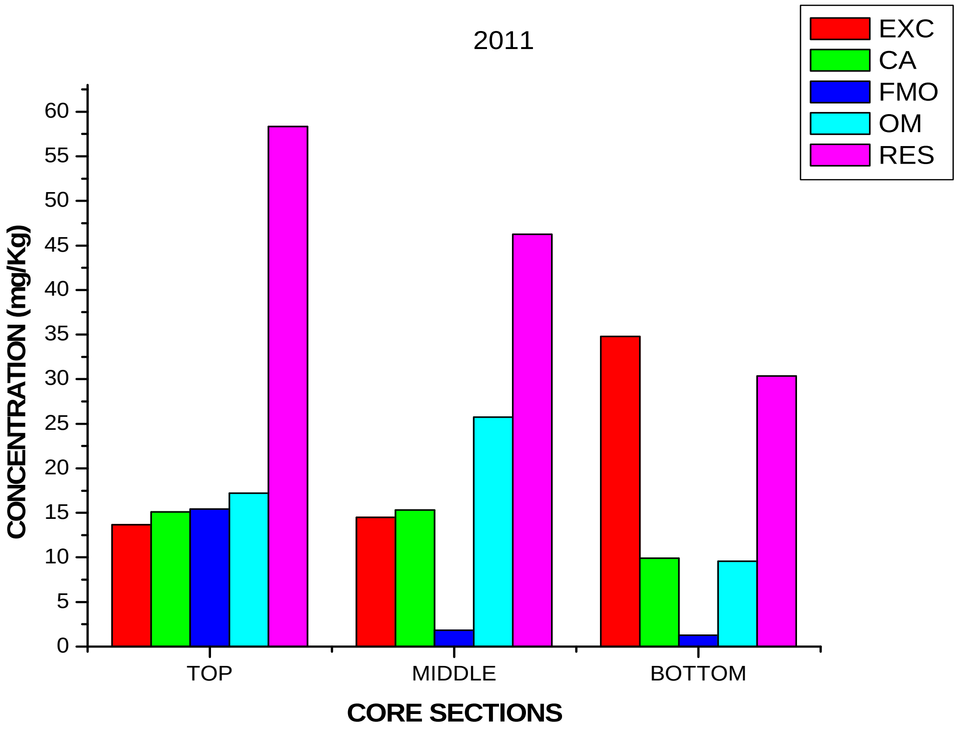


Figure 5.65 Fractionation profile of Mn in the core sediment N_1 (2011)

f. N_2:

Fractionation profile was given in Figure 5.66. Exchangeable and bound to organic matter fraction were greater to the mid section of the core and lesser to the bottom section. Bound to carbonate was slightly less on top portion of the core and increased towards the bottom. Fe- Mn oxide and residual fractions were high on top division of the core and less towards the bottom.

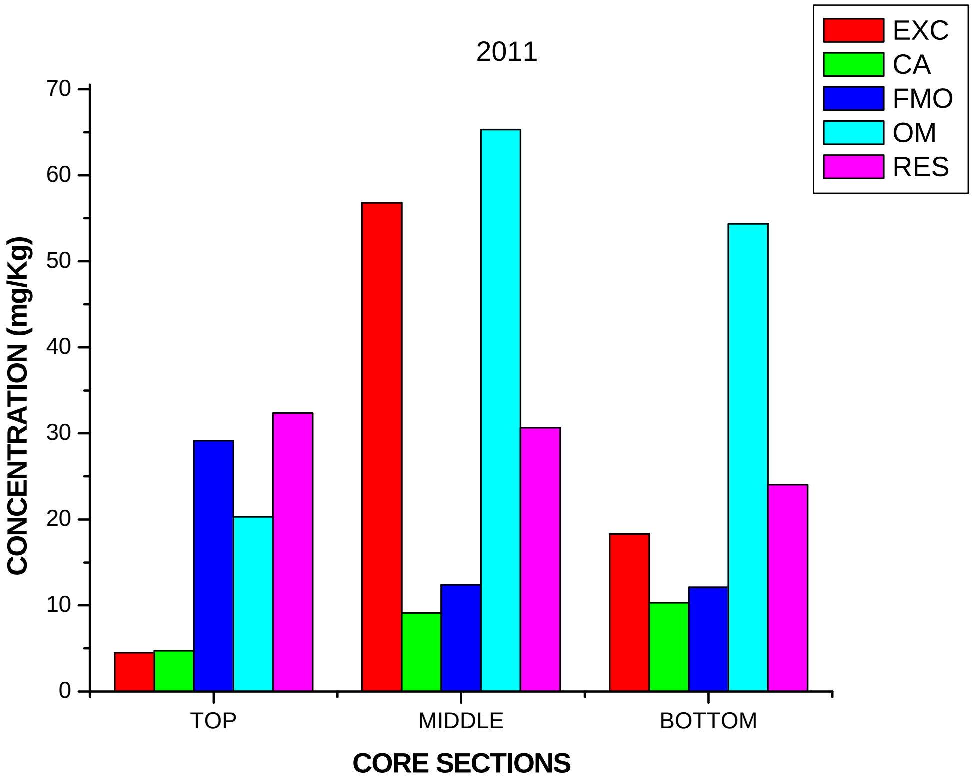


Figure 5.66 Fractionation profile of Mn in the core sediment N_2(2011)

5.2.2.6 Nickel

a. S_1:

Fractionation profile was given in Figure 5.67. Exchangeable fraction was greater to the mid section of the core and less towards heavier depth. Bound to carbonate and Fe- Mn oxide bound fraction were diminished to the mid section of the core and intensified towards the heavier depth. Bound to organic matter fraction and residual fraction were lgreater to the top section of the core and increase towards the bottom.

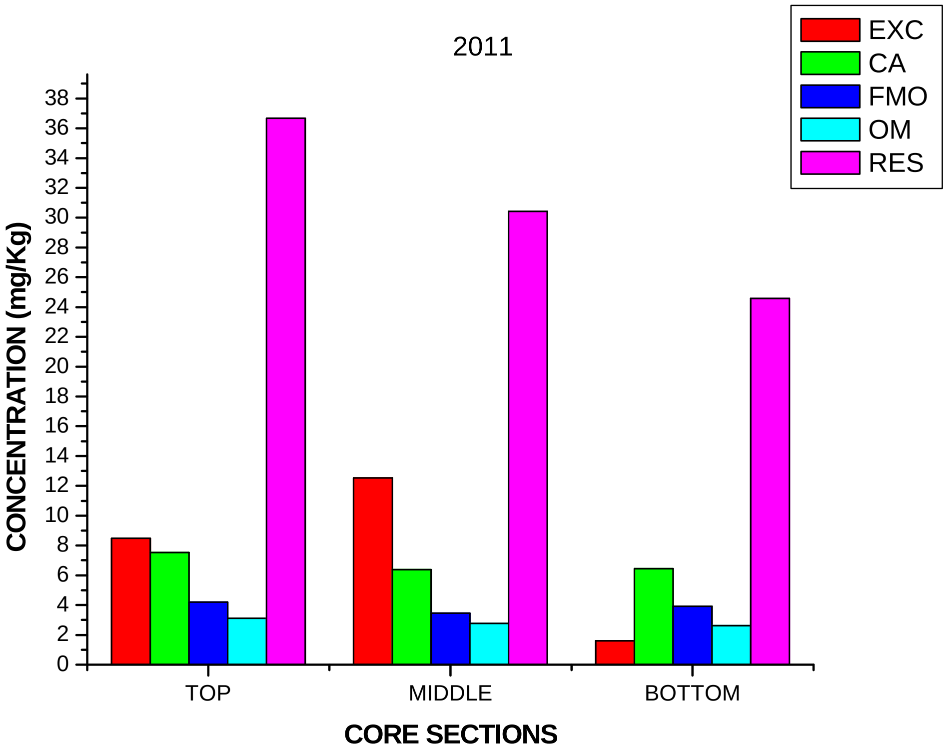


Figure 5.67 Fractionation profile of Ni in the core sediment S_1 (2011)

b. S_2:

Fractionation profile was given in Figure 5.68. Exchangeable, bound to carbonate and bound to organic matter were slightly major in the mid section of the core and minor to the heavier depth. Fe- Mn oxide fraction was low in the mid section of the core and increases towards the bottom. Residual fraction was augmented top portion of the core and lessens towards the bottom.

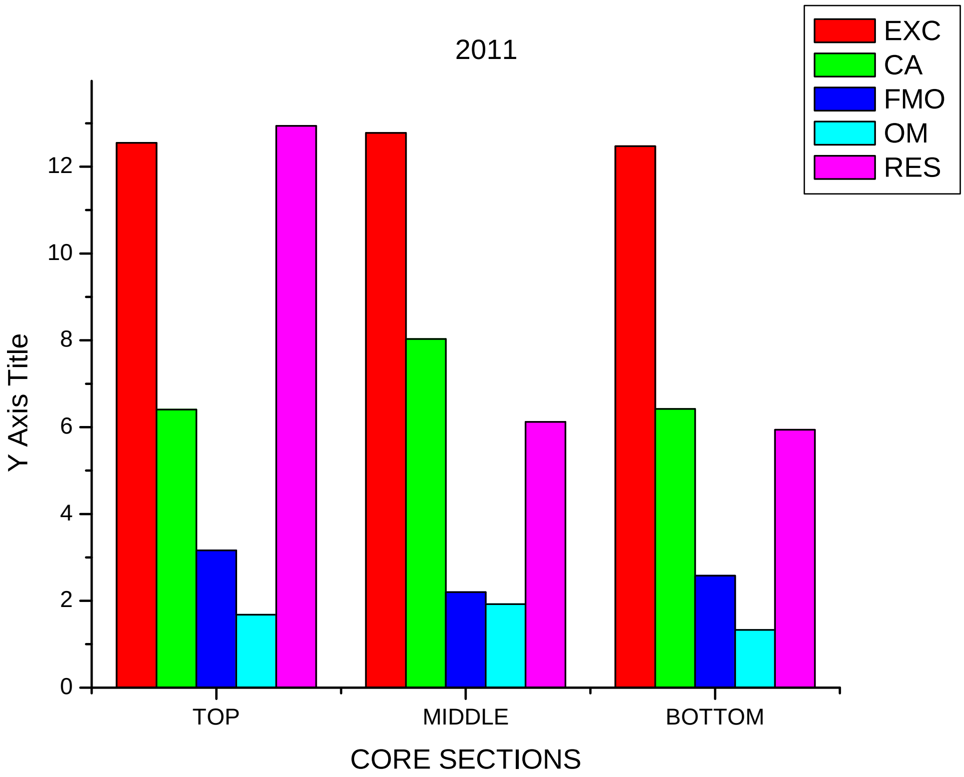


Figure 5.68 Fractionation profile of Ni in the core sediment S_2(2011)

c. M_1:

Fractionation profile was given in Figure 5.69. Exchangeable fraction was slightly less on top portion of the core and increased towards the bottom. Bound to carbonate, bound to organic matter and residual fraction were high to the mid section of the core and smaller to the bottom part. Fe and Mn oxide fraction was minor in the mid section of the core and major to the deeper layer.

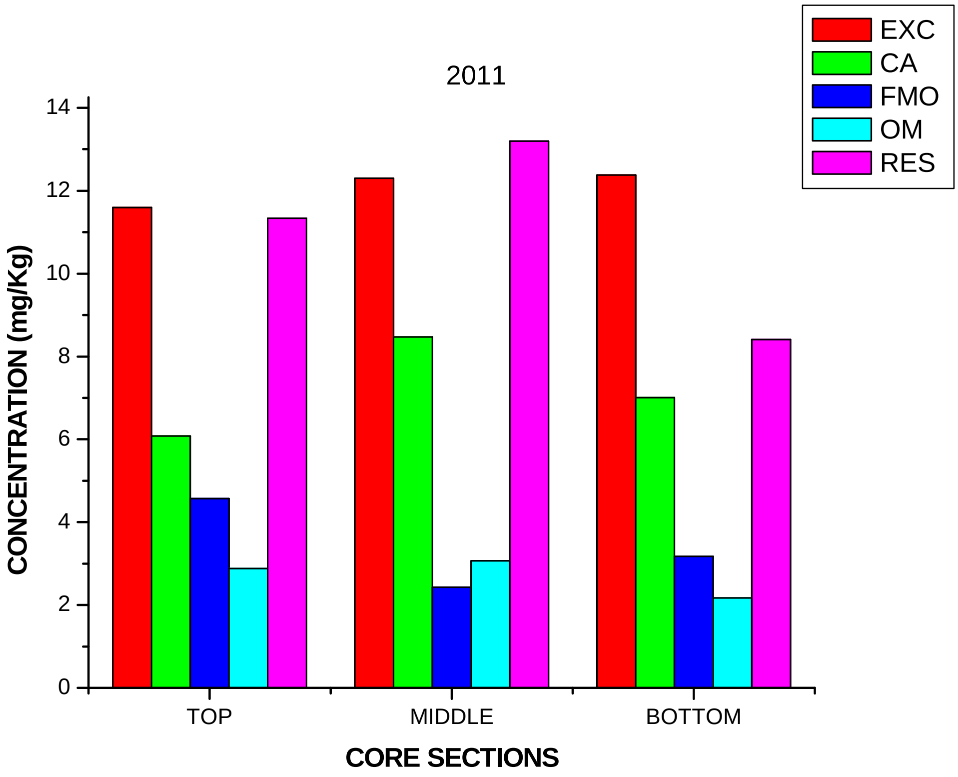


Figure 5.69 Fractionation profile of Ni in the core sediment M_1 (2011)

d. M_2:

Fractionation profile was given in Figure 5.70. Exchangeable fraction was high in the mid section of the core and smaller towards the bottom. Bound to organic matter and residual fraction were greater towards the bottom portion of the core. Bound to carbonate and Fe and Mn oxide , were diminished towards the bottom of the core.

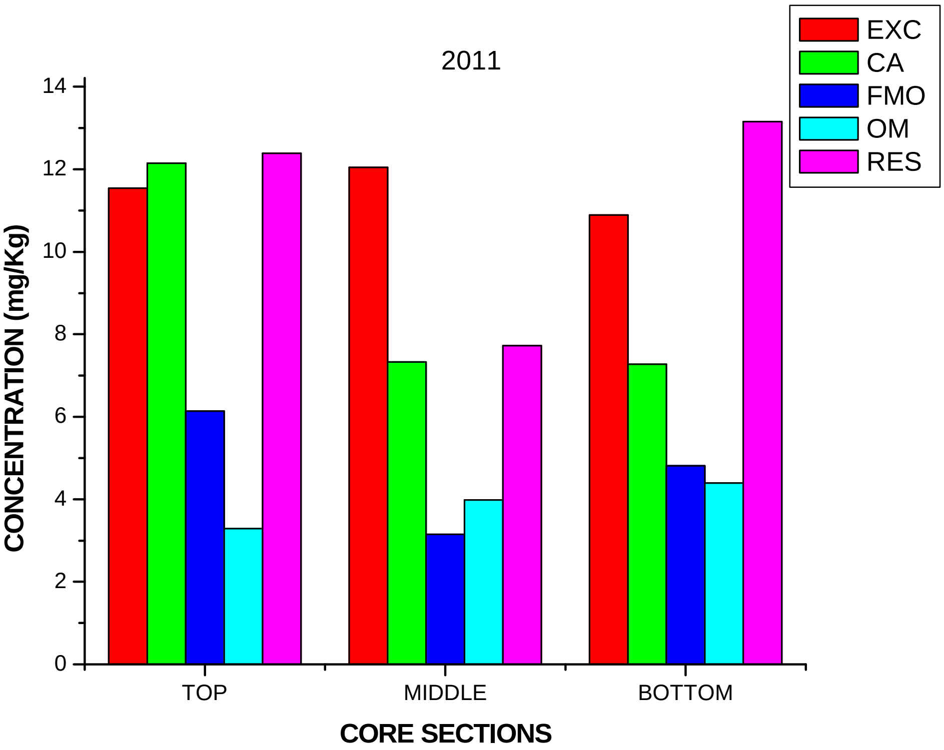


Figure 5.70 Fractionation profile of Ni in the core sediment M_2(2011)

e. N_1:

Fractionation profile was given in Figure 5.71. Exchangeable, Fe - Mn oxide fractions and residual fraction were slightly high on top sector of the core and was limited towards the bottom. Bound to carbonate was weakly decreased to the mid section of the core and increased to the bottom section. Bound to organic matter were faintly high to the mid segment of the core and decreased to the bottom.

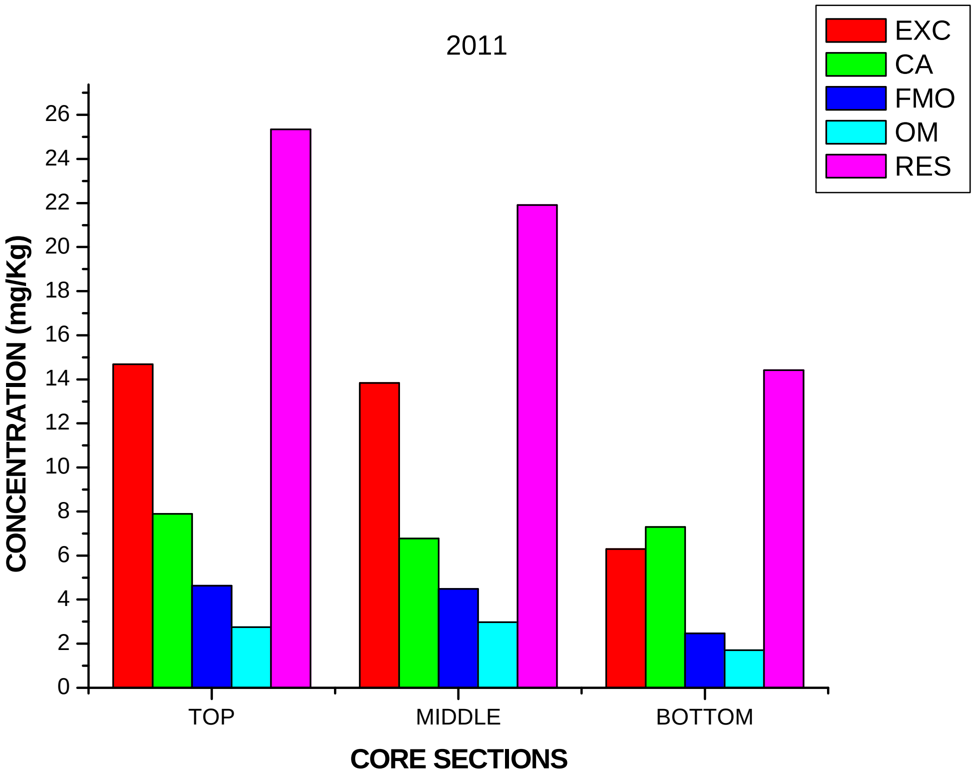


Figure 5.71 Fractionation profile of Ni in the core sediment N_1 (2011)

f. *N_2:*

Fractionation profile was given in Figure 5.72. Exchangeable fraction was less on mid partition of the core and increased towards the bottom. Bound to carbonate, bound to organic matter and residual fractions were weakly greater to the mid section of the core and lesser to the heavier depth. Fe- Mn oxide was found slightly greater on top division of the core and less towards the bottom.

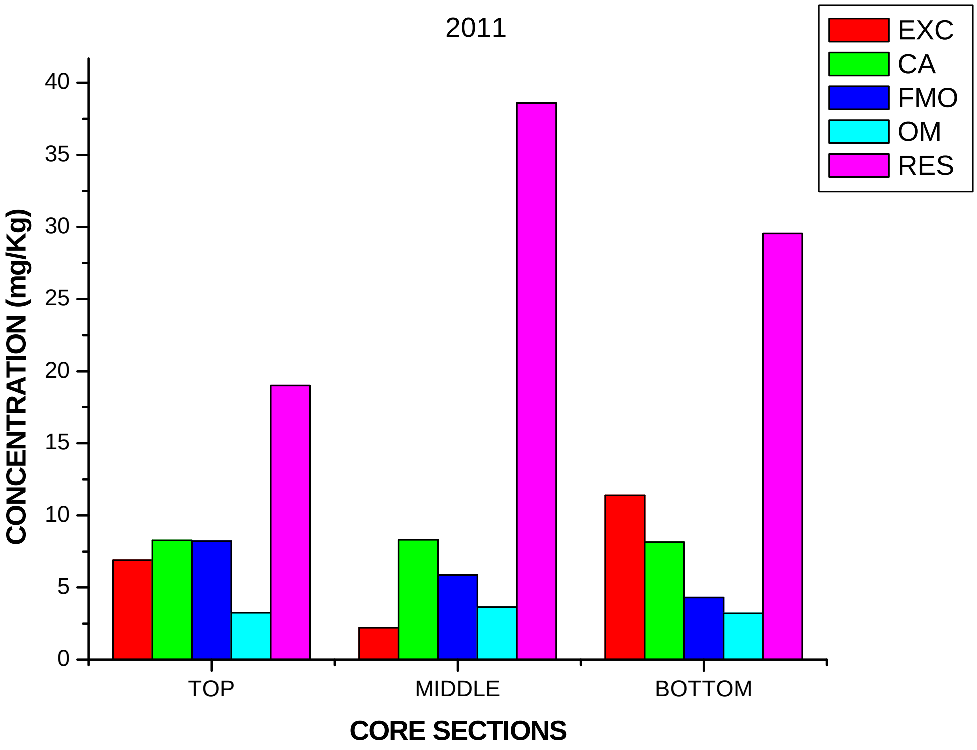


Figure 5.72 Fractionation profile of Ni in the core sediment N_2(2011)

Salient features outweighed from the above said results are shortlisted as: Among the six cores, top sections were enriched mainly with exchangeable or carbonate bound fraction. The cores from the northern part of the estuary were enriched with exchangeable fraction may be due to the fine grain size of the sediments. Cd was abundant in this fraction suggesting substantial input from urban runoff and other manmade sources. Cadmium and its compounds are mainly from industrial effluents, sewage sludge, domestic waste; pigments, petrol additives, steel products and combustion of fossil fuels are likely to be reach in the aquatic environment (Fergusson. 1990; Mathew et al. 2003). High Cd content in the exchangeable fraction was also found in the river sediments by Morillo et al. (2002) and in the marine sediments by Guevara-Riba et al. 2004 and Cuong and Obbard. 2006. The metals in EXC fraction include metals weakly adsorbed on sediments or on their essential components namely clays, Fe and Mn hydrated oxides, and humic acids. These metals can be released by ion-exchange processes and or metals that can be co-precipitated with carbonates present in many types of sediment (Marin et al. 1997; Tokaliog˘lu et al. 2000). This mechanism could effectively support the intensification of Cd in the study area. Changes in the ionic composition, influencing adsorption-desorption reactions, or lowering of pH could cause remobilization of metals in EXC fraction (Marin et al. 1997). In the present study, north zone had low pH values generating the high concentration of metals in the EXC fraction.

Major portion of Cu was found in the residual fraction in the core sediment of the CES in both periods of study (2009 and 2011). Bound to organic matter fraction represent as the second most dominant fraction in these sediment. Carbonate bound was the next abundant component of the sediment. Exchangeable and Fe- Mn oxide fractions were accounted the fourth and fifth place in the fractionation analysis. Most of the cores studied were enriched with residual fraction creating less threat in the estuary. High copper content in the residual fraction was also found in the river sediments by Budimir and Marko.1995 and marine sediments by Yuan et al. 2004, respectively. Major anthropogenic source of Cu include agrochemicals, wood preservatives, electroplating and antifouling paints. A significant amount of Cu is associated with the reducible fractions either by co-precipitation or by sorption onto pre existing coatings under existing physicochemical conditions (Panda et al. 1995). Ho. 2000 suggested that the high affinity of organic ligands makes Cu in sediments more stable, leading to the suppression of diffusion and dispersion of Cu. In addition, organic compounds under the reduced condition may be more active to bind with Cu by complexation rather than by ion exchange (Balasoiu. 2001; Wu et al. 1999). This strong effect can also be attributed to the fact that copper easily forms complexes with the organic matter due to high stability constant of organic Cu compounds (Kotoky et al. 2004). Organic matter exhibits a high degree of selectivity for divalent ions and hence the organic bound Cu fraction is an important fraction in the sediments and is not available for biological activity (Mcbride. 1994). Thus, the organic matter plays an important role in the immobilization of Cu, but mineralization of the host organic material under oxidizing conditions will release Cu into the overlying water column (Jain et al. 2007). Significantly high Cu concentration analysed in both organic and sulfide fraction in the sediments of Periyar River and Cochin estuary can be attributed to the high stability constant of organic-Cu compounds and supports the earlier works of Lasheen and Ammar. 2008.

Mostly Pb content was identified in the non-residual fraction specific to FMO. It has been reported that Pb exist in the stable forms with Fe hydroxide and Mn dioxide (Ramos et al. 1994), Which has been proved to be sensitive to anthropogenic inputs (Modak et al. 1992). This is in agreement with the previous results reported by Morillo et al. 2004 which showed that Fe and Mn hydrous oxides are important scavengers of Pb in sediments. Abundance of Pb in this fraction suggests the substantial input from urban runoff and other manmade sources and supported by Taylor and Owens. 2009. Thus, a high element percentage in the reducible fraction is a hazard for the aquatic environment because Fe and Mn species can be reduced into the pore waters during early diagenesis through microbially mediated redox reactions (Canfield. 1989 a,b.). Dissolution will also release Pb associated with oxide phases to the pore water possibly to the overlying water column (Petersen et al. 1995) and to benthic biota (Jones and Turki. 1997). The major sources of Pb are from the nonpoint sources, intensive human activities, including agriculture waste in the drainage basin and previous report also support the same inference (Monbet. 2006). The metal sources are mainly from industrial effluents, sewage sludge, domestic waste, pigments, petrol additives, steel products and combustion of fossil fuels (Fergusson. 1990; Mathew et al. 2003).

The residual fraction was the most dominant fraction of Fe in the sediment of the CES in both periods of study (2009 and 2011) and the next phase is the Fe –Mn oxide bound fraction in these sediment. Bound to organic matter was the third most abundant component of the sediment. Carbonate bound and exchangeable fractions noted were the fourth and fifth place in the fractionation analyses. These results are in good agreement with data reported by several studies carried out worldwide in marine coastal areas (Usero et al. 1998; Martin et al. 1998; Yuan et al. 2004; Takarina et al. 2004). The high percentage of Fe in the residual phase indicates that most of the iron exists as crystalline iron peroxides (goethite, limonite, magnetite, etc.). Large amounts of Fe accumulate in the residual phase probably because it is basically of natural origin (it is the most common element in the earth's crust). The major sources of Fe were from fertilizer, other chemical plant and agrochemical runoff (Wolters et al. 1989).

On comparing between the fractions, exchangeable and carbonate bound were intensified in the fractionation profile showing severe pollution in the study area. This is probably because of the known close association of Mn with carbonates (Dassenakis et al. 2003) as endorsed by other workers (Kiratli and Ergin. 1996; Morillo et al. 2004). Mn is the most mobile element since it is present with the highest percentage in the labile phase. In this phase, weakly sorbed Mn retained on sediment surface by relatively weak electrostatic interactions which may be released by ion exchange processes and dissociation of Mn-carbonate phase (Tessier et al. 1979). Zonal comparison revealed that northern part of the estuary was dominant with bioavailable fraction. Mn was derived mainly from fertilizer and agrochemical runoff and report by Wolters et al.1989 also justifies there inferences.

Most of the fractions of Ni was identified in the RES form. The dominant proportion of Ni in the residual phase is in agreement with the results of other studies (Martin et al. 1998; Mester et al. 1998). Main sources of Ni in the aquatic environment are electroplating and metallurgical industries, burning of fossil fuels, municipal wastewater, and geological weathering.

The relative distribution of metal in different fractions revealed Cd,Cu ,Pb and Mn had elevated concentration in nonresidual fraction, whereas Fe and Ni had increased content in residual fraction. Anthropogenically sourced metals preferential partition to the non residual phase of the sediment and the residual phase generally describes the background geochemical conditions. This supports the anthropogenic origin of metals Cd, Cu, Pb and Mn in the studied area under consideration.

5.3 Risk Assessment

The mobility, transport and partitioning of metals in an aquatic system is a function of the chemical form which in turn is controlled by the physicochemical and biological characteristics of that system. Fractionation of metal identification in sediment is more instructive than any total metal concentration. Both risk assessment code (RAC) and mobility factor (MF) showed risk in the top section of the core and it was diminished towards the bottom. Non residual enrichment factor (KNRF) also showed extreme anthropogenic loading in the top section of all the cores than the remaining division.

5.4 Conclusion

Sequential extraction procedure was applied for the partioning of selected metals in specific core sediments of the Cochin Estuary which shows its strong association with various geochemical forms. The north zone derived core sediment showed significant metal pollution than the other zones in the estuary, suggesting that industrial activities were the major contributing source for the metal pollution. Although lithogenic fraction dominated in the fractionation profile of Fe and Ni metals, Fe–Mn oxides and organic matter also played notable scavenging roles in most of the sampling sites. Significant level of EXC and CA-bound fractions of Cd, Cu, Pb and Mn gain much attention due to their bioavailable nature and susceptibility to release back into the water column. High RAC and MF values were recorded at a few sampling sites suggesting that certain pockets of the Cochin Estuary are polluted by metals due to human influences and interferences. The results of this study can be further used to help for designing the impact of remediation strategies and highlights the need for the in depth investigation of certain metal distribution and their fractionation.These concentrations are nearer or exceeding the threshold limits as prescribed by the recognized agencies in certain hot spot areas of the CES in order to get precise information on the behaviour and transport of these xenobiotic elements in the fluvial environment. The inferences and data sets derived from the CES are very significant and need to be addressed immediately which have greater role in modifying the global budget of metal concentration in the world oceans.

****

Chapter 6

SUMMARY

Contents

Spatial and temporal distribution of the concentrations of metals (Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn) existing within the sediments of CES has been investigated. Besides, individual sediment bound metal fractionations and in turn analysis was carried out for the surface and core sediments of CES. The raw data has been presented and interpreted with conclusions are put forward to explain the distribution patterns both spatially and temporally.

6.1 Spatial Distribution (Metal in Surface Sediment)

Distribution of metal concentration in the surface sediments collected from 17 prominent stations (grouped in to three zones – south, middle and north) of CES were deliberate for the ecological risk assessment in the study area. Results showed that the distribution of metals in the sediment was not uniform over the whole study area and revealed extreme contamination in the northern region than the southern region. According to the sediment quality guideline and previous literature comparison, CES showed to be polluted in heavy rate. This study inferred that the enhanced concentration of metals in northern part of the CES is due to strong anthropogenic influences. On the basis of GCI, northern zone has been identified as critical point of contamination.

6.2 Temporal Distribution (Metal in Core Sediment)

This compiles the ecological risk of metals in the estuary with reference to the biennial depth profile of core sediment in CES. Twelve core sediments were extracted from the South, Middle and North regions of the CES, six in each year of sample collection. Investigation on the influence of anthropogenic activities using GCI resulted in moderate to severe pollution for all the metals and specifically for Cd. SQG comparison generate severe contamination for Cd , Co, Cr, Pb, Mn, Zn and moderate for Cr and Ni. Except elements Ni and Zn, all the metals showed enrichment in comparison with previous reports placing the region as one among the impacted estuaries around the world. This study generates an authority on metal distribution and their chemical control in the estuarine core sediments.In CES, due to the excessive sand mining and dredging activities may influence the interpretation of chronological pollution status in the ecosystem. Metal concentrations showed irregular pattern in the entire sections (Top, Middle and Bottom) of the core showing the non homogenous anthropogenic input of these metals.

6.3 Geochemical Metal Fractionation

Sequential extraction procedure (SEP) was applied for the biennial partioning of selected metals in seventeen surface and specific six core sediments of the CES which shows its strong association with various geochemical forms. The north zone derived sediments showed significant metal pollution than the other zones in the estuary, suggesting that industrial activities were the major contributing source for the metal pollution.

6.3.1 Surface Sediment

Fractionation profile showed intensified content of metal in non residual fraction, creating severe threat to the aquatic system. EXC and CA fractions dominated in the fractionation profile in most of the metals which gain attention due to their bioavailable nature and susceptibility to release back to the water column in the entire zones of the estuary. RAC and MF revealed that certain pockets of the three zones of the estuary are polluted by metal either from human activities and industrial wastes or sewage disposal influences. EF and KNRF revealed extreme contamination in these surface sediments.

6.3.2 Core Sediment

Lithogenic fraction dominated in the fractionation profile of Fe and Ni. Fe–Mn oxides and organic matter also played notable scavenging roles in most of the sampling sites. Significant level of EXC and CA-bound fractions of Cd, Cu, Pb and Mn gain much attention due to their bioavailable nature and susceptibility to release back into the water column.The top section of the core mainly enriched with bioavailale fraction.High RAC and MF values were recorded at a few sampling sites suggesting that certain pockets of the CES are polluted by metals due to human influences and interferences.

6.4 Conclusion

The high concentration and bioavailability of metals in the CES indicate that there is a need to conduct more detailed and continuous monitoring studies in this region and to take necessary steps to reduce the sources of pollution. Further, deterioration of geochemical parameters may enhance the bioavailability of metals and will adversely affect the aquatic system and health of human, as they are depend on the system for their livelihood. Hence, the findings in this study will indicate the need for proper industrial planning and the safe disposal of industrial and urban waste, which would otherwise lead high levels of pollutants into the coastal ecosystem of Kerala, and would greatly invite socioeconomic disaster. The results of this study can be further used to help for designing the impact of remediation strategies. Also highlights the need for in depth investigation of certain metal distribution and their fractionation which were nearer or exceeding the threshold limits as prescribed by the recognized agencies in certain hot spot areas of the CES to get precise information on the behaviour and transport of these xenobiotic elements in the fluvial environment. Attention should therefore be drawn to fast developmental activities and habitation in and around the estuarine area. Thus proper management is needed to avoid the spreading of contaminants within and outside the estuary, by adopting stringent measures to control before any catastrophic event affects this area.The inferences and data sets derived from the CES are very significant and need to be addressed immediately which have greater role in modifying the global budget of metal concentration in the world oceans.

6.5 Recommendations

The thesis “Geochemical metal fractionation profile of the core sediment in the Cochin Estuarine System” has put serious attention of researchers for the conservation, management and restoration of the Cochin

Estuarine System. To maintain the natural quality of the system, the present study endorses the following recommendations and policy guidelines.

There are six approaches suggested through which pollution can be reduced:

1. Reducing consumption or usage of a polluting product and use alternate product which is less harmful to the ecosystem.
2. Treatment of wastes, discharges and disposal of a pollutant before dumping.
3. Develop effective appropriate methods and plans to control point and nonpoint sources of pollutants.
   - ➢ Remedial measures should adopt in the inskirts of factoty location itself.
   - ➢ Implement pollution prevention through education programs to reduce nonpoint source pollutants generated from the following activities, where applicable:
     - The improper storage, use, and disposal of household hazardous chemicals, including automobile fluids, pesticides, paints, solvents, etc.
     - Lawn and garden activities, including the application and disposal of lawn and garden care products, and the improper disposal of leaves and yard trimmings.
     - Discharge of pollutants into storm drains including floatables, waste oil, and litter.

4. Prepare policies and guidelines to prevent pollution
5. Adoption of land use practices designed to minimize soil erosion, land degradation and runoff. Greeneries in and around and plantation of mangroves near coastal areas.
6. Use the combined expertise and legislative responsibilities of Government agencies to ensure the acceptance of pollution prevention standard.

- ➢ Regional and local government
  - Develop control measures for pollution sources arising in and around industry
  - Eliminate contaminants through treatment and purification
- ➢ National government
  - Ensure that industry is committed to controlling environmental pollution and promoting health
  - Provide information and warnings on sources of pollution
  - Organize studies by experts and research groups
  - Provide official certification and monetary relief for pollution victims
- ➢ Scientists and researchers
  - Substantiate causal relationship between pollution and illness

- Provide diagnosis and treatment of pollution-related health problems
- The results of the pollution and their treatment study should be published in the form of articles for local and universal communication

Thus the creation of public awareness in this aspect is very important. Greater interaction between scientists, technologists and media is needed. School education can be a mechanism for creating awareness. Since India is at the stage of development transition, which eats up resources and adds to pollution burden should be discouraged. We need to remember an old proverb that "We did not inherit the Earth from our Ancestors, but borrowed it from our Children”. Their future has to be considered, before plundering the earth and contaminating it.

The present study therefore emphasizes the researchers for further studies to develop a suitable sediment quality guideline which would be appropriate to the coastal - estuarine conditions of Kerala, with the support of different Scientific Organization. More attention should be given for the toxicity and their impacts on the aquatic life in the ecosystem. Future research should also incorporate the above findings and its causative effect and impact on Human beings.

Some of the research findings were published in both national and international renowned journals and few more are yet to be published. The research articles published and communicated are appended in the Publication list.

****

- Presented a paper on **“Geochemical Assessment of Metal Contamination in the Core Sediments of Cochin Estuarine System”** in the National Conference of Ocean Society of India (OSICON’13) held during 26th-28th November 2013 at Indian Institute of Tropical Meteorology, Pune.
- Presented a paper on **“Heavy Metal Fractionation in the Sediments of Cochin Estuarine System (CES)”** in the UGC sponsored National seminar on Green Chemistry and Environmental Conservation organized by the Department of Chemistry, Morning Star Home Science College Angamaly South on 18 – 19 July 2013.
- Presented a paper on **“Fractionation of Phosphorus in the Cochin Estuary- South west coast India”** in Symposium on Coastal Oceanographic Studies Modelling and Observations [COSMOS] held at NPOL, Cochin on 9th and 10th May 2013.
- Participated in the two day workshop on “**Material Characterization at Nanoscales"** organized by the Sophisticated Test and Instrumentation Centre (STIC), Cochin University of Science and Technology, Cochin during 25-26 March 2013.
- Presented a paper on “**Geochemical Characteristics of Sediment core Pore water Particulate matter from Cochin Estuary”** in the National seminar **Aquasem’13** on Recent Developments in Water Chemistry with Specific Reference to Water Resources and

Management organized by the Department of Chemical Oceanography CUSAT, Society of Aquatic Chemists Kochi on 21 – 23 March 2013.

- Presented a paper on "**Nutritional Quality of Cochin Estuary"** in the International Conference on Nutritional Medicine Health and Wellness organized by the Department of Zoology, St.Teresa's College, Ernakulum in collaboration with Dr. Rath Research Institute, USA, on 7th and 8th June 2012 at St.Teresa's College, Ernakulum.
- Presented a paper on "**Core sediment metal distribution in the prominent areas of Cochin Estuary"** in the National Conference on Mangrove wetlands and near shore marine ecosystems from sustainability issues to management and restoration held at JNU , New Delhi on 5th and 6th March 2012.
- Attended a one day workshop on "**Profiling Research Publications for Quality Research"** organized by the University Library, Cochin University of Science and Technology, Kochi-22 on 3rd January 2012.
- Presented a paper on "**Core sediment organic matter distribution of in the coastal region of Antarctica"** in OSICON -2011 held at NIOT, Chennai (July 2011).
- Presented a paper on **"Contribution of women in improving the quality of the environment –A general perspective"** in the National seminar on Role of Women in the protection and promotion of Environment held at the Women's Studies Centre, CUSAT, Kochi 22 on 8th March 2011.

- Presented a paper on **“Biogeochemistry of sediment organic matter in selected stations of Kerala coast”** in Symposium on Indian Ocean Marine Living Resources [IndoMLR] held at Cochin on 2nd and 3rd December 2010.
- Presented a paper on **“Distribution of sediment organic matter (Protein & Lipid) in selected stations of Kerala coast”** in Kerala’s Ist Women Science Congress (2010) held at St.Teresa’s College, Ernakulam from10-12 August 2010.

****

REFERENCES

Abdel-Ghani, N. T. and Elchaghaby, G. A. (2007). Influence of operating conditions on the removal of Cu, Zn, Cd and Pb ions from wastewater by adsorption. International Journal of Environmental Science and Technology., 4(4), 451-456.

Abdel-Ghani, N. T. Hefny, M. and El-Chaghaby, G. A. F. (2007). Removal of lead from aqueous solution using low cost abundantly available adsorbents. International Journal of Environmental Science and Technology., 4 (1), 67-74.

Abrahim, G. and Parker, R. (2002). Heavy metal contaminants in Tamaki Estuary: Impact of city development and growth, Auckland, New Zealand. Environmental Geology., 42, 883–890.

Ahmad, M. K. Islam, S. Rahman, S. Haque, M. R. and Islam, M. M. (2010). Heavy Metals in Water, Sediment and Some Fishes of Buriganga River, Bangladesh. International Journal of Environmental Research., 4 (2), 321-332.

Akcay, H. Oguz, A. and Karapire, C. (2003). Study of heavy metal pollution and speciation in Buyak Menderes and Gediz river sediments, Water Research., 37 (4), 813-822.

Al-Juboury, A.I. (2009). Natural Pollution by Some Heavy Metals in the Tigris River, Northern Iraq. International Journal of Environmental Research., 3 (2), 189-198.

Al-Masri, M. S. Aba, A. Khalil, H. and Al-Hares, Z. (2002). Sedimentation rates and pollution history of a dried lake: Al-Oteibeh Lake. Science of the Total Environment., 293 (1-3), 177-189.

Allen Burton, G. 2002. Sediment quality criteria in use around the world. Limnology., 3, 65–75.

Aloupi, M. and Angelidis, M. O. (2002). Normalization to lithium for the assessment of metal contamination in coastal sediment cores from the Aegean Sea, Greece. Marine Environmental Research., 52(1),1-12.

Alvarez, E.A. Mochón, M.C. Jiménez Sánchez, J.C. and Ternero Rodríguez, M. (2002).Heavy metal extractable forms in sludge from wastewater treatment plants. Chemosphere., 47, 765-775.

Anithamary,I. Ramkumar,T. and Venkatramanan, S. (2012). Distribution and accumulation of metals in the surface sediments of Coleroon river estuary, East coast of India. Bulletin of Environmental Contamination and Toxicology., 88 (3), 413-417.

Anju, A.K. Dipu,S. and Sobha,V. (2011). Seasonal Variation of Heavy Metals in Cochin Estuary and Adjoining Periyar and Muvattupuzha Rivers, Kerala, India. Global Journal of Environmental Research., 5 (1),15-20.

Atkinson, M. J. and Smith, A.S.V. (1983). C:N:P ratios of benthic marine plants. Limnology and oceanography., 28, 568-574.

Balachandran, K. K. Laluraj, C. M. Nair, M. Joseph, T. Sheeba, P. and Venugopal, P. (2005). Heavy metal accumu-lation in a flow restricted tropical estuary. Estuarine Coastal and Shelf Science., 65, 361– 370.

Balachandran, K. K. Laluraj, C. M. Martin, G. D. Srinivas, K. and Venugopal, P. (2006). Environmental analysis of heavy metal deposition in a flow-restricted tropical estuary and its adjacent shelf. Environmental Forensics., 7, 345–351.

Balachandran, K. K. Reddy, G. S. Revichandran, C. Srinivas,K. Vijayan, P. R. and Thottam ,T. J.(2008). Modelling of tidal hydrodynamics for a tropical ecosystem with implications for pollutant dispersion (Cochin Estuary, Southwest India). Ocean Dynamics., 58(3-4), 259–273.

Balasoiu, C. F. Zagury, G. J. and Deschenes, L. (2001). Partitioning and speciation of chromium, copper and arsenic in CCA-contaminated soil: Influence of soil composition. Science of the Total Environment., 280, 239–255.

Banerjee, A. D. K. (2003). Heavy metal levels and solid phase speciation in street dusts of Delhi, India. Environmental Pollution., 123(1), 95–105.

Banerjee, K. Senthilkumar, B. Purvaja, R. and Ramesh, R. (2012). Sedimentation and trace metal distribution in selected locations of Sundarbans mangroves and Hooghly estuary, Northeast coast of India. Environmental Geochemistry and Health., 34, 27–42.

Baolin Liu. Ke Hu. Zhenglong Jiang. Juan Yang. Ximing Luo. And Aihua Liu. (2011). Distribution and enrichment of heavy metals in a sediment core from the Pearl River Estuary. Environmental Earth Science., 62,265–275.

Baptista, N. J.A. Smith, B.J. and Mcalliste, J.J. (2000). Heavy metal concentrations in surface sediments in a nearshore envi ronment, Jurujuba Sound, SE Brazil. Environmental Pollution .,109(1),1–9.

Bellucci, L. G. El Moumni, B. Collavini, F. Frignani, M. and Albertazzi, S. (2003). Heavy metals in Morocco Lagoon and river sediments. Journal of Physics., 107 (1), 139-142.

Belzunce-Segarra, M.J. Bacon, J.R. Prego, R. and Wilson, M.J. (1997). Chemical forms of heavy metals in surface sediments of the San Simon inlet, Ria de Vigo, Galicia. Journal of Environmental Science and Health, Part A – Environmental Science and Engineering and Toxic and Hazardous Substance Control., 32, 1271–1292.

Berner, R. A. (1980). Early Diagenesis: A Theoretical Approach Princeton. Princeton University Press.

Berner, R. and Raiswell, R. (1983). C/S method for distinguishing fresh water from marine sedimentary rocks. Geology., 12, 365–368.

Bertolotto, R. M. Tortarolo, B. Frignani, M. Bellucci, L. G. Albanese, S.and Cuneo, C. (2003). Heavy metals in coastal sediments of the Ligurian sea off Vado Ligure. Journal of Physics., 107 (1), 159-162.

Bijoy, N. S. Sumitha, C.M. and Girish, K.B. (2013). Manganese induced haematological and histopathological changes in Oreochromismassambicus (Peters, 1852). Pollution Research., 32, 555-562.

Birth, G. (2003). A scheme for assessing human impacts on coastal aquatic environments using sediments. (In: Woodcofie, C. D., Furness, R. A. (Eds.) Coastal GIS 2003) . Wollongong University Papers in Center for Maritime Policy, 14, Australia.

Blomqvist, S. Larsson, U.and Borg, H. (1992). Heavy metal decrease in the sediments of a Baltic Bay following tertiary sewage treatment. Marine Pollution Bulletin., 24, 258–266.

Bowen,R.E. Crumbly,C. (1999). Evolving principles in coastal management from concept to action In, Soden DL, Steel BS (eds) Hand book of global environment policy and administration. Marcel Dekkar, New York.

Buccolieri, A. Buccolieri, G. Cardellicchio,N. Dell'Atti, A. Di Leo, A. and Maci, A. (2006). Heavy metals in marine sediments of Taranto Gulf (Ionian Sea, Southern Italy). Marine Chemistry., 99, 227-235.

Budimir, S. and Marko, B. (1995). Distribution of Cd, Pb, Cu and Zn in carbonate sediments from the Krka river estuary obtained by sequential extraction. Science of the Total Environment.,170, 101–118.

Canfield D.E. (1989 a). Reactive iron in marine sediments. Geochimica et Cosmochimica Acta ., 53, 619-632.

Canfield, D.E. (1989 b). Sulfate reduction and oxic respiration in marine sediments: implications for organic carbon preservation in euxinic environments. Deep-Sea Research., 36, 121-138.

Chakraborty, P. Babu, P.V.R. and Sarma, V.V. (2012). A study of lead and cadmium speciation in some estuarine and coastal sediments. Chemical Geology., 294–295, 217–225.

Chakraborty, P. Raghunadh Babu, P.V. Acharyya, T. and Bandyopadhyay, D. (2010). Stress and toxicity of biologically important transition metals (Co, Ni, Cu and Zn) on phytoplankton in a tropical freshwater system: An investigation with pigment analysis by HPLC. Chemosphere., 80, 548–553.

Chapman, P. and Wang, F. (2001). Assessing sediment contamination in estuaries. Environmental Toxicology and Chemistry., 20, 3–22.

Chibunda, R. T. (2009). Chronic Toxicity of Mercury ($HgCl_2$) to the Benthic Midge Chironomus riparius. International Journal of Environmental Research., 3 (3), 455-462.

Chibunda, R.T. Pereka, A.E. Phiri, E.C.J. and Tungaraza. C. (2010). Ecotoxicity of Mercury Contaminated Sediment Collected from Mabubi River (Geita district, Tanzania) to the Early Life Stages of African Catfish (Clarias gariepinus). International Journal of Environmental Research., 4 (1), 49-56.

Church, T.M. (1986). Biogeochemical factors influencing the residencetime of microconstituents in a large tidal estuary, Delaware bay. Marine Chemistry., 18, 393-406.

Ciji, P.P. and Bijoy, N. (2014). Toxicity of Copper and Zinc to Puntius parrah (day, 1865). Marine Environmental Research., 93, 38-46.

Coban, B. Balkis, N. and Aksu, A. (2009). Heavy metal levels in sea water and sediment of Zonguldak, Turkey. Journal of the Black Sea/Mediterranean Environment., 15, 23-32.

Cobelo,G. Antonio. Prego. and Ricardo.(2004). Influence of point sources on trace metal contamination and distribution in a semienclosed industrial embayment: the Ferrol Ria (NW Spain).Estuarine Coastal and Shelf Science., 60, 695-703.

CPCB. (1996) Pollution potential of industries in coastal areas of India, Coastal Pollution Control Series, Central Pollution Control Board Report COPOCS/9/1995-96, Estuarine Coastal and Shelf Science., 54, 1051–1070.

Cundy, A.B. Croudace, I.W. Cearreta, A. and Irabien, M.J. (2003). Reconstructing historical trends in metal input in heavily-disturbed, contaminated estuaries: studies from Bilbao, Southampton Water and Sicily. Applied Geochemistry.,18, 311– 325.

Cuong, D.T. and Obbard, J.P. (2006). Metal speciation in coastal marine sediments from Singapore using a modified BCR-sequential extraction procedure. Applied Geochemistry., 21(8),1335–1346.

Das, A.K. Chakraborty, R. Cervera, M.L. de la Guardia, M.(1995). Metal speciation in solid matrices. Talanta., 42, 1007–1030.

Daskalakis, D. K. and O’Connor, T. P. (1995). Normalization and elemental sediment contamination in the coastal United States. Environmental Science and Technology., 29, 470-477.

Dassenakis, M. Adrianos, H. Depiazi, G. Konstantas, A. Karabela, M., Sakellari, A. and Scoullos, M. (2003). The use of various methods for the study of metal pollution in marine sediments, the case of Euvoikos Gulf, Greece. Applied Geochemistry., 18, 781–794.

Deepulal, P.M. Gireeshkumar, T.R. Sujatha, C.H. and Rejomon, G. (2012). Chemometric study on the trace metal accumulation in the sediments of the Cochin Estuary-Southwest coast of India. Environmental Monitoring and Assessment., 184, 6261–6279.

Dhanakumar, S. Murthy, K.R. Solaraj, G. and Mohanraj, R. (2013). Heavy-metal fractionation in surface sediments of the Cauvery River Estuarine Region, Southeastern coast of India. Archives of Environmental Contamination and Toxicology., 65, 14–23.

Doner, H.E. (1987). Chloride as a factor in mobilities of Ni(II), Cu(II) and Cd(II) in soil. Soil Science Society of America Journal., 42,882–885.

Everrarts, J.M. and Fischer, C.V. (1992). The distribution of heavy metals(Cu, Zn, Cd, Pb) in the fine fraction of surface sediments of the North Sea. Netherlands. Journal of Sea Research., 29,323–331.

Faganelli, J. Ogorolec, B. Misic, M. Dollenen, T. and Pezdic J. (1987). Organic geochemistry of two 40m sediment cores from the Gulf of Trieste Northern Adriatic). Coastal Shelf Science., 25, 157-167.

Fan, W. Wang, W.X. Chen, J. Li, X. and Yen, Y.F. (2002). Cu, Ni and Pb speciation in surface sediments from a contaminated bay of northern China. Marine Pollution Bulletin.,44, 816– 32.

Feng, H. Han, X. Zhang, W. and Yu, L. (2004). A preliminary study of heavy metal contamination in Yangtze River intertidal zone due to urbanization. Marine Pollution Bulletin., 49, 910-915.

Ferguson, E. J. (1990). Heavy metals in plants.(In:Ferguson (Ed))The heavy elements, Chemistry, Environmental Impact and Health Effects. Pergamon Press, Oxford, UK.

Fernex, F.E. Migon, C. and Chisholm, J.R.M.(2001). Entrapment of pollutants in Mediterranean sediments and biogeochemical indicators of their impact. Hydrobiologia .,450, 31-46.

Forstner, U. Ahlf, W. Calmano, W. Kersten, M. and Schoer, J. (1990). Assessment of metal mobility in sludges and solid wastes, In: Metal Speciation in the Environment, NATO ASI Series, J. A. C. Broeckaert, S. Gucer and Adams, F. series G, Ecological Sciences., 23. Springer, Berlin.

Förstner, U. and Wittmann, G. (1983). Metal Pollution in the Aquatic Environment. Springer-Verlag, Berlin.

Forster, U. and Whittmann, G.T.W. (1998). Metal Pollution in the Aquatic Environment. Springer- Handbook of Ecotoxicology. Blackwell Science, Oxford, 543-569.

Geetha, R. Chandramohanakumar, N. and Mathews, L. (2008). Geochemical Reactivity of Surficial and Core Sediment of a Tropical Mangrove Ecosystem.). International Journal of Environmental Research., 2(4), 329-342.

Gleyzes, C. Tellier, S. and Astruc, M. (2002). Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures. Trends in Analytical Chemistry., 21 (6–7), 451–467.

Gopalan, U.K. Doyil, T. Vengayil, P. Udaya, V. and Krishnakutty, M. (1983). The shinking backwaters of Kerala. Journal of Marine Biological Association of India., 25, 131-141.

Guevara-Riba, A. Sahuquillo, A. Rubio, R. and Rauret, G. (2004) Assessment of metal mobility in dredged harbour sediments from Barcelona, Spain, Science of Total Environment., 321,241–255.

Hakanson, L. (1980). An ecological risk index for aquatic pollution control, a sedimentological approach. Water Research., 14, 975–1001.

Harikumar, P.S. and Jisha, T.S. (2010). Distribution pattern of trace metal pollutants in the sediments of an urban wetlands in the southwest coast of India. International Journal of Engineering Science and Technology ., 2(5), 840-850.

Harikumar, P. S. Nasir, U. P. and Mujeebu Rahman, M. P. (2009). Distribution of heavy metals in the core sediments of a tropical wetland system. International Journal of Environmental Science and Technology., 6 (2), 225-232.

Harikumar, P. S. and Nasir, U. P. (2010). Ecotoxicological impact assessment of heavy metals in core sediments of a tropical estuary. Ecotoxicology and Environmental Safety., 73(7), 1742–1747.

Ho, T.L.T. (2000). Heavy metal pollution of agricultural soil and river sediment in Hanoi, Vietnam. Ph.D. thesis, Kyushu University, Fukuoka, Japan

Holm, N.G. (1988). Arsenic regeneration from estuarine sediments of the Bothnian Bay, weden. Chemical Geology., 68, 89-98.

Howari,F.M. and Banat,K.M.(2001). Assessment of Fe, Zn, Cd, Hg and Pb in the Jordan and Yarmouk river sediments in relation to their physicochemical properties and sequential extraction characterization. Water Air Soil Pollution., 132,43–59.

Jain, C. K. (2004). Metal fractionation study on bed sediments of River Yamuna, India, Water Research., 38, 569-578.

Jayasree, P. and Nair, S.M. (1995). Spatial diversity of trace metals in recent sediments of Cochin estuary (India). Toxicology and Environmental Chemistry., 51, 243–254.

Jenne, F. A. (1968). Controls of Mn, Fe, Co, Ni, Cu and Zn concentrations in the soils and water:The significance of hydrous Mn and Fe oxides', in: R. F. Gould (ed.), Trace in Organics in the Waters, Advances in Chemistry Series 73,Washington DC, American Chemistry Society. 337–387.

Jiya,J. Rajesh,G. Abdulaziz,A. Loka Bharathi, P.A. and Shanta Nair. (2011). Heavy metal pollution exerts reduction/adaptation in the diversity and enzyme expression profile of heterotrophic bacteria in Cochin Estuary, India. Environmental Pollution., 159, 2775-2780.

Jones, B. and Turki, A. (1997). Distribution and speciation of heavy metals in surfacial sediments from Tees Estuary, North-East England. Marine Pollution Bulletin., 34, 768–779.

Kabala, C. and Singh, B.R. (2011). Fractionation and mobility of copper, lead and zinc in soil profiles in the vicinity of a copper smelter. Journal of Environmental Quality., 30, 485-492.

Kaladharan, P. Krishnakumar, P.K. Prema, D. Nandakumar, A. Khambadkar,L. and Valsala, K.K. (2011). Assimilative capacity of Cochin inshore waters with reference to contaminants received from the backwaters and the upstream areas. Indian Journal of Fisheries., 58, 75-83.

Kaladharan, P. Prema, D. Valsala, K.K. Leelabhai, K.S. and Rajagopalan, M. (2005). Trends in heavy metal concentrations in sediment, fin fishes and shellfishes, in inshore waters of Cochin, southwest coast of India. Journal of the Marine Biological Association of India., 47,1 – 7.

Karbassi, A.R. (1996). Geochemistry of Ni, Zn, Cu, Pb, Co, Cd, V, Mn, Fe, Al and Ca in sediments of north western part of the Persian Gulf. International Journal Environmental Studies., 54,205-212.

Karbassi, A. R. (1989). Geochemical and magnetic studies of riverine, estuarine and marine sediments. Ph.D. thesis, Mangalore University, India.

Karbassi, A. R. and Amirnezhad, R. (2004). Geochemistry of heavy metals and sedimentation rate in a bay adjacent to the Caspian Sea. International Journal of Environmental Science and Technology., 1 (3), 199- 206.

Karbassi, A. R. and Shankar, R. (2005). Geochemistry of two sediment cores from the west coast of India. International Journal of Environmental Science and Technology., 1 (4), 307-316.

Karbassi, A. R. Nabi-Bidhendi, G. R. and Bayati, I. (2005). Environmental geochemistry of heavy metals in a sediment core off Bushehr, Persian Gulf. Iran. Journal of Environmental Health Science and Engineering., 2 (4), 255-260.

Kheboian, C. and Bauer, C.F. (1987). Accuracy of selective extraction procedures for metal speciation in model aquatic sediments. Analatical Chemistry., 59, 1417-1423

Kiratli, N. and Ergin, M. (1996). Partitioning of heavy metals in surface Black Sea sediments. Applied Geochemistry., 11, 775–788.

Kotoky, P. Bora, B. J. Baruah, J. and Borah, G. C. (2004). Chemical fractionation of heavy metals in soils around oil installations, Assam. Chemical Speciation and Bioavailability.,15(4), 115–126.

Krupadam, R.J. Ahuja, R. Wate, S.R. (2007). Heavy metal binding fractions in the sediments of the Godavari estuary, East Coast of India. Environmental Modeling and Assessment.12, 145–155.

Lakshmanan, P.T. and Nambisan, P.N.K. (1989). Bioaccumulation and Depuration of Some Trace Metals in the Mussel. Perna viridis (Linnaeus)., 43, 131-138.

Lasheen, M.R. and Ammar, N.S. (2008). Speciation of heavy metals in River Nile sediments, Cairo, Egypt. Environmentalist., 29,8-16.

Lee, S. V. and Cundy, A. B. (2001). Heavy metal contamination and mixing process s in sediments from the Humber estuary, Eastern England. Estuarine Coastal and Shelf Science., 53 (5), 619-636.

Leivuori, M. (1998). Heavy metal contamination in surface sediments in the Gulf of Finland and comparison with the gulf of Bothina. Chemosphere., 36,43–59.

Lewis, D.W. (1984). Practical sedimentology, Huchinson Ross publishing Co. Stroudsburg, 229.

Liaghati, T. Preda, M. and Cox, M. (2003). Heavy metal distribution and controlling factors within coastal plain sediments, Bells Creek Catchment, southeast Queensland, Australia. Environment International., 29, 935–948.

Li, X. D. Wai, O. W. H. Li, Y. S. Coles, B. J. Ramsey, M. H. and Thornton, I. (2000). Heavy metal distribution in the sediment profiles of the Pearl River Estuary, South China, Applied Geochemistry., 15, 567–581.

Long, E.R. Bin, C. Smith, S.L. and Calder, F.D. (1995). Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environmental Management.,19, 81–97.

Lopez, P.and Lluch, X. (2000). Sediment geochemistry of a meromictic coastal lagoon, Escibollar(Majorca, Spain). Limnetica., 18, 15-27.

Lopez Sanchez, J. F. Rubio, R. Samitier, C. and Rauret, G. (1996). Trace metal partitioning in marine sediments and sludges deposited off the coast of Barcelona (Spain). Water Research ., 30, 153–159.

Loring, D. H. and Rantala R. T. T. (1992). Manual for the geochemical analyses of marine sediments and suspended matter. Earth-science reviews., 32, 235-283.

MacDonald, D.D. Scott Carr, R. Calder, F.D. Long, E.R. and Ingersoll, C.G. (1996). Development and evaluation of sediment quality guidelines for Florida coastal waters. Ecotoxicology., 5, 253–278.

Mahesh, M. Toms, A. Jayasooryan, K. K. Shylesh Chandran, M. S. Jayasooryan,K. K. Shylesh,C.M. S. and Ramasamy, E. V. (2012). Fractionation of selected metals in the sediments of Cochin estuary and Periyar River, southwest coast of India. Environmentalist., 32,383–393

Makino, T. Kamiya, T. Takano, H. Itou, T. Sekiya, N. Sasaki, K. Maejima,Y. and Sugahara,K. (2007). Remediation of cadmium contaminated paddy soils by washing with calcium chloride: verification of on-site washing. Environmental Pollution., 147,112–119.

Manju, P. Nair. and Sujatha C.H. (2012). Biogeochemical quality assessment of the sediments in Kerala coast, International Journal of Environmental Sciences., 3(1), 707-719.

Manju, P.Nair. and Sujatha,C.H. (2013 a). Environmental Geochemistry of Core Sediment in the Cochin Estuary (CE), India. Research Journal of Chemical Sciences., 3, 65-69.

Manju,P.Nair. and Sujatha,C.H. (2013 b). Biennial metal discrepancy in the surface sediment of Cochin Estuarine System. International Journal of Recent Scientific Research., 4, 1365-1369.

Manju, P. Nair. Akhil, P.S. and Sujatha, C.H. Geochemistry of Core Sediment from Antarctic Region, Research journal of chemistry and environment., 17(2), 8-12 (2013) .

Marchand, C. Lalliet, V. E. Baltzer, F. Alberic, P. Cossa, D. and Baillif, P. (2006). Heavy Metals Distribution in Mangrove Sediments along the mobile coast line of French Guiana. Marine Chemistry ., 98, 1-17.

Marin, B. Valladon, M. Polve, M. and Monaco, A. (1997). Reproducibility testing of a sequential extraction scheme for the determination of trace metal speciation in a marine reference sediment by inductively coupled plasma-mass spectrometry. Analytica Chimica Acta., 342,91–112.

Martin,G.D. Rejomon George, Shaiju, P. Renjith K.R. Muraleedharan Nair, S.M. and Chandramohanakumar,N. (2012). Toxic metals enrichment in the surficial sediments of a eutrophic tropical estuary (Cochin Backwaters, Southwest Coast of India). Scientific World Journal., 2012,1-17.

Martin, R. Sanchez, D. M. and Gutierrez, A. M. (1998). Sequential extraction of U, Th, Ce, La and some heavy metals in sediments from Ortigas River, Spain. Talanta., 46, 1115–1121.

Mathew, M. Mohanraj, R. Azeez, P. A. and Pattabhi, S. (2003). Speciation of heavy metals in bed sediments of wetlands in urban Coimbatore, India. Bulletin of Environmental Contamination and Toxicology., 70, 800-808.

Mcbride, M. B. (1994).Environmental Chemistry of Soils. Oxford University Press, New York.

Menon, N. Balachand, N. and Menon, A.N.(2000).Hydrobiology of Cochin Backwater system-A review.Hydrobiologia.,430,149-183.

Mester, Z. Cremisini, C. Ghiara, E. and Morabito, R. (1998). Comparison of two sequential extraction procedures for metal fractionation in sediment samples. Analytica Chimica Acta., 259, 133–142.

Meyers, P. A. and Lallier-Verge, S. E. (1999). Lacustrine sedimentary organic matter records of Late Quaternary paleoclimates. Journal of Paleolimnology., 21, 345–372.

Modak, D.P. Singh, K.P. Chandra, H. and Ray, P.K. (1992). Mobile and bound forms of trace metals in sediments of the lower Ganges. Water Research., 26(11),1541–1548.

Mohamed, A. W. (2005). Geochemistry and sedimentology of core sediments and the influence of human activities, Qusier, Safaga and Hasighada Harbors, Red sea coast, Egyptian Journal of Aquatic Research., 31 (1), 92-103.

Mohapatra, B. C. and Rengarajan, K. (2000). Heavy metal toxicity in the estuarine, coastal and marine ecosystems of India, Central Marine Fisheries Research Institute Special Publication., 69, 1-121

Mohiuddin,K.M. Zakir, H. M. Otomo, K. Sharmin, S. and Shikazono, N. (2010). Geochemical distribution of trace metal pollutants in water and sediments of downstream of an urban river. International journal of Environmental Science and Technology., 7 (1), 17-28.

Monbet, P.H. (2006). Mass balance of lead through a small macrotidal estuary: the Morlaix river estuary (Brittany, France). Marine Chemistry., 98, 59-80.

Morillo, J. Usero, J. and Gracia, I. (2002). Partitioning of metals in sediments from the Odiel River (Spain). Environment International., 28, 263–271.

Morillo, J. Usero, J. and Gracia, I. (2004). Heavy metal distribution in marine sediments from the southwest coast of Spain. Chemosphere., 55,431–442.

Mossop, K.F. and Davidson, C.M. (2003). Comparison of original and modified BCR Sequential Extraction procedures for the fractionation of copper, iron, lead, manganese and zinc in soil and sediments. Analytica Chimica Acta ., 478, 111-118.

Muller, G. (1969). Index of geoaccumulation in sediments of the Rhine River. Geo J. 2, 108–118.

Muller, P. J. (1997). C/N ratios in Pacific deep sea sediments: Effect of inorganic ammonium and organic nitrogen compound sorbed by clays. Geochimica et Cosmochimica Acta., 41,765–776.

Muniz, P. Venturini, N. and Gomez-Erache, M. (2004). Spatial distribution of chromium and lead in the benthic environment of coastal areas of the Rio De La Plata estuary (Montevideo, Uruguay). Brazilian Journal of Biology., 64(1),103–116.

Nair, C.K. Balchand, A.N. and Namisan, P.N.K. (1991). Heavy metal speciation in sediments of Cochin estuary determined using chemical extraction techniques. Science of the Total Environment., 102,113–128.

Nair, C.K. (1992). Chemical Partitioning of Trace Metals in Sediments of a Tropical Estuary. Ph.D. thesis,Cochin University of Science and Technology.

Nair, C.K. and Balchand, A.N. (1993). Speciation of trace metals in sediments of a tropical estuary. Environmental Geology**.,** 21,96–102.

Nair, S. M. Balchand, A. N. and Nambisan, P. N. K. (1990). Metal concentrations in recently deposited sediments of Cochin backwaters, India, Science of the Total Environment., 97-98, 507–524.

Narwal, R.P. Singh B.R. and Salbu. (1999). Association of cadmium, zinc, copper and nickel with components in naturally heavy metal-rich soils studied by parallel and sequential extractions Commun. Soil Science and Plant Analysis., 30, 1209-1230.

Niffy Benny. (2009) Unravelling a benchmark for sulphur akin in the Cochin Estuarine System. Ph.D Thesis, Cochin University of Science and Technology.

Nolting, R. F. Ramkema, A. and Everaats, J. M. (1999). The geochemistry of Cu, Cd, Zn, Ni and Pb in sediment cores from the continental slope of the Banc d'Arguin (Mauritania). Continental Shelf Research., 19, 665-691.

Ouseph, P.P. (1978). Status report of Marine Pollution along Kerala Coast, Proceedings of the Interdepartmental Seminar on Status of marine pollution in India, Department of Ocean Development, New Delhi.86-105.

Ouseph, P. P. (1987). Heavy metal pollution in the sedimentsof Cochin estuarine system. National seminar on estuarine management, 123-127.

Ouseph, P.P. (1992). Dissolved and particular trace metals in Cochin estuary. Marine Pollution Bulletin., 24, 181.

Padmalal, D. Maya, K. and Seralathan, P. (1997). Geochemistry of Cu, Co, Ni, Zn, Cd and Cr in the surficial sediments of a tropical estuary, southwest coast of India: a granulometric approach. Environmental Geology., 31 (1/2), 85-93.

Panda, D. Subramanian, V. and Panigrahy, R. C. (1995), Geochemical fractionation of heavy metalsin Chilka Lake (East Coast of India) – a tropical Coastal lagoon, Environmental Geology., 26, 199–210.

Paneer Selvam, A. Laxmi Priya,S. Kakolee Banerjee. Hariharan,G. Purvaja,R. and Ramesh,R. (2012) . Heavy metal assessment using geochemical and statistical tools in the surface sediments of Vembanad Lake, southwest coast of India. Environmental Monitoring Assessment.,184, 5899–5915.

Paul, A.C. and Pillai, K.C. (1976). Studies on pollution aspects of Periyar river, Project Report.

Paul, A.C. and Pillai, K.C. (1983). Trace metals in a tropical river environment: speciation and biological transfer. Water, Air and Soil Pollution, 19, 75- 86.

Pekey, H. (2006). Heavy Metal Pollution Assessment in Sediments of the Izmit Bay, Turkey. Environmental Monitoring Assessment., 123, 219-31.

Peng, Y.H. Yang, W.K. Lin, W.H. Lai, T.T. and Chien, C.T. (2009). Supplementary material. Biochemical And Biophysical Research Communications., 382(1) (Export to RIS).

Perdue, E.M. and Koprivnjak, J..F. (2007). Using the C/N ratio to estimate terrigenous inputs of organic matter to aquatic environments. Estuarine Coastal and Shelf Science., 73, 65–72.

Perin, G. Bonardi, M. Fabris, R. Simoncini, B. Manente, S. Tosi, L. and Scotto, S. (1997). Heavy metal pollution in central Venice Lagoon bottom sediments: evaluation of the metal bioavailability by geochemical speciation procedure. Environmental Technology., 18, 593-604 .

Petersen, W. Wallman, K. Li, P. Schroeder, F. and Knauth, H.O. (1995). Exchange of trace elements at the sediment–water interface during early diagenetic processes. Marine and Freshwater Research., 46, 19–26.

Pillai, V.K. and Valsala, K. K. (1995). Seasonal variations of some metals in bivalve mollusc Sunetta scripta from the Cochin coastal waters, Indian Journal of Marine Sciences., 24, 113-115.

Prasad, M.B.K. Ramanathan, A.L. Shrivastav, S.K. and Anshumali, R.S. (2006). Metal fractionation studies in surficial and core sediments in the Achenkovil river basin in India. Environmental Monitoring Assessment., 121,77–102.

Pratheesh, V. B. (2011). Ecotoxic Metal Records and its Degree of Geochemical Symphony in the Niche of Cochin Estuarine System- A Theraptic Perspective. Ph.D. thesis, Cochin University of Science and Thechnology, India.

Praveena, S. M. Ahmed, A. Radojevic, M. Abdullah, M. H. and Aris, A. Z. (2008). Heavy Metals in Mangrove surface Sediment of Mengkabong Lagoon, Sabh: Multivariate and Geo-Accumulation Index Approaxcches. International Journal of Environmental Research., 2 (4), 139-148.

Priju, C. P. and Narayana, A. C. (2007). Heavy and Trace Metals in Vambanad Lake Sediments. International Journal of Environmental Research., 4, 280-289.

Purushothaman, P. and Chakrapani, G.J. (2007). Heavy Metals Fractionation in Ganga River Sediments, India, Environmental Monitoring and Assessment., 132, 475–489.

Quevauviller, (1998). Operationally defined extraction procedures from soil and sediment analysis I. Standardization. Trends in Analytical Chemistry., 17 (5), 289–298.

Rajamani Amma, V. (1994). The distribution and partition of some of the trace metals in sediments and waters on the coastal environment, Ph.D Thesis, Cochin University of Science and Technology.

Rajendran and Kurian, C.V. (1986). Crassostrea madrasensis (Preston)- Indicator of Metal pollution at Cochin backwaters. National Seminar on Mussel Watch, 1, 121-126.

Rainey, M. P. Tyler, A. N. Gilvear, D. J. Bryant, R. G. and Mcdonald, P. (2003). Mapping Intertidal Esturiane Sediment Grain Size Distribution through Airborne Remote Sensing. Remote Sensing Environment., 86, 480-490.

Ramanathan, A.L. Subramanian, V. and Vaithiyanathan, P. (1988). Chemical and sediment characteristics of the upper reaches of Cauvery estuary, East coast of India. Indian Journal of Marine Science.,17, 114–120.

Ramanathan, A.L. Vaithiyanathan, P. and Subramanian, V. (1993). Geochemistry of the Cauvery Estuary, east coast of India. Estuaries., 16, 459–474.

Ramasamy, E. V. Toms, A., Shylesh, C. M. S., Jayasooryan, K. K. and Mahesh, M. (2012). Mercury fractionation in the sediments of Vembanad wetland, west coast of India, Environmental Geochemistry and Health., 34, 575-586.

Ramesh, R. Ramanathan, A.L. James, R.A. Subramanian, V. Jacobsen, S.B. and Holland, H.D. (1999). Rare earth elements and heavy metal distribution in estuarine sediments of east coast of India. Hydrobiologia., 89–99.

Ramesh, R. Subramanian, V. Van Grieken, R. and Van't Dack, L. (1989). The elemental chemistry of sediments in the Krishna river basin, India. Chemical Geology., 74, 331–341.

Ramos, L. Hernandez, L.M. and Gonzalez, M.J. (1994). Sequential fractionation of copper, lead, cadmium and zinc in the soil from or near Donana National Park. Journal of Environmental Quality., 23,50–57.

Ranjitha, Raveendran. and Sujatha, C.H. (2011). Quantization of specific trace metals in bivalve, Villorita cyprinoides Var Cochinensis in the Cochin Estuary. Indian Journal of Geo- Marine Sciences., 40, 424-429.

Rasa, K. Peltovuori ,T. and Hartikainen, H. (2006). Effects of de-icing chemicals sodium chloride and potassium formate on cadmium solubility in a coarse mineral. Soil Science and Total Environment., 366,819–825.

Ratheesh Kumar, C . S. Joseph, M. M. Gireesh Kumar, T .R. Renjith, K.R. Manju, M.N. and Chandramohanakumar, N.(2010) .Spatial variability and contamination of heavy Metals in the inter-tidal systems of a tropical environment. International journal of environmental research., 4(4), 691–700.

Ray, A.K. Tripathy, S.C. Patra, S. and Sarma, V.V. (2006). Assessment of Godavari estuarine mangrove ecosystem through trace metal studies. Environmental International., 32,219–223.

Redfield, A.C. B.H. Ketchum, and Richards,F.A. (1963). The influence of organisms on the composition of sea-water, In Hill N (Ed), In the Sea, second ed. Wiley, New York, 26-77.

Renjith, K. R. and Chandramohanakumar, N. (2009) . Distribution of heavy metals in the surficial sediments of a complex micro-tidal estuarine system in southwest India. Research journal of chemistry and environment., 13(2), 34–44.

Remani, K.N. Saraladevi, K. Venugopal, P. and Unnithan, R.V. (1983). Indicator organism of pollution in Cochin backwaters, Mahasagar Bulletin of National Institute of Oceanography., 16, 199-207.

Ridgway, J. and Shimmield, G. (2002). Estuaries as repositories of historical contamination and their impact on shelf seas. Estuarine Coastal and Shelf Science., 55, 903–928.

Robin, R.S. Pradipta, R. Muduli, K. Vishnu Vardhan, K.R. Abhilash, A. Paneer Selvam, B. Charan Kumar, and Balasubramanian. (2012). Assessment of Hydrogeochemical Characteristics in an Urbanized Estuary using Environmental Techniques, Geosciences., 2, 81-92.

Rokade, M.A. (2009). Heavy Metal Burden in Coastal Marine Sediments of North West Coast of India Related to Pollution. Ph.D. thesis, University of Mumbai.

Sahu, K.C. and Bhosale, U. (1991). Heavy metal pollution around the island city of Bombay, India. Part I: Quantification of heavy metal pollution of aquatic sediments and recognition of environmental discriminates. Chemical Geology., 90,263–283.

Sahuquillo, A. Rigol, A. and Rauret, G. (2003). Overview of the use of leaching/extraction tests for risk assessment of trace metals in contaminated soils and sediments. Trends in Analytical Chemistry., 22(3),152-159.

Salomon, D. Saurat, J.H. and Meda, P. (1988).Cell-to-cell communication within intact human skin. Journal of Clinical Investigation., 82, 248–254.

Salomons,W. and Fo¨rstner,U. (1984). Metals in the hydrocycle, 11. Springer, Heidelberg, 166–167.

Salomons, W. and Stigliani, W.M. (1995). Biogeodynamics of Pollutants in Soils and Sediments: Risk Assessment of Delayed and Non-Linear Responses Springer-Verlag, Heidelberg, Germany .

Sankaranarayanan, V. N. Jayalakshmy, K. V. and Tresiamma J. (1998). Particulate trace metals in Cochin backwaters: distribution of seasonal indices. Indian Journal of Fisheries., 45 (3), 321- 329.

Santamaria-Fernandez, R. Cave, M.R. and Hill, S.J. (2005) Trace metaldistribution in the Arosa estuary (N.W. Spain): the application ofa recently developed sequential extraction procedure for metalpartitioning. Analytica Chimica Acta ., 557(1–2),344–352.

Santos, J.C. Beltra´n R. and Go´mez, J.L. (2003) Spatial variations of heavy metals contamination in sediments from Odiel river (Southwest Spain). Environmental International., 29,69–77.

Saraladevi, K. Venugopal, P. Remani, K. N. Lalitha, S. and Unnithan, R. V. (1979). Hydrographic features and water quality of Cochin backwaters in relation to industrial pollution, Indian Journal of Marine Sciences., 8,141-145.

Saraladevi, K. and Venugopal P. (1989). Benthos of Cochin backwaters receiving industrial effluents. Indian Journal of Marine Sciences., 18, 165-169.

Saraladevi, K. Venugopal, P. and Sankaranarayanan, V.N. (1992). Organic carbon in the sediments of the lower reaches of Periyar River. Journal of Fisheries Association., 22, 61-68.

Seralathan, P. (1987). Trace element geochemistry of modern deltaic sediments of the Cauvery River, east coast of India. Indian Journal of Marine Sciences., 16, 235–239.

Shajan, K. P.(2001) . Geochemistry of bottom sediments from a river-estuary- shelf mixing zone on the tropical southwest coast of India. Bulletin of the geological survey of Japan., 52, 371–382.

Sharma, S.K. and Subramanian, V. (2010). Source and distribution of trace metals and nutrients in Narmada and Tapti river basins, India. Environmental Earth Science., 61, 1337–1352.

Shibu, M. P. Balchand, A. N. and Nambisan, N. P. K. (1990). Trace metal speciation in a tropical estuary: significance of environmental factors. Science of the Total Environment., 97/98, 267-287.

Shibu, M. P. Jacob Chacko, and Balchand, A. N. (l995). Speciation and estuarine modification of zinc during transport in a tropical fluvial environment. Toxicological and Environmental Chemistry., 47, 23-36.

Shiowatana, J. McLaren, R.G. Chanmekha, N. and Samphao, A. (2001). Fractionation of arsenic in soil by a continuous-flow sequential extraction method, Journal of Environmental Quality., 30, 1940-1949.

Singh, S. K. and Subramanian, V.(1984). Hydrous Fe and Mn oxides-scavengers of heavy metals in the aquatic environment, CRC Critical Reviews in Environmental Science and Technology .,14(1), 33–90.

Singh, V.K. Singh, K.P. and Mohan, D. (2005).Status of heavy metals inwater and bed sediments of the River Gomati—a tributary of Ganga River, India. Environment Monitoring Assessment., 105,43–67.

Spencer, K.L. and MacLeod, C.L. (2002).Distribution and partitioning of heavy metals in estuarine sediment cores and implications for the use of sediment quality standards. Earth System Sciences., 6,989–998.

Staelens, N. Parkpian, P. and Polprasert, C. (2000). Assessment of metal speciation evolution in sewage sludge dewateredin vertical flow reed beds using a sequential extraction scheme. Chemical Speciation and Bioavailability., 12, 97–107.

Stephens, S.R. Alloway, B.J. Parker, A. Carter, J.E. and Hodson, M.E. (2001). Changes in the leachability of metals from dredged canal sediments during drying and oxidation. Environmental Pollution., 114, 407-413.

Subramanian, V. Van't Dack, L. and Van Grieken, R. (1985). Chemical composition of river sediments from the Indian sub-continent. Chemical Geology., 48, 271–279.

Subramanian, V. Jha, P.K. and Van Grieken, R. (1988). Heavy metals in the Ganges Estuary. Marine Pollution Bulletin., 19, 290–293.

Subramanian, V. Ramanathan, A.L. and Vaithyanathan, P. (1989). Distribution and fractionation of heavy metals in the Cauvery Estuary, India. Marine Pollution Bulletin., 20, 286–290.

Subramanian,V. (1993). Phosphorus, silicon, and some trace contaminants in the Ganges Estuary. Estuaries., 16, 453–458.

Sudhanandh, V.S. Udayakumar, P. Ouseph, P.P. Amaldev, S. and Narendra Babu, K. (2011). Dispersion and Accumulation Trend of Heavy Metals in Coastal and Estuarine Sediments and its Textural Characteristics, a case Study in India. Journal of Human Ecology., 36, 85-90.

Sugirtha Kumar, P. and Patterson Edward, J.K. (2009). Assessment of metal concentration in the sediment cores of Manakudy estuary, southwest coast of India. Indian Journal of Marine Science., 38(2),235–248.

Sulivan, P. and Taylor, K.G. (2003). Sediment and pore water geochemistry in a metal contaminated estuary, Dulas Bay, Anglesey. Environmental Geochemistry and Health., 25,115–122.

Sundararajan, M. Usha-Natesan. Babu, N. and Seralathan, P. (2009). Sedimentological and Mineralogical investigation of beach sediments of a fast prograding cuspate foreland (Point Calimere), Southeast coast of India. Research Journal of Environmental Sciences., 3 (2), 134-148.

Sundararajan, M. and Natesan, U. (2010). Geochemistry of core sediments from Mullipallam creek, South East coast of India the southeast coast of India. Environmental Earth Science., 61(5),947-961.

Sutherland, R.A. Tack, F.M.G. Tolosa, C.A. and Verloo, M.G. (2000). Operationally defined metal fractions in road deposited sediment, Honolulu, Hawaii. Journal of Environmental Quality., 29, 1431-1439.

Svete, P. Milacic, R. and Pihlar, B. (2001).Partitioning of Zn, Pb and Cd inriver sediments from a lead and zinc mining area using the BCR three-step procedure. Journal of Environmental Monitoring., 3,586–590.

Szefer, P. Glassby, G.P. and Pempkowiak, J. (1995). Extraction studies of heavy metal pollutants in surficial sediments from the southern Baltic Sea off Poland. Chemical Geology., 120, 111–126.

Tack, F.M. and Verloo, M.G. 1995. Chemical speciation and fractionation in soil and sediment heavy metal analysis: a review. International Journal of Environmental Analytical Chemistry., 59, 225–238.

Tack, F.M.G. and Verloo, M.G. (1999).Single extraction versus sequential extraction for the estimation of heavy metal fractions in reduced and oxidized dredged sediments. Chemical Speciation and Bioavailability., 11, 43–50.

Takarina, N. D. Browne, D. R. and Risk, M. J. (2004). Speciation of heavymetals in coastal sediments of Semarang, Indonesia. Marine Pollution Bulletin., 49, 854–874.

Tessier, A.P. Campbell, G.C. and Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. Analytical Chemistry., 51, 844–851.

Thomson, K. T. (2002). Economic and social issues of biodiversity loss in Cochin backwaters, Technical Report, Cochin University of Science and Technology, Cochin, India.

Tokaliog˘lu, S. Kartal, S. and Latif, E. (2000). Determination of heavy metals and their speciation in lake sediments by flame atomic absorption spectrometry after a four-stage sequential extraction procedure. Analytica Chimica Acta., 413, 33–40.

Tomlinson, D.L. Wilson, J.G. Hariis, C.R. and Jeffrey, D.W.(1980). Problems in the Assessment of Heavy Metal Levels in Estuaries and the Formation of a Pollution Index, Helgolander Meeresunters., 33, (1-4), 566-575.

Tuncer, G. Tuncel, G. and Balkas, T.I. (2001). Evolution of metal pollution in the Golden Horn (Turkey) sediments between 1912–1987. Marine Pollution Bulletin., 42 (5), 350–360.

Turekian, K.K. and Wedepohl, K.H. (1961). Distribution of the elements in some major units of the earth crust. Bulletins of Geological Society of America., 72, 175-192.

Turki, A. J. (2007). Study on the Speciation and Relative Mobility of Some heavy Metals in the Sediments of Al Shabab Lagoon. Report ,King Abdul Aziz University. Scientific Research Council, Research Grant No. 426/254.

Turner, A. and Olsen, Y.S. (2000). Bioavailability of trace metal in contaminated estuarine sediments: A comparison of chemical and enzymatic extractants. Estuarine, Coastal and Shelf Sciences., 51,717-728.

Tyson, R.V.(1995). Sedimentary Organic Matter: Organic Facies and Palynofacies. Chapman and Hall, London.

Usero, J. Gamero, M. Morillo, J. and Gracia, I. (1998). Comparative study of three sequential extraction procedures for metals in marine sediments. Environment International., 24, 478–496.

Velimirović, D.S. Mitić, S.S. Tošić, S.B. Pavlović, A.N. and Stojković, M.D. (2012). Determination of the content of some trace elements in particular samples of grains, flours and breads by ICP-OES. Oxidation Communication.,35(1), 160–171.

Venugopal, P. Devi, K.S., Remani, K.N., Unnithan, R.V. (1982). Trace metal levels in the sediments of the Cochin backwaters. Mahasagar., 15, 205–214.

Weis, D. A. Callaway, J. C. and Gersberg, R. M. (2001). Vertical accretion rates and heavy metal chronologies in wetland sediments of the Tijuana Estuary. Estuaries., 24 (6A), 840- 850.

Wolters, E.C. Huang, C.C. and Clark, C. (1989). Positron emission tomography in manganese intoxication. Annals of Neurology., 26, 647-651.

Wu, J. Laird, D. A. and Thompson, M. L. (1999).Sorption and desorption of copper on soil claycomponents, Journal of Environmental Quality., 28, 334–338.

Yuan, C.G. Shi, J.B. He, B. Liu, J.F. Liang, L.N. and Jiang, G.B. (2004). Speciation of heavy metals in marine sediments from the East China Sea by ICP-MS with sequential extraction. Environment International., 30,769–783.

Zakir, H.M. Shikazono, N. and Otomo, K. (2008). Geochemical distribution of trace metals and assessment of anthropogenic pollution in sediments of Old Nakagawa River, Tokyo, Japan. American Journal of Environmental Sciences., 4(6),661-672.

Zhang, J. and Liu, C. L. (2002). Riverine composition and estuarine geochemistry of particulate metals in China -Weathering features, anthropogenic impact and chemical fluxes. Estuarine Coastal Shelf Sciences., 54(6), 1051–1070.

Zhai, M. Kampunzu, H. A. B. Modisi, M. P. and Totolo, O. (2003). Distribution of heavy metals in Gaborone urban soils (Botswana) and its relationship to soil pollution and bedrock composition. Environmental Geology., 45, 171–180.

Zourarah, B. Maanan, M. Carruesco, C. Aajjane, A. Mehdi, K. and Conceicao Freitas, M. (2007). Fifty year sedimentary record of heavy metal pollution in the lagoon of Oualidia (Moroccan Atlantic coast). Estuarine Coastal Shelf Sciences., 72, 359–369.

****

PUBLICATIONS

- **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.
- **Manju. P. Nair.,** P. S. Akhil, C.H **.**Sujatha 2013.Geochemistry of Core Sediment from Antarctic Region. *Research journal of chemistry and environment* 17(2), 8-12.
- **Manju.P.Nair** and Sujatha.C.H. 2013 Environmental Geochemistry of Core Sediment in the Cochin Estuary (CE). *Research Journal of Chemical Sciences* 3(4), 65-69.
- **Manju.P.Nair** and Sujatha. C.H. 2013 Biennial Metal Discrepancy in the Surface Sediment of Cochin Estuarine System. *International Journal of Recent Scientific Research* 4(9) 1365- 1369.
- 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 Sciences. 122(6) 1557-1570.
- **Manju.P.Nair** and Sujatha. C.H.2013 Iron fractionation in the Sediments of Kerala Coast. *International Journal of Green and Herbal Chemistry* 2(3) 555-561.
- **Manju.P.Nair** and Sujatha. C.H. 2013 Fractionation of Phosphorus in the Sediments of Kerala Coast. *Journal of Chemical, Biological and Physical Sciences* 3(3) 2274-2278.

- **Manju.P.Nair** and Sujatha.C.H**.** 2013 Organochlorine Pesticide residues in the sediments of Kerala coast. *Global Journal of Applied Environmental Sciences* 3(1), 31-40.
- **Manju.P.Nair** and Sujatha. C.H. 2013 Nutrient Dynamics in the Sediments of Kerala Coast. *International Journal of Environmental Sciences* 3(5) 1562-156.
- **Manju.P.Nair** and Sujatha. C.H. 2012. Biogeochemical quality assessment of the sediments in Kerala coast. *International Journal of Environmental Sciences.* 3(1), 707-719.
- **Manju.P.Nair** and Sujatha. C.H. Metal Distribution and Fractionation Profile of Surface Sediment in the Specific Zones of CES. *Biogeochemistry.* **(**Communicated).
- **Manju.P.Nair** and Sujatha. C.H. Fractionation Profile of Metal in the Core Sediments of CES. *Environmental Sciences and Technology.* **(**Communicated).

****