DYNAMICS OF TRACE METALS, RARE EARTH ELEMENTS AND NUTRIENTS IN COCHIN ESTUARY, SOUTH WEST COAST OF INDIA

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By

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JUNE, 2017

Certificate

This is to certify that the thesis entitled **"DYNAMICS OF TRACE METALS, RARE EARTH ELEMENTS AND NUTRIENTS IN COCHIN ESTUARY, SOUTH WEST COAST OF INDIA"** *is an authentic record of the research carried out by* **Mrs. LALLU K R** *(Reg: No: 4113), under my supervision in CSIR-National Institute of Oceanography, Regional centre, Cochin- 18, in partial fulfillment of the requirement for the degree of Doctor of Philosophy in Faculty of Marine Sciences, Cochin University of science and Technology and that no part of this thesis has previously formed the basis for the award of any other degree, diploma or associateship in any university.*

I also certify that all the relevant corrections and modifications suggested by the audience during the pre-synopsis seminar and recommended by the doctoral committee of the candidate have been incorporated in this thesis.

Kochi -18
June, 2017

Dr. P. S. Parameswaran
(Supervising Guide)

DECLARATION

I hereby declare that the thesis entitled " **DYNAMICS OF TRACE METALS, RARE EARTH ELEMENTS AND NUTRIENTS IN COCHIN ESTUARY, SOUTH WEST COAST OF INDIA** *" submitted by me is an authentic record of the research carried out by me, under the supervision of* ***Dr. P. S. Parameswaran****, Chief Scientist, CSIR - National Institute of Oceanography, Regional Centre, Kochi- 18, in partial fulfillment of the requirement for the degree of Doctor of Philosophy in Faculty of Marine Sciences, Cochin University of science and Technology and that no part of this thesis has been presented before for any other degree diploma or associateship in any university.*

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Lallu K R

Dedicated to My Dear Father, whose advice urged
me to grasp his dream of my Doctoralship

PREFACE

Estuarine and coastal areas are complex and dynamic aquatic environment. Physical, chemical, geological and biological interactions between freshwater and salt water systems can have profound influence on the transport and fate of materials (nutrients, trace metals and rare earth elements) in the estuary. The distribution of nutrients and elements through complex processes of material exchange within these aquatic environments are also influenced by anthropogenic inputs. Now-a-days, such influences are more apparent in estuaries and surrounding coastal areas, than in open ocean, due to intense human activities.

Over the past several decades, there has been rapid increase in human settlement along coastal regions / estuaries of the world. Consequently, many estuarine systems have been affected by the serious environmental deterioration and increased encroachment. Estuaries serve as important interfaces between rivers and the coastal sea, where inputs of terrestrial materials can be significantly modified and recycled before entering the coastal zone. A greater knowledge of the biogeochemical cycling of metals and nutrients in estuaries, such as transport, fate and transformation of chemical substances, is important to understand the intensity of the perturbations in these regions.

Understanding of the input/export fluxes of nutrients and trace metals on coastal seas requires monitoring of their inputs through rivers and measuring their transport across the inlet to the coastal seas. However, while it is relatively straightforward to monitor a river's material flux to its receiving estuary, estimation of the subsequent material flux to the coastal zone is much more difficult, owing to the complex biogeochemical processes involved and varied intensity.

Freshwater input in to a tidal system can bring about substantial changes in the water quality (salinity, nutrients, trace metals and plankton) even on short time scales. Temporal (intertidal and intra-tidal), spatial and seasonal variations in nutrients and trace metals are found to be appropriate to explain the fate and transport of nutrients and trace metals in an ecosystem. Moreover, fractionation (physical and chemical) of sediments for their different heavy metal species will be an appropriate step to estimate their dynamics in the estuarine and coastal region. Likewise, changes in salinity, freshwater input, currents and tides are very useful to explain the physical behavior and transport properties of these materials in an estuary. Redox potential can successfully provide the oxidizing or reducing conditions prevailing in the estuary. The mineralogy and texture of the estuary adds to the geochemical processes in the sediments of both estuarine and coastal areas.

Cochin estuary is one of the largest tropical estuaries along the southwest coast of India sustaining rich bio-resources. There are several studies delineating the environmental changes in the Cochin estuary caused by anthropogenic activities. However, no studies have so far accomplished quantification of material transport across the estuary. This is the first attempt to quantify the fluxes of nutrients and heavy metals across the Cochin estuary.

Scheme of Presentation

Following an introductory chapter, the thesis is divided into the following six chapters.

Chapter II. Hydrography and nutrient fluxes
Chapter III. Fractionation of trace metals in sediment
Chapter IV. Fractionation of rare earths in sediment
Chapter V. Input and export fluxes of trace metals in the Cochin Estuary

Chapter VI. Summary and Conclusion.

Chapter I provides information on the importance of fractionation and flux studies in coastal marine regions. It also elaborates on the objectives and scope of the study. Chapter 2 deals with the dynamics and fluxes of nutrients through Cochin estuary. It also explains the inter-tidal, intra-tidal and seasonal changes in nutrients at different locations in the Cochin estuary.

Chapter 3 discusses the fractionation of heavy metals in exchangeable, carbonate bound, reducible, organic bound and residual phases and the metal availability to biota. Chapter 4 covers the fractionation of rare earth elements and its depositional characteristics.

Chapter 5 explains the partitioning of heavy metals between dissolved and particulate phases in from 6 major rivers and Cochin estuary and it also discusses the heavy metal fluxes through rivers into Cochin estuary and the net transport to the adjacent coastal sea. Chapter 6 provides the summary and conclusion of the thesis.

CONTENTS

Abbreviations

ADP	-	Acoustic Doppler Profiler
ADCP	-	Acoustic Doppler Current Profiler
APDC	-	Ammonium Pyrrolidine dithiocarbamate
Al	-	Aluminium
BIS	-	Bureau of Indian Standard
CE	-	Cochin Estuary
CH_3COOH	-	Acetic acid
CCME	-	Canadian Council of Ministers of the Environment
Cr	-	Chromium
Cd	-	Cadmium
Co	-	Cobalt
Cu	-	Copper
Ce	-	Cerium
CeO_2	-	Cerium dioxide
C/g	-	Carbon per gram
cm	-	Centimeter
CTD	-	Conductivity Temperature Depth Profiler
DO	-	Dissolved oxygen
DIN	-	Dissolved Inorganic Nitrogen
Dy	-	Dysprosium
DDDC	-	Diethyl ammonium diethyl dithiocarbamate
E	-	East
Eu	-	Europium

Er - Erbium

Fe - Iron

Fr - Fraction

Gd - Gadolinium

HCl - Hydrochloric acid

H_2O_2 - Hydrogen peroxide

HNO_3 - Nitric acid

HF - Hydrofluoric acid

$HClO_4$ - Perchloric acid

Hf - Hafnium

HREE - Heavy Rare Earth Elements

Ho - Holmium

Hg - Mercury

hr - Hour

HHW - Highest High Water

IUPAC - International Union of Pure and Applied Chemistry

ICP-MS - Inductively Coupled Plasma-Mass Spectrometer

ICP-OES - Inductively Coupled Plasma Optical Emission Spectrometer

kg - Kilogram

kg/day - Kilogram per day

kg/m^3 - Kilogram per meter cube

km - Kilometer

KC - Kerala Coast

km^2 - Kilometre square

LREE - Light Rare Earth Elements

La - Lanthanum

Lu - Lutetium
MREE - Middle Rare Earth Elements
ml - Millilitre
m/kg - Milligram per kilogram
mg/g - Milligram per gram
m^2 - Meter square
m^3 - Meter cube
mm - Millimeter
m^3/s - Meter cube per second
m/s - Meter per second
m^3s^{-1} - Meter cube per second
m^3d^{-1} - Meter cube per day
mg - Milligram
mg/m^3 - Milligram per meter cube
Mg - Magnesium
mgC/g - Milligram carbon per gram
mg/l - Milligram per litre
ml/l - Millilitre per litre
Mn - Manganese
NF - Normalisation Factor
N - Nitrogen
NH_4-N - Ammonia- nitrogen
N - North
Ni - Nickel
Nb - Niobium
Nd - Neodymium
nm - Nanometer
NO_2^- - Nitrite
NO_3^- - Nitrate

^{o}C	-	Degree Celsius
OC	-	Organic Carbon
OMZ	-	Oxygen Minimum Zone
OH	-	Hydroxide
Pb	-	Lead
Pr	-	Praseodymium
P	-	Phosphorus
PO_4^{3-}	-	Phosphate
PELs	-	Probable Effect Levels
ppm	-	Parts per million
REE	-	Rare Earth Elements
rpm	-	Rotation per minute
RAC	-	Risk Assessment Code
Si	-	Silicon
SiO_4^{4-}	-	Silicate
Sn	-	Tin
SQG	-	Standard Sediment Quality Guidelines
SEP	-	Sequential Extraction Procedure
Sc	-	Scandium
Sm	-	Samarium
SPM	-	Suspended Particulate Matter
S	-	South
TOM	-	Total Organic Matter
TEL	-	Threshold Effect Levels
Tb	-	Terbium
Tm	-	Thulium
V	-	Vanadium
W	-	West

WHO - World Health Organization
WRSPM - World Rivers Average Suspended Particulate Matter
wt. - Weight
XRD - X -ray Diffraction
Yb - Ytterbium
Y - Yttrium
Zn - Zinc
Zr - Zirconium
μg/g - Micro gram per gram
μg/l - Micro gram per litre
μg/kg - Micro gram per kilogram
μl - Micro litre
μm - Micro meter
μmol/g - Micro mole per gram
μmol/l - Micro mole per litre
β - Beta
r - Gamma
μ - Micron
% - Percentage

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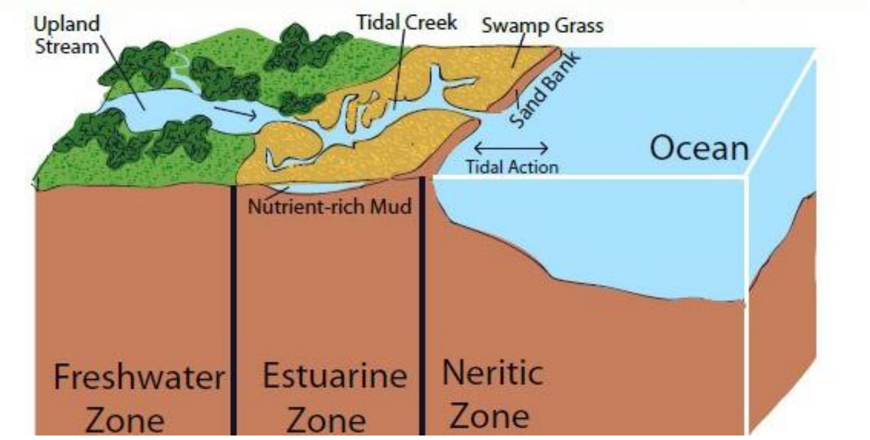
Chapter 1

GENERAL INTRODUCTION

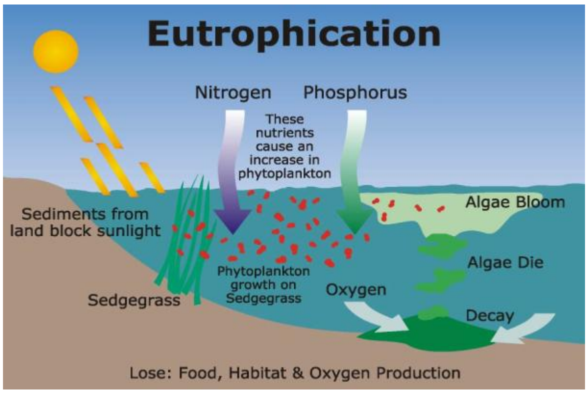
Contents

1.1 INTRODUCTION

An **estuary** is a partially enclosed coastal body of brackish waters, with one or more rivers or streams flowing into it and having a free connection to the open sea. Estuaries serve as important interfaces between rivers and the coastal ocean, where inputs of terrestrial materials get significantly modified and recycled before entering the coastal waters. The dominant feature controlling the distribution, speciation and reactivity of chemical components within estuaries is the mixing of fresh and saline waters. Coastal waters form a multi-dimensional system wherein the dynamic processes are rarely in equilibrium. Unlike the open ocean where nutrients are mainly supplied from subsurface waters, estuarine and coastal systems receive nutrient load from river and land run-off, atmospheric deposition and benthic remineralization. This makes coastal systems highly productive as compared to open oceans. Although the ocean marginal area comprising of estuaries, coastal and continental shelves occupy only about 10% of the global oceanic area, between 30% and 50% of the marine primary production and almost 90% of the fishery production are reported from these regions (Romankevich, 1984; Walsh, 1988, 1991).



The exponential development of human activities during the last century has caused a negative impact on all environmental compartments, including aquatic environments. However, the impact of these changes in the estuarine system on the coastal waters, are still not fully known. Nutrient enrichment (eutrophication) is perhaps the most widespread problem in estuaries around the world (Howarth et al., 2000, 2002).



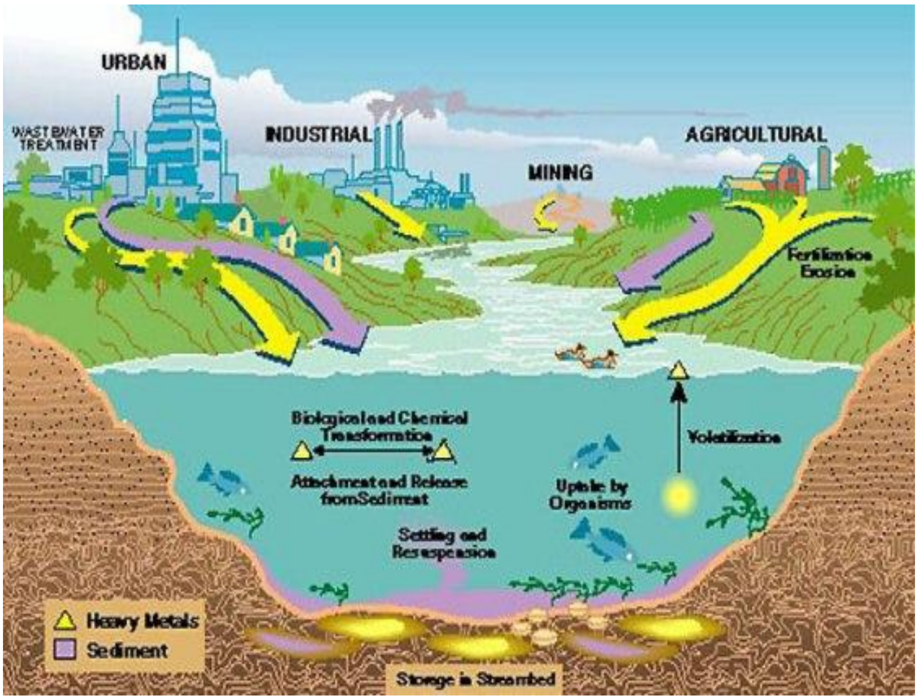
Nutrients, especially nitrogen, have increased in rivers and estuaries resulting in harmful algal blooms with consequent reduction in dissolved oxygen in those waters. Understanding the behavior of nutrients and hydrographic conditions in estuaries has important implications for global nutrient budgets and for controlling eutrophication of these systems (Pereira et al., 2001; Shen et al., 2003). Estuarine systems are capable of significantly modifying the flux of nutrients from land to sea (Falco et al., 2010). The effectiveness of the estuarine retention/transport depends at least in part on the geography of the estuary (Jickells et al., 2014) and internal nutrient cycling (Longphuirt et al., 2015).

Industrially important trace metals and their compounds find a variety of uses in different fields of human endeavour, including agriculture, engineering, electronic equipments, health, hygiene, etc. The increasing use of trace metals in everyday life is generally viewed with great concern as it has been established that most of these trace metals are potentially toxic to aquatic organisms.

Metals are introduced into the water column under different forms: particulate, colloidal and dissolved (Kennish, 2002). Upon entering the environment, many of these pollutants are subjected to a variety of physical, chemical, geological and biological processes, bringing about their disintegration or sometimes, even ultimate removal. Persistent chemicals that do not breakdown under above conditions remain in the water columns, leading to serious environmental and human health problems (Shibu, 1992).

In estuaries, trace metals generally exist in two phases: *i.e.*, in the dissolved phase in the water column and also in the particulate phase adsorbed on to sediments. The behaviour of trace metals in the aquatic environment is strongly influenced by adsorption to organic and inorganic particles. The dissolved fraction of the trace metals may be transported through the water column *via* the processes of advection and dispersion, while the adsorbed particulate fraction may be transported with the sediments, which are governed by sediment dynamics.

The partition of a trace metal between its dissolved and adsorbed particulate fractions depends on the physical and chemical characteristics of the suspended particles, together with various ambient conditions, such as salinity, pH, type and concentration of dissolved organic matter (Turner et al., 2001; Turner and Millward, 2002). Resuspension of contaminated bed sediments caused by strong tidal currents or dredging operations may release a significant amount of trace metals into the water column, and this desorption of toxic metal contaminants from their particulate phase will have pronounced impact on the aquatic environments and ecosystems.



The rare earth elements (REE) of sediments and sedimentary rocks naturally reflect the mineral content of these deposits and reveal the process of their formation/incorporation. REE contents of most sediments and sedimentary rocks are similar in the relative abundance of individual elements although they differ in absolute concentration (Balashov et. al., 1964 and Spirn, 1965). REE are considered as useful tracers of various geological and oceanographic processes (Piper, 1974, Murray and Leinen, 1993). Concentration of these elements in sediments are influenced by (1) particulate supply from the adjacent land masses (Piper, 1974, McLennan, 1989; Nath et al., 2000; Hannigan et al., 2010), (2) biogenic sedimentation from overlying seawater (Murphy and Dymond, 1984) and (3) oxygenation conditions in the water column (Liu et al., 1988; Pattan et al., 2005).

Physical, chemical and biological processes within an estuary vary over a broad spectrum, both in space and time (Morris, 1990; Dyer, 1991). Spatial variations depend on the topography of the estuary, on the gradients in salinities and on the fine sediment concentration (Nair et al., 1992). While annual and seasonal variations depend on the climatological factors, fortnightly and diurnal variations are caused by tidal actions (Holmes, 1986; Vale, 1990).

An estuary provides a particularly unique chemical environment for element cycling (Burton and Liss, 1976; Elderfield, 1978; Morris et al., 1982; Martin and Whitfield, 1983). Within an estuary, the suspended matter carried by rivers is subjected to varying salinity and pH, often causing (1) precipitation of the suspended particles by flocculation (Sholkovitz, 1976, 1978; Sholkovitz and Copland, 1981) and (2) chemical exchange between the suspended sediment and estuarine waters that changes the chemistry of both (Vander Weijden et al., 1977). Gradients in the chemical environment, *e.g.*, in the salt or oxygen content, may change the partitioning of trace metals and their transport mechanisms (Carey, 1990). Estuarine physicochemical gradients, biogeochemical processes, and organism physiology are jointly co-ordinating the fate and potential effects of metals in estuaries (Machado et al., 2016).

The Cochin estuary is one of the largest tropical estuarine systems along the west coast of India, spreading over 250km^2 (10°10' N, 76°15'E in the north to 09° 30'N, 76°25'E in the south), and providing a good nursery ground for a wide variety of flora and fauna. Cochin estuary has unique topography; oriented parallel to the coastline and connected to the sea through 2 inlets at Munambam and Kochi (Madhupratap et al., 1987; Srinivas et al., 2004). The Cochin barmouth is 450 m wide and is dredged to a depth of 10-13 m through which tides act within the estuary. Major portion of the estuary has a depth in the range of 2-7 m. The condition of the substrata is predominantly muddy (Balachandran, 2001). The freshwater runoff into the estuary is primarily contributed by the rivers Periyar, Pampa, Achankovil, Manimala, Meenachil, and Muvattupuzha. The river runoff is high during wet season (June - September) characterized by Indian Summer Monsoon (ISM). This period is followed by a moderate runoff period (October - December), and the rest of the year is relatively dry period. The hydrography of the Cochin estuary is greatly influenced by tides, freshwater water flow and estuarine circulation (Revichandran et al., 2011; Shivaprasad et al., 2013). The flushing timescale of the estuary ranged from 1 to 2.5 days during the wet season and were 8.7 days during the dry season (Vinita et al., 2015a). The flow characteristics and the mixing pattern of Cochin estuary are very peculiar and have great influence in the bio-resources, transportation, waste disposal and plankton dynamics (Balachandran et al., 2005; Sooria et al., 2015).

A number of multidisciplinary studies have been undertaken in the Cochin estuary during past several decades. The hydrography of the estuary was investigated by several investigators including Sankaranarayanan and Qasim, 1969; Qasim and Gopinathan, 1969; Sankaranarayanan et al., 1986; Madhupratap et al., 1987; Udayavarma et al., 1981; Gopalan et al., 1983; Chandramohan, 1989; Balachandran, 2001; Srinivas et al., 2003, 2005; Revichandran et al., 2011. The information available includes spatial and seasonal distributions of temperature, salinity, dissolved oxygen, pH, alkalinity, and suspended solids of surface and bottom waters of the region. Recent studies reported the seasonal stratification, tidal intrusion length and spatial tidal asymmetry in Cochin estuary (Shivaprasad et al., 2013; Bincy et al., 2013; Vinita et al., 2015b).

Qasim and Madhupratap, 1979; Nair et al., 1975; Madhupratap et al., 1977; Saraladevi, 1979; Pillai, 1977; Kurup, 1983; Madhu et al., 2007, 2010; Jyothibabu et al., 2006; Vineetha et al., 2015 and several others have investigated the biological characteristics of the estuary in detail. Recent studies reveal the seasonal dynamics of plankton food web, trophic status and the response of autotrophic pico- and nano plankton to summer monsoon (Sooria et al., 2015; Rajaneesh et al., 2015 Arya et al., 2016). The diurnal variations in bacterial and viral abundance in Cochin estuary has been studied (Parvathy et al., 2015). The microbial diversity in the Cochin estuary and their effect on nitrogen fixation and nitrification has been reported recently (Vipin et al., 2015; Jabir et al., 2017).

The greater awareness on the potential health hazards due to the industrial and domestic effluents added to this estuary prompted several researchers to study on the pollution aspects, its carrying capacity, disruption in the life cycle of organisms (Unnithan et al., 1977; Azis and Nair, 1981, Maheswari et al., 2006; Harikumar et al., 2009; Laluraj 2009; Sreekanth et al., 2015; Ramaswamy et al., 2017), morphological changes (Dineshkumar et al., 2014), destruction of natural habitat (Gopalan et al., 1983; Kurup, 1992; Shibu et al., 1990; Sujatha, 1999; Balachandran et al., 2003, 2006), diversity of bio-resources (Jiya et al., 2011; Priju et al., 2007), salt water intrusion (Shivaprasad et al., 2013; Vinita et al., 2015a), flow restrictions (Balachandran et al., 2005), environmental impact of dredging (Balchand et al., 2000), eutrophication and changes in biogenic properties (Gopinathan et al., 1984; Balachandran, 2001; Nair et al., 2010; Gupta et al., 2009; Martin et al., 2011, 2013), changes in the quality of organic matter (Renjith et al., 2013; Gireeshkumar et al., 2013a), over exploitation and declining resources (Balchand, 2001; Menon et al., 2000; Balchandran et al., 2003, 2005, 2008b; Martin et al., 2011) *etc*. The above studies clearly stressed the need for the conservation of the ecosystem for better aquatic life. Rapid industrialization along the estuarine/riverine coasts during the past few decades and the resultant increase in human settlements have led to emergence of several large cities in these areas. These developments and the consequent high pollution load released into the estuary necessitate a critical evaluation of the ecosystem with a view to suggest appropriate remedial measures for its mitigation.

1.2 AIM AND SCOPE OF THE STUDY

A greater knowledge of the biogeochemical process in estuary, which involves the transformation and transport of chemical substances, is critical in understanding the effects of these environmental alterations. The effective management of the input of nutrients and trace metals on coastal seas require continuous monitoring of their riverine inputs and their effective transmission through estuaries, thereby providing a realistic estimate of inputs to the coastal sea. Although several studies, delineating the environmental changes of the Cochin estuary caused by anthropogenic activities have been studied, only Naik et al., 2000 has reported on quantification of the material transport across the estuary. In the present study, we measured the nutrient fluxes through different locations in the Cochin estuary over successive spring and neap tidal cycles of a post-monsoon, monsoon and pre-monsoon seasons. This is the first attempt to quantify the fluxes of nutrients from the Cochin estuary into the sea. Fractionation of rare earths was performed to access the geochemical variability and depositional condition affecting their fate and transport in the estuarine and coastal environment. For unraveling the trace metal dynamics, the metal fluxes through 6 major rivers discharging into estuary and from different locations in the Cochin estuary over a complete tidal cycle were computed. Environmental impact of metal pollution in sediment depends not only on the total concentration of the metals, but also on their mobility and availability, which influence their release / interaction with other components of the ecosystem such as water, plankton and air. Different sequential extraction methods were employed for estimation of the mobility of trace metal in sediments.

1.3 PRIME OBJECTIVES

- To understand the intra-tidal, inter-tidal, spatial and seasonal variations in the dissolved nutrients in the Cochin estuary and their transport to the sea (input and export fluxes of nutrients in the Cochin estuary).
- To study the present status of trace metals in the sediments of the Cochin estuary and adjacent coastal sea and their chemical

fractionation to identify the mechanism of trace metal accumulation and their mobility.

- To study the distribution and fractionation of rare earths and radioactive uranium and thorium in the sediments of Cochin estuary and adjacent coastal regions to infer their provenance, behaviour and depositional conditions.
- To study the input and export fluxes of trace metals in the Cochin estuary.

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Chapter 2

HYDROGRAPHY AND NUTRIENT FLUXES

Contents

2.1. INTRODUCTION

It has been estimated that 61% of the world population lives along the coastal margin (Alongi, 1998). These demographic changes have detrimental effects on the overall biogeochemical cycling in estuaries. Nutrient enrichment is perhaps the most widespread problem in estuaries around the world (Howarth et al., 2000, 2002). Physical processes play an important role in regulating the chemistry and biology of estuaries (Bianchi et al., 1999; Hobbie, 2000). An estuary is a semi-enclosed body of water, where seawater is measurably diluted by freshwater (Hobbie, 2000). The biogeochemical cycles of estuaries are mainly controlled by the river and groundwater discharge, tides, re-suspension and exchange flow characteristics (Leonard and Luther, 1995).

The physical and chemical environment is commonly expressed in terms of water quality parameters such as temperature, salinity, dissolved oxygen, pH and nutrients. The mixing of river water and seawater can be quite varied in different estuarine systems. The tidal mixing and salinity gradients can significantly affect concentrations of both dissolved and particulate constituents in the adsorption/desorption, flocculation and biological processes. In short, estuarine processes are highly variable with respect to time and space that also influence the water quality.

Nutrients are the raw materials for the marine food chain, as they are essential to the primary production. The elements required in relatively large amounts are generally referred as macro nutrients that constitute carbon, oxygen, hydrogen, nitrogen, and phosphorus. Macronutrients constitute 0.2 to 1% of dry organic weight which also includes sulfur, chlorine, potassium, sodium, calcium, magnesium, iron, and copper. Nutrients needed in trace amounts are generally called micronutrients. These elements often constitute less than 0.2% of dry organic matter. Some common micronutrients required by living organisms include aluminum, boron, bromine, chromium, cobalt, fluorine, gallium, iodine, manganese, molybdenum, selenium, silicon, strontium, tin, titanium, vanadium, and zinc.

Nutrient inputs to estuarine waters come from land, rivers, groundwater, atmospheric deposition, sewage and other anthropogenic activities. Nutrient concentrations have been significantly increased in global rivers by human activity through waste discharge and agriculture (Seitzinger et al., 2002; Statham, 2011; Moore et al., 2003), leading to eutrophication of estuarine and coastal ecosystems (Jickells, 1998; Diaz and Rosenberg, 1995). Anthropogenic inputs have caused many estuarine-coastal systems to shift to N surplus leading to eutrophication (Bricker et al., 1999; Hoch and Kirchman, 1995; Gattuso et al., 1998; Middelburg and Nieuwenhuize, 2000). Increased heterotrophic activities have been observed in such ecosystems due to anaerobic processes such as denitrification, anammox and methanogenesis (Fasham, 2003). The effects include impacts on species diversity, appearance of harmful algal blooms and development of hypoxia (Jickells, 1998). Though water quality management emphasizes control on the point sources such as wastewater treatment, most of these inputs are “nonpoint sources”.

2.2 NUTRIENT FLUX AND ITS IMPORTANCE

In transport phenomena (heat transfer, mass transfer and fluid dynamics), flux is defined as the rate of flow of a property per unit area, which has the dimensions [quantity] x $[\text{time}]^{-1}$x $[\text{area}]^{-1}$. Both natural and anthropogenic activities have significant influence on the transport of nutrients to estuaries and to coastal waters. Estuaries are the intermediate zones of land-sea interactions contributing significantly to the nutrient fluxes in to the ocean on varying time scales (Simpson et al., 2001). The nutrient delivery is influenced by catchment hydrology, freshwater flow and tides (Pennock et al., 1994; Justic et al., 1995; Doval et al., 1997; Mackas and Harrison, 1997). Anthropogenic activities enhance nutrient levels lead to eutrophication and oxygen depletion (Beukema, 1991; Parker and O’Reilly, 1991) and often upset the coastal water ecology. Hence, transport measurements are important to study the nutrient economy and productivity patterns of coastal marine systems (Dehairs et al., 2000; McManus et al., 2001).

2.3 STUDY REGION AND METHODOLOGY

2.3.1 Regional Setting

Cochin estuary is the second largest estuary along the west-coast of India that spreads over 250km^2 (10°10′ N, 76° 15′ E in the north to 09° 30′ N, 76° 25′ E in the south) and length of ~80 km providing a nursery ground for a wide variety of aquatic plants, shell and fin-fishes.

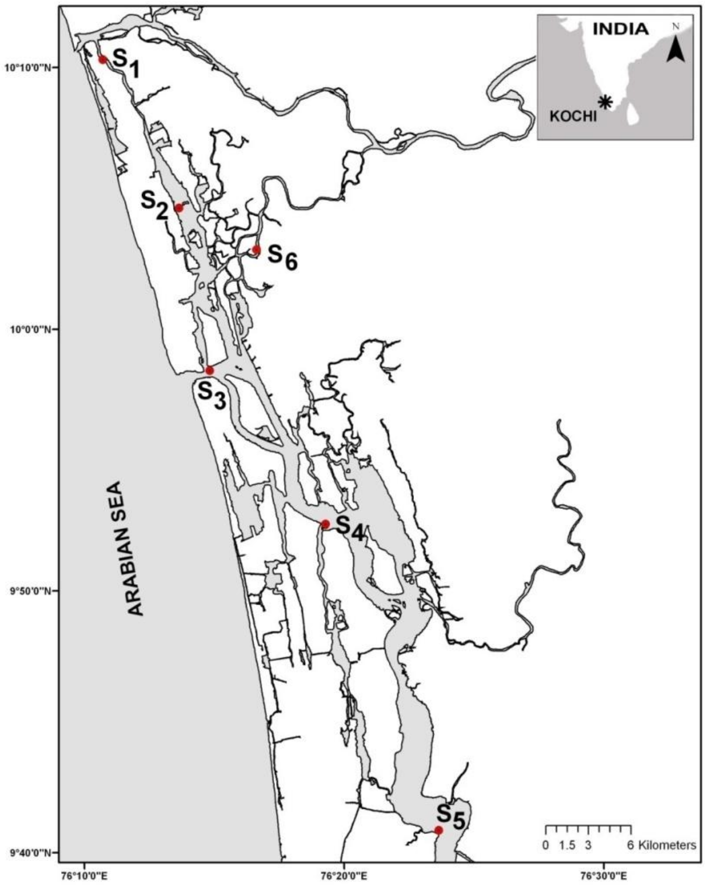

Fig 2.1: Cochin backwaters and the stations for the time-series observations

The annual rainfall over the region is about 3200mm of which, nearly 75% occurs during the summer monsoon (June to September). The predominant winds are south-westerly (10 to 12km/h) from June to September and north-easterly from October to January. For the rest of the year, the winds generally remain weak. Cochin estuary has unique topography; oriented parallel to the coastline and connected to the sea through 2 inlets, Munambam and Kochi (Madhupratap et al., 1987; Srinivas et al., 2003). The tides entering the backwaters are predominantly of mixed semidiurnal (~ 1 m). The depth of the backwater varies considerably from place to place. Along the main channel it is maintained at about 10 to 12 m for navigational purposes while at other places it ranges from 2 to 6 m. The condition of the substrata is predominantly muddy (Balachandran et al., 2001).

The estuary receives nutrients from 6 major rivers namely Periyar, Muvattupuzha, Pamba, Manimala, Achankoil and Meenachil. The increased flushing considerably reduces the salinity of the estuary during monsoon (Shivaprasad et al., 2013). The erratic fluctuations in river run off and rhythmic tidal cycle make the sampling of such estuaries very difficult to study estuarine processes and quantification of fluxes. Cochin estuary has distinct zones based on the tidal excursions a dynamic central zone sandwiched between two relatively weak zones on the north and south (Balachandran et al., 2005). The estuary changes from stratified to partially mixed and completely mixed type while progressing from monsoon, post-monsoon and pre-monsoon seasons (Bincy et al., 2013).

In recent years, increased human interference has led to severe ecological disturbance to the estuary affecting its hydrographical functioning. As a consequence, the estuary has shrunken its area from 315km^2 in 1912 to 256km^2 in 1980 (Gopalan et al., 1983). The inter-basin transfer of water from river Periyar to river Muvattupuzha has changed the estuarine circulation. The construction of Thanneermukkam bund has virtually cut off the estuary from the south Vembanad Lake (Kuttanad). Closure of the bund (mid-December to March) arrests tidal propagation further to the south estuary. Consequently, the south estuary became a trap of agricultural wastes to support the growth of water hyacinth (*African payal*).

The ecological studies in the Cochin Estuary were pioneered by Sankaranarayanan and Qasim, 1969 and Sankaranarayanan and Panampunnayil, 1979. They observed a marked seasonal rhythm in the distribution of nutrients induced by precipitation and runoff. The studies of Balachandran et al., 1999 identified the control of freshwater on the dissolved silicate levels in Cochin estuary. Nitrogen loading to this estuary has increased due to increased industrial and agricultural practices, apart from aqua-tourism (Martin et al., 2010, 2013). High nitrification rate has been noticed recently in the intermediate salinities of the Cochin estuary (Miranda et al., 2008). The enrichment of nutrients during pre-monsoon is due to point sources while nonpoint sources are dominant during monsoon (Joseph et al., 2010). Though nutrients are not limiting the chlorophyll production, their physiological responses to nutrients, pH, temperature and salinity are crucial for the biological production in the coastal waters (Balachandran et al., 2008b). To sum up, over the past 5 decade, this estuary has evolved from an autotrophic to a heterotrophic system due to urbanization causing organic enrichment (Shoji et al., 2008; Gupta et al., 2009). The estuarine sediments are found to accumulate organic matter to act as a potential source of P (Gireesh et al, 2013a, b). This has also increased the sediment oxygen demand in the estuary (Abhilash et al., 2012).

The effluents from unprocessed industrial units and domestic sectors have been estimated as 0.104×10^6 and $0.26\times10^3 m^3 d^{-1}$ respectively, besides the seepage from agricultural, aquaculture fields, port activities, coconut husk retting yards and aqua tourism (Saraladevi et al., 1983, 1991; KSPCB, 1982, 1986; Dineshkumar, et al., 1994). The hydrography of Cochin estuary has deteriorated due to the loading of pollutants exceeding its carrying capacity

(Menon et al., 2000; Balachandran et al., 2001, 2005; Miranda et al., 2008; Martin et al., 2008; Robin et al., 2012). This has caused changes in microbial activity affecting the biota (Martin et al., 2008; Miranda et al., 2008; Shoji et al., 2008). The influence of anthropogenic activities on soft benthic community and frequent fish kills are common in recent time (Martin et al., 2011). Accordingly, the major objective of present study was as follows.

- To understand the inter-tidal, intra-tidal, spatial and seasonal variations in the dissolved nutrients in the Cochin estuary and their transports to the sea.

2.3.2 Data collection and analysis

In general, there are three distinct seasons: monsoon (June-September), post monsoon (October-January) and pre-monsoon (February-May). Monsoon season is characterized by high precipitation and river discharge, while post and pre-monsoons are considered as moderate and least discharge periods respectively.

The mean daily river discharge during the study period was obtained from Central Water Commission (CWC). During summer monsoon of 2010, the river discharge was 702 and 652.4m^3/s on 26th and 27th July (spring phase). During neap phase, the discharges on 2nd and 3rd August were 605.4 and 525.3m^3/s respectively. During post monsoon (spring), the daily discharges were 207 and 151m^3/s on 6th and 7th October 2009, while during neap phase (13th and 14th October), the discharges were very low (80 and 94m^3/s). Similarly for the pre-monsoon spring (22nd and 23rd February) and neap (1st and 2nd March), the discharges were very low (14.79, 14.84, 20.59 and 20.21m^3/s respectively).

A total of six stations were selected for the time series measurements based on the circulation and input characteristics of the estuary (Fig 2.1). They were S_1 (minor inlet in the north), S_3 (major inlet at Cochin), S_2 (between S_1 and S_3), S_4 (22 km south of S_3), S_5 (43 km south near Thanneermukkom bund) and S_6 (21 km NE in the Periyar River entrance). The stations were selected in such a way that S_5 receives freshwater from 4 rivers, whereas S_6 receives freshwater from the River Periyar. It is also relevant to note that the region between S_3 and S_4 is quite dynamic due to the presence of strong rectilinear currents whereas the water movement is weak between S_4 and S_5 (Balachandran et al., 2008c). Similarly, the position of S_2 is very important, as it represents the stagnant north estuary due to the synchronous tides entering from the two inlets at S_1 and S_3 (Ramamirtham and Muthusamy, 1986).

Six Aanderaa current meters (RCM 9) were deployed at mid-depth of the channel at each location continuously for 30 days for all seasons to record the current speed and direction at 10-min intervals. Considering the deep channel at Cochin inlet, two current meters were moored at the center of the channel at 2 m and near bottom during post-monsoon. During other seasons (pre-monsoon and peak summer monsoon), the current velocity and total cross-sectional discharge through the Cochin inlet were measured using an Acoustic Doppler Profiler (ADP) with bottom-tracking. Water level variation at each location was recorded at 10-min intervals using SBE 26 plus Tide Recorder for the entire period (30 d) of observation. Cochin estuary, being a micro tidal estuary, the maximum tidal amplitude is approximately one meter. The phase of tide with maximum tidal amplitude is the spring period and that with minimum amplitude is the neap period. The selection of spring and neap phase observations are made based on the monthly variations in the water level at the Cochin inlet obtained from Indian Tide Tables. These are again checked during the simultaneous tidal measurements made at this location during the entire observational period (Appendix 1b). It can be seen that the low/high tides of spring/neap phases are different at different locations in the estuary and also during different seasons (though the difference is marginal).

Hourly profiles of salinity and temperature were measured using a conductivity-temperature-depth profiler (CTD19 plus, Sea-Bird Electronics). From all the 6 locations, water samples were collected from 0.5 m below the surface and 0.5m above the bottom at 3-h intervals using 5 L Niskin sampler (Hydro-Bios, Kiel-Holtenau, Germany). The sampling was continued for 24 hours during spring and neap tides and this scheme was adopted for all the three seasons. The sample for dissolved oxygen (DO) was collected without air bubbles in a glass bottle, fixed onboard and later analyzed according to Winkler’s method (Grasshoff et al., 1983). The water samples for the determination of various dissolved inorganic nutrients were collected in 500 mL PVC bottles kept in ice boxes and brought to the laboratory within 4 h for analysis. The samples were passed through Whatman GF/F filter paper (pore size 0.7 µm) prior to analysis. Nitrite-N was determined through the formation of a reddish purple azo dye following the method of Bendschneider and Robinson, 1952. Nitrate-N was measured by reduction to nitrite in a copper-cadmium reduction column, APHA, 2000. Ammonia-N and silicate-Si were estimated by phenate method, APHA, 2000 and by ascorbic acid method Koroleff, 1983, respectively. Phosphate-P was measured using ascorbic acid as reducing agent, APHA, 2000. All the dissolved nutrients were analyzed using a UV-Vis Spectrophotometer (Shimadzu 1650PC) calibrated with respective standard solutions.

2.3.3 Nutrient flux computation

The cross-section transport Q (kg/day), for each variable can be obtained by integrating the instantaneous flux as

$$Q = \mathrm{A}' \int_{t1}^{t2} \mathrm{c}\bar{\mathrm{u}}\,dt$$

Where A′ is the cross-section area (m^2), c is the concentration of the parameter (kg/m^3), and ū is the current speed (m/s). The over bar denotes the average speed of water column. The net transport was calculated by integrating the three hourly transports over one tidal cycle. The positive values denote export fluxes (seaward fluxes) and negative values denote import fluxes (landward fluxes). The cross-sectional area of each location was calculated from the respective bathymetry data using Triangulated Irregular Network Programme (Priyakant et al., 2003). A constant value was taken for each cross-sectional area neglecting the tidal variations and the recorded current velocity was corrected with respect to the channel orientation (Appendix 1a).

The nutrient fluxes across the four sampling locations, viz S_1 (minor inlet), S_3 (Cochin inlet), S_5 and S_6 (river boundaries) were calculated (Table 2.1 - Table 2.3) for monsoon, post monsoon and pre-monsoon seasons. The significance of this study is that it is the first attempt to quantify the fluxes of nutrients in the Cochin estuary. We used the current meter data for the post monsoon period, while ADP data was used during pre-monsoon and peak summer monsoon seasons to compute the fluxes of nutrients. The instantaneous discharge (m^3s^{-1}) obtained from ADP was multiplied by the corresponding nutrient concentration (μM converted to kgm^{-3}) to obtain the instantaneous nutrient flux. The input fluxes were calculated as the sum of fluxes across S_5 and S_6, whereas the export fluxes were calculated as the sum of fluxes across S_1 and S_3. The net flux was obtained as the difference between input and export fluxes. The positive values for net flux denote a net addition and negative values denotes a net removal of nutrients in the estuary.

2.4 GENERAL HYDROGRAPHY

Estuary is a region where elements are recycled at a faster rate to support living organisms. These elements are to be kept in balance to maintain the health of an estuary. Characterizing the role of estuaries as a nutrient trap or a source requires information regarding the input and flushing qualities of estuaries with their exchange capacities**.** The general hydrography of Cochin estuary is specified here to evaluate the status of the estuary during the time series observations.

2.4.1 Salinity:-Intra-tidal, diurnal and seasonal variations

Salinity distribution in an estuary is influenced by fresh water discharge, tides, precipitation, evaporation and estuarine circulation (Jassby et al., 1995). Moreover, it is also governed by the morphologic, bathymetric and hydrodynamic characteristics of an estuary. The variation in salinity at the Cochin inlet is found to follow tidal rhythm (Balachandran et al., 2001; Srinivas et al., 2003; Shivaparasad et al., 2013; Vinita et al., 2015b). Fig 2.2 depicts the diurnal variation of surface and bottom salinity along the channel S_1-S_5 in the Cochin estuary during three different seasons. The diurnal variation of salinity in S_6, northern upstream is represented in Fig 2.4. It is evident that during peak summer monsoon, heavy rainfall results in high fresh water discharge which eventually reaches estuarine mouth. Freshwater flow during spring tide (58.5×10^6 m^3d^{-1}) was relatively high as compared to that ($48.9\ \times10^6$ m^3d^{-1}) during neap tide (CWC). The maximum tidal range at the

Cochin inlet was 0.39m during spring tide and 0.26m during neap tide (Appendix 1b). The surface (0.52m/s) and bottom (0.53m/s) currents at the inlet were stronger during spring flood and directed landwards. The advection of saltier water towards surface during spring flood probably resulted in an increase in salinity in the surface. Thus, there was salinity stratification at the Cochin inlet during spring tide with surface fresh water (salinity 2.29-11.36) and saltier bottom (19.16- 33.22).

Fresh water discharge was less during neap period, but inlet showed greater stratification during neap with a salinity gradient 16.5-31.8. The salinity at the surface and bottom varied as (1.93 to 4.76) and (20.17 to 33.73) respectively. During neap flood, relatively weaker surface currents (0.29m/s) and bottom currents (0.34m/s) weakens the advection of bottom water towards the surface and favoured intense stratification. Similar observation was reported in earlier studies (Balachandran, 2001). At the minor inlet S_1 (Maliankara) also, salinity remained higher during spring tide as compared to neap tide due to increased tidal activity. All other stations (S_2, S_4, S_5 and S_6) remained fresh water dominant during both spring and neap tides.

During the post monsoon period, there was heavy rain (~126mm) in the study area during the spring tide, while there was no rain (~1 mm) during the successive neap observation (Data obtained from website of Indian Meteorological Department, http://www.imd.gov.in/). This was well reflected in the daily river discharge data as well as in the salinity distribution in the study region.

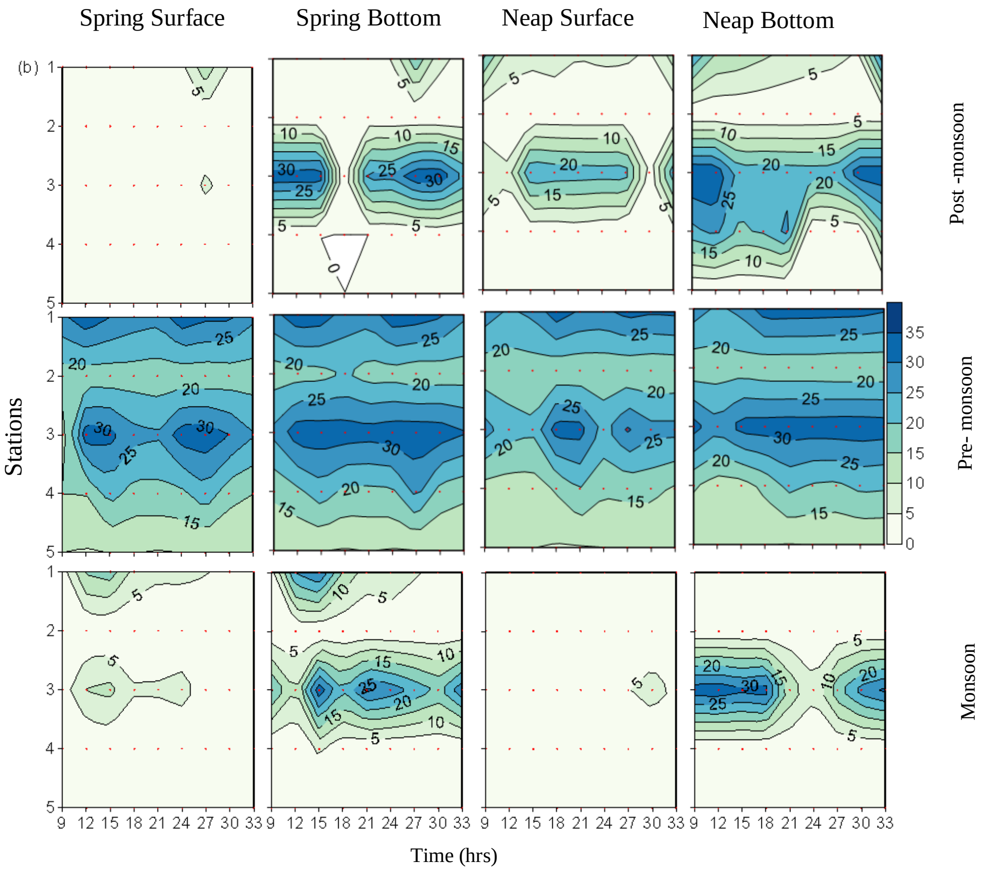

Fig 2.2: Diurnal salinity variations in the Cochin estuary during different seasons. The stations S_1 to S_5 are represented by number 1 to 5

The fresh water flow during spring ($15.5\times10^6 m^3 d^{-1}$) was much higher than during neap tide ($7.5\times10^6 m^3 d^{-1}$). As a consequence, the water column at the Cochin inlet was well stratified during spring with freshwater (0.63-5.96) stratified over the saltier (3.40-34.31) water. However, during neap the stratification at the Cochin inlet was limited only for a short period (flood), as well-mixed conditions prevailed over for the next 12 h and then regained the stratification for the next 6 h. During neap tide, the seawater intruded into the estuary up to Arookutty S_4 (22km away from inlet) when the fresh water flow was low (Fig 2.3) which supports the view that salinity intrusion mostly depends on fresh water discharge rather than spring-neap tidal oscillations (Bincy et al., 2013).

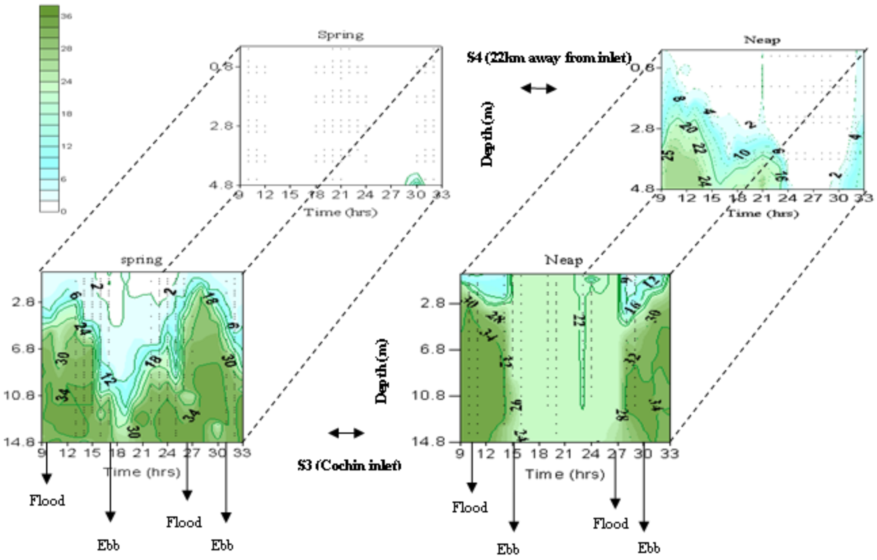

Fig 2.3: Diurnal variation in salinity across the Cochin inlet (S_3) and Arookutty (S_4) during a spring and neap tide of summer monsoon.

Intrusion of seawater up to 22km towards the south estuary is an interesting feature to be noted, as indicated by the increase in the bottom salinity at S_4 (salinity gradient > 26) especially during neap tide. During post monsoon however, there was a contrasting behavior at the minor inlet, S_1 as it showed high salinity during neap tide due to very low fresh water flow. Other estuarine stations S_2, S_5 and S_6 remained fresh water dominated during both tides.

During pre-monsoon observation, the river discharge was at its minimum (spring: 1.763 x $10^6 m^3 d^{-1}$; neap: 1.28 x $10^6 m^3 d^{-1}$) while the tidal influence was the maximum, enabling a well-mixed and homogeneous condition in the entire estuary (except at S_6). At the inlet, surface salinity (12.23-33.09) varied in accordance with the bottom salinity (26.33-33.20) during spring tide, while the ranges were 22.19-32.3 and 26.67-32.93 during neap tide. There was stratification at S_6 (Varapuzha) due to the moderate fresh water flow from the River Periyar. Consequently, the northern upstream (Varapuzha) contained freshwater in the surface (neap: 0.99-1.77: spring: 0.66-1.38) and salt water in the bottom (neap: 7.98-12.25; spring: 0.52-11.98). The seawater intrusion into the south estuary resulted in the maximum salinity (9.56-10.35) at S_5 (Thanneermukkam) during this period. The salinity variation generally followed the tidal amplitude.

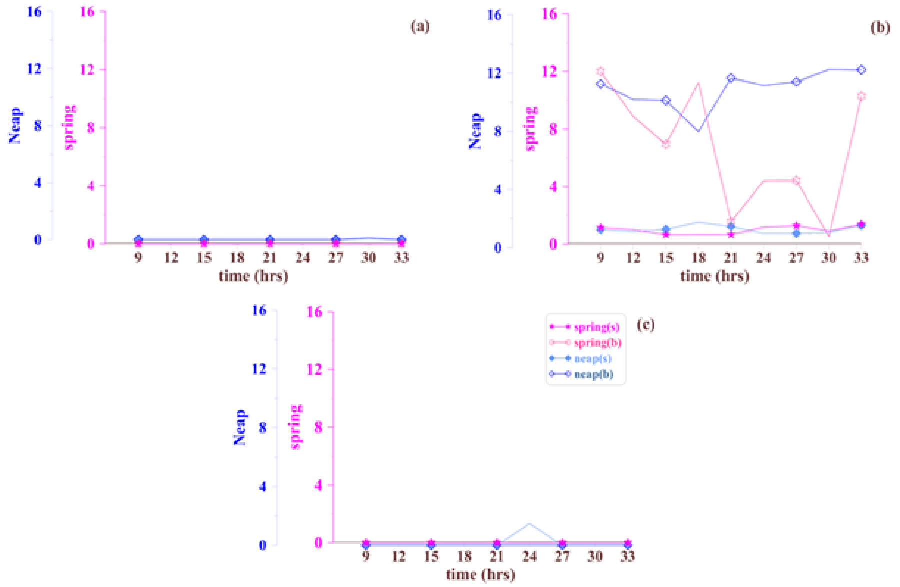

Fig 2.4: Diurnal variation in salinity at S_6 (northern upstream) during three different seasons: (a) Post Monsoon, (b) Pre Monsoon, (c) Monsoon

2.4.2 Dissolved Oxygen

The dissolved oxygen (DO) is the oxygen that dissolved in water due to diffusion from atmosphere, aeration and photosynthesis. Saturated dissolved oxygen levels are necessary for good water quality. Oxygen is an essential element for all forms of life. Aquatic life is put under stress when the dissolved oxygen levels drop below 5.0mg/l. Dissolved oxygen below 1-2mg/l can result in fish mortality. Numerous scientific studies suggest that 4-5ppm DO is the minimum level that will support a large, diverse fish population. The DO level in good fishing environment generally averages about 9.0ppm. Moreover, oxygen affects a number of esthetic factors like the odor, clarity and taste.

Fig 2.5 depicts the diurnal variation of dissolved oxygen (DO) along S_1-S_5 channel in Cochin estuary during three seasons. Similar variation for S_6 (northern upstream) is represented in Fig 2.6. Dissolved oxygen was generally high in the surface and low in the bottom throughout the study region. Higher values were observed during ebb compared to flood periods. DO showed an increasing trend from pre-monsoon to post monsoon and to monsoon season in the upstream. Due to bidirectional characteristics, the bottom saltier layer at Cochin inlet showed a lower DO during monsoon and post monsoon periods.

During the peak summer monsoon period, there was substantial reduction in dissolved oxygen (0.61-1.82mg/L) at the inlet during 2nd phase of diurnal tidal cycle during spring phase. There was hypoxic condition in the bottom layer for a short period during spring phase (flood), possibly due to the coastal upwelling. It was more perceptible during neap phase, as the dissolved oxygen further decreased to 0.56-1.16mg/L during flood tide. The intrusion of saline water into the estuary was least during this period, as evidenced from the low oxygen levels limited to the inlet. The DO levels generally increased towards northern and southern estuarine regions with peak values at S_5 (Thannermukkam), especially during neap tide in the surface (7.29-8.37mg/L) and bottom (6.55-8.82mg/L). During spring tide, there was slight reduction in the DO at surface (6.63-7.94mg/L) and bottom (6.42-7.66mg/L).

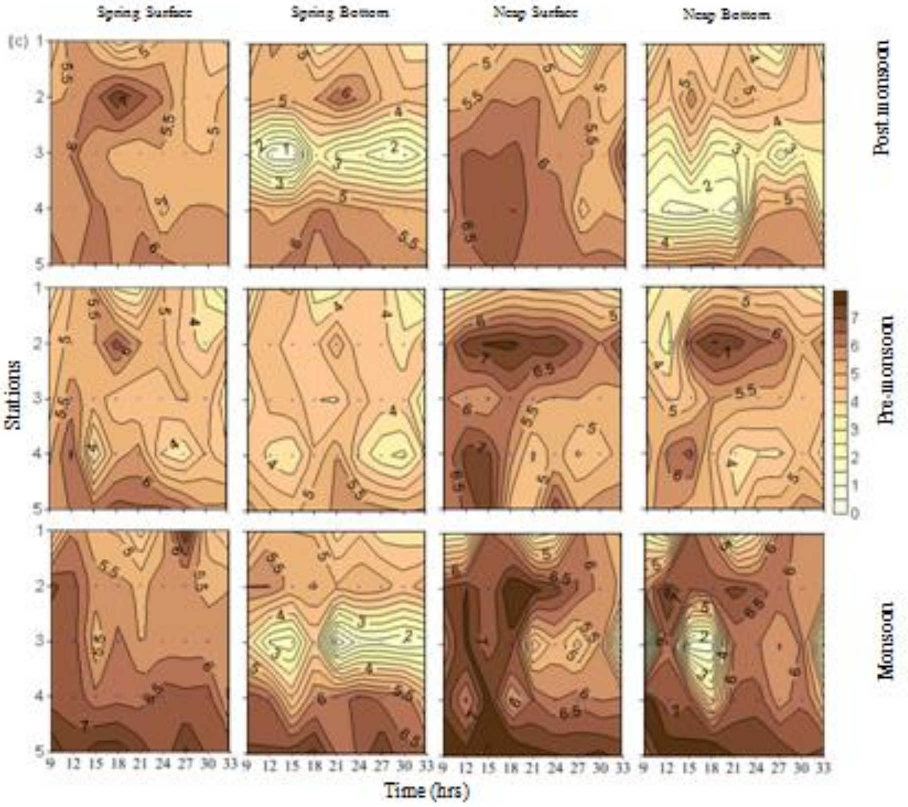

Fig 2.5: Diurnal variations in DO (mg/l) in the Cochin estuary during different seasons. The stations S_1 to S_5 are represented by number 1 to 5

During post monsoon, DO showed saturated levels in southern upstream throughout spring and neap tides, especially during neap tides, The average DO in northern upstream during spring tide was 5.83mg/L (surface) and 5.95mg/L (bottom), while during neap tide, it was 6.15mg/L (surface) and 6.27mg/L (bottom). Similarly, in southern upstream, the DO during spring tide was 6.04mg/L (surface) and 5.91mg/L (bottom), while during neap, it was

6.32mg/L (surface) and 6.04mg/L (bottom). The stagnant north estuary (S_2) exhibited lower DO than S_6 during this period, probably due to the flow restrictions (Balachandran et al., 2008c).

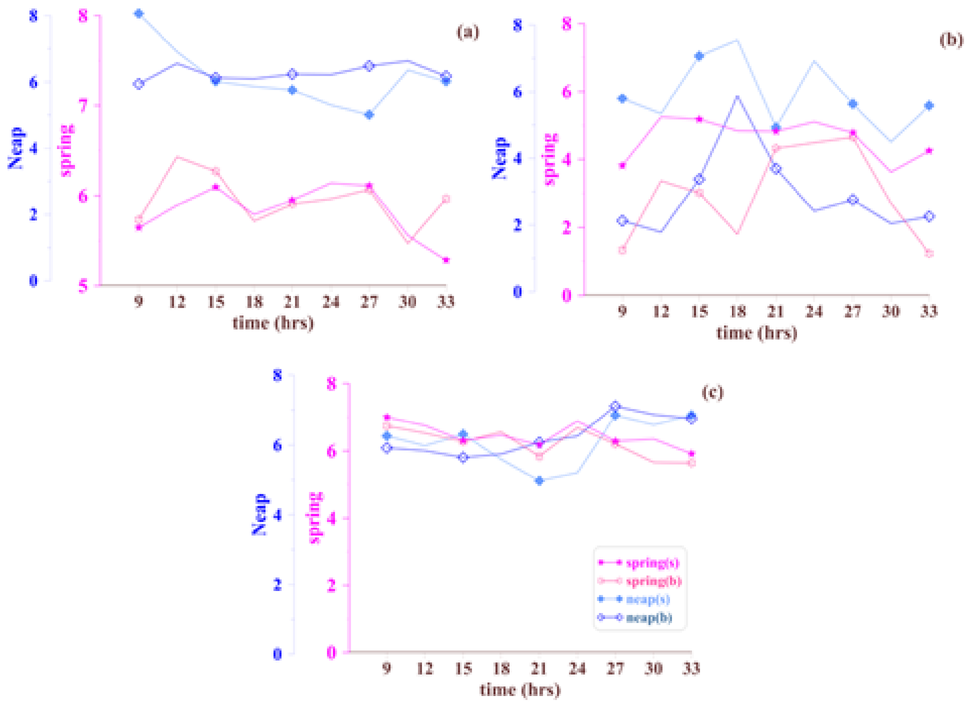

Fig 2.6: Diurnal variations in DO (mg/L) at S_6 (north upstream) during (a) Post Monsoon (b) Pre Monsoon (c) Monsoon

The Cochin inlet (S_3) was relatively cooler (24-26°C) in the sub surface during spring flood period of the post monsoon. The sub surface waters were also high saline (34.9) and oxygen-deficient (0.53-0.55mg/l), which continued during neap tide to spread further up to S_4 (Arookutty) owing to low fresh water flow. It is an established fact that during the monsoon upwelling, the cool, oxygen-deficient and nutrient-rich waters rise to the surface along the southwest coast of India (Naqvi and Jayakumar, 2000;

Habeebrehman et al., 2008). As the upwelled waters advances into the coastal zone, it is further depleted in oxygen due to the increased demand for the oxidation of organic matter (Naqvi and Jayakumar, 2000).

The presence of hypoxic waters (DO < 1.51mg/l) in the bottom was observed in the Cochin estuary during peak summer monsoon (July) of 2009 (Shivaprasad et al., 2013). The present study during post monsoon could further delineate the spatial extent of these hypoxic waters up to 22km inside the estuary. Sub surface hypoxia under prolonged stratification can even result in the development of anoxic conditions (Rabalais and Gilbert, 2009), which will severely affect the biological organisms (Zhang et al., 2010). Another factor that has contributed to the oxygen deficiency in Cochin estuary is the intense bacterial respiration (Shoji et al., 2008). Dissolved oxygen concentration < 2mg/L can induce stress on many aquatic organisms. However, it can be seen from Fig. 2.5 that the oxygen saturation was quickly regained due to the dynamic nature of the estuary.

The estuary remained well mixed during pre-monsoon, when the estuarine inlet recorded maximum oxygen saturation. It was slightly higher during neap phase (surface: 5.10 - 6.37 mg/L; bottom: 4.34 - 5.58mg/L) than during spring phase (surface: 3.41-5.81mg/L; bottom: 2.98 - 4.89mg/L). However, the DO at northern inlet (Munambam, S_1) was < 4mg/L during both spring and neap tides.

During pre-monsoon period, the oxygen deficiency observed in the bottom (spring avg 2.99mg/L; neap avg 2.93mg/L) in the northern upstream (S_6) has not been previously reported (Sankaranarayanan and Qasim, 1969; Saraladevi et al., 1983; Anirudhan et al., 1988; Nair et al., 1988; Kunjikrishna

Pillai, 1991; Sheeba et al., 2000; Robin et al., 2012). While the surface layer at S_6 was oxygenated during spring (3.63 - 5.35mg/L) and neap tides with slightly higher values during neap (4.50 - 7.55mg/L) tide. The oxygen regained saturation at S_6 (Varapuzha) during wet period (monsoon and post monsoon) due to increased fresh water discharge.

During pre-monsoon, the north estuary (S_2) was well oxygenated (surface 5.82-7.65mg/L and bottom 3.16-7.55 mg/L) during neap tide, which was reduced during spring tide (surface 3.77-6.78 and bottom 3.64-5.44mg/L). Although the south estuary remained vertically mixed during this period, (S_4 and S_5), oxygen deficiency was felt in the S_4 bottom, possibly due to increased oxygen demand. The oxygen levels at S_4 in the surface (spring: 3.59-6.57; neap: 4.44-7.26mg/L) during pre-monsoon was slightly lower than that during monsoon. The oxygen deficiency in the bottom at S_4 during neap (3.69-6.64mg/L) and spring (2.86-5.54mg/L) phase was not intense as that in post-monsoon period. However it was well saturated at southern upstream (S_5) during both spring (surface 6.17, bottom 5.47mg/L) and neap (surface 5.96; bottom 5.27mg/L) observations.

2.4.3 Nitrate-N

The dominant dissolved nitrogen species are nitrate, nitrite, and ammonia. In well oxygenated water body, the most abundant and stable inorganic form of nitrogen is nitrate. It is chemically stable, but can be reduced by microbial action. Nitrate enters the water body through surface flow and groundwater as a consequence of agricultural activity (fertilizers and manures), wastewater and oxidation of nitrogenous wastes including septic tanks and other activities. Nitrate stimulates the growth of plankton and water weeds that may increase the fish population. However, excess growth of algae due to high nutrients cause eutrophication, which will deplete the oxygen levels and cause fish mortality.

Fig 2.7 depicts the diurnal variation of nitrate along the channel S_1-S_5 during three seasons. The variation at S_6 (northern upstream) is represented in Fig 2.8. The results show that apart from the freshwater discharge and tidal activity, nonpoint sources and internal processes are also contributing to the spatial distribution of nitrate in the estuary. Periyar River is a major source of nitrate in to Cochin estuary, as indicated by its high concentration in the northern upstream (S_6) compared to southern upstream (S_5) even though freshwater discharge (from 4 rivers) provided a well oxygenated conditions in the latter. This evidenced the additional supply of nitrate from the industrial activities at S_6.

During monsoon (spring) period, increased freshwater discharge resulted in high nitrate levels over the entire study region (except S_1 & S_4). Nitrate concentration at S_6 ranged from 28.86-38.89µM in the surface and 9.88 25.01µM in the bottom. The low nitrate levels at S_4 (Arookutty) during spring tide (surface 8.17-17.14µM; bottom 9.24-19.67µM) were concomitant to high NH_4 contents, indicating the dominant internal processes in the estuary. During neap tide, nitrate was maximum (surface 27.26-40.17µM; bottom 31.20-39.12µM) at the minor inlet (S_1) due to nonpoint sources, while it was minimum at southern upstream S_5 (surface 9.69-16.82µM; bottom 9.92-16.93 µM) following its uptake by plankton (high photosynthesis), indicated by saturated water column.

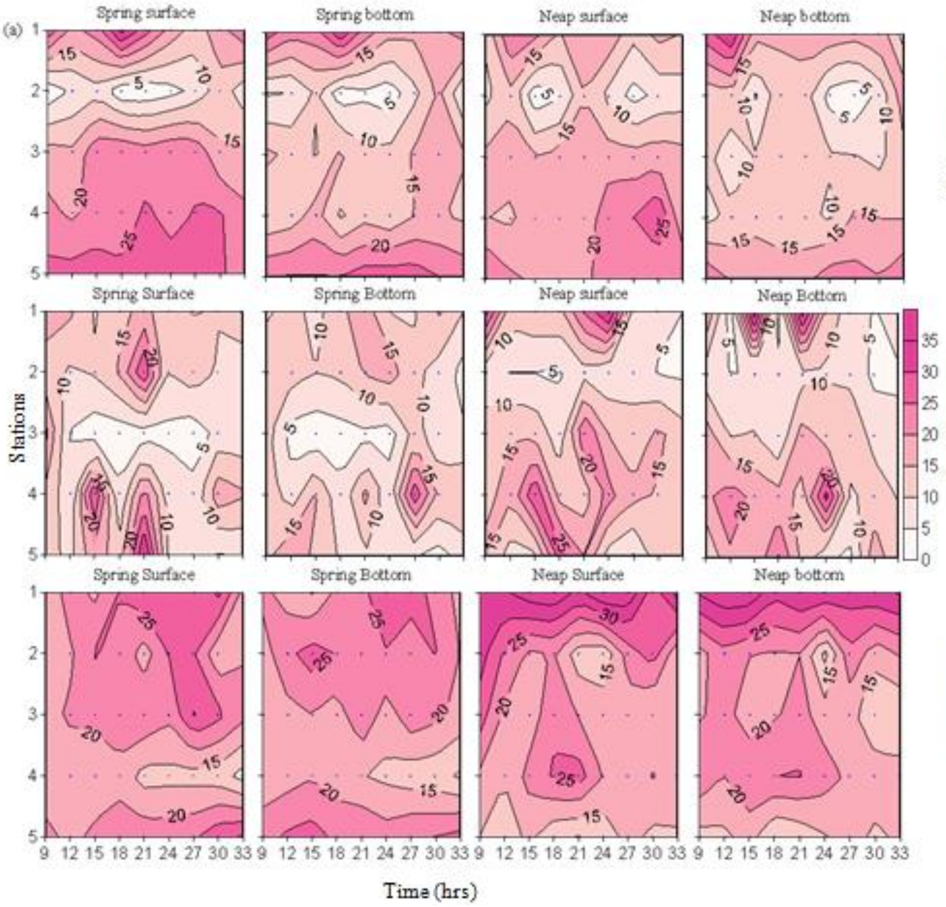

Fig 2.7: Diurnal variations in nitrate (µM) in the Cochin estuary during different seasons. The stations S_1 to S_5 are represented by number 1 to 5

Nitrate concentrations at the Cochin inlet were higher during ebb and lower during flood periods. The stratification was responsible for the differences in the vertical distribution of nitrate at the inlet, with bottom concentrations (spring 20; neap 17.19µM) lower than the surface concentrations (spring 23.19; neap 19.63µM).

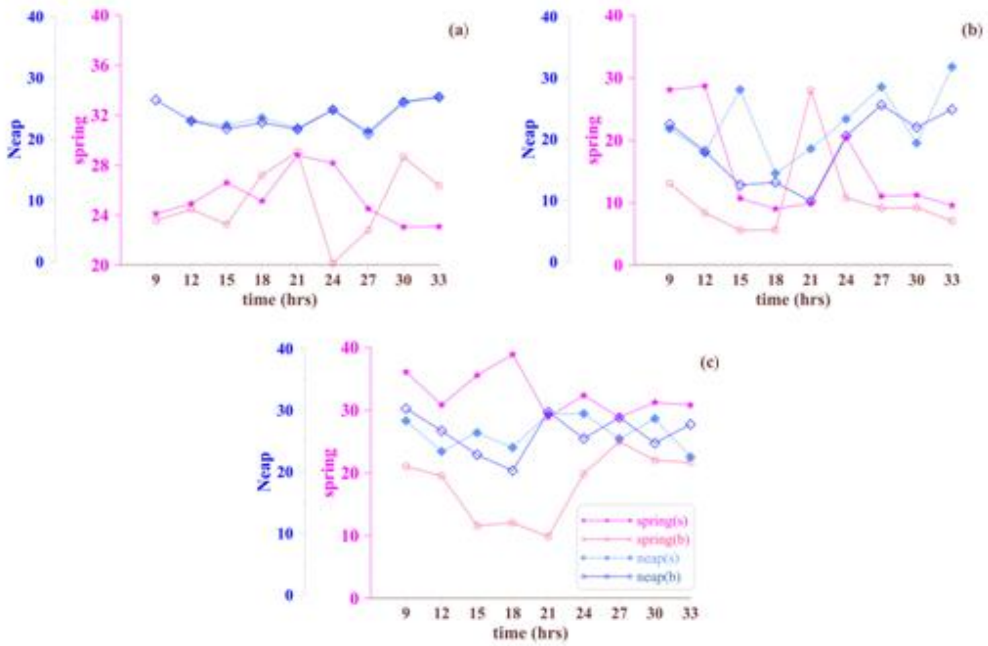

Fig 2.8: Diurnal variations in NO_3 (µM) at S_6 (northern upstream) during three seasons (a) Post Monsoon (b) Pre Monsoon (c) Monsoon.

Irrespective of spring neap tidal oscillations, the northern upstream (S_6) was enriched with nitrate during post monsoon following its low uptake. However, S_2 the stagnant north estuary was depleted in nitrate due to the increased productivity of the region. The chlorophyll *a* was consistently high at S_2 (spring: 18.6; neap: 9.4mg/m^3), whereas it remained <5mg/m^3 in other regions.

Even though river discharge was more during spring phase, the nitrate concentration was generally high in the estuary during neap phase of post monsoon period. The average nitrate at S_6 during spring was 24.34µM (surface) and 24.8µM (bottom) while during neap, it was 34.32µM (surface) and 25.92µM (bottom). Nitrate at the Cochin inlet varied inversely with salinity and was lower than that monsoon season. Nitrate levels were low in the bottom (spring 17.4; neap 12.3µM) than at the surface (spring 22.7; neap 31.4µM).

As rivers are the major source of nitrate, the concentration was very low in the estuary during low discharge period (pre-monsoon). However, high nitrate (15.41µM) was observed towards the northern upstream (S_6) in the surface compared to the bottom (10.77µM). During pre-monsoon spring, the nitrate at the inlet was 1.25-22µM (surface) and 1.89-11.7µM (bottom). During low tidal amplitudes (neap tide), more freshwater reached the inlet, when there was an increase in nitrate levels (surface 6.83-25.10µM and bottom 5.65-17.68 µM). Nitrate was consistently low at S_2 (surface 4.09- 8.56; bottom 3.61-9.6µM) during neap tide when oxygen was high due to increased productivity.

2.4.4 **Nitrite**-N

The nitrite (NO_2^-) is a relatively unstable oxidation state of N. Chemical and biological reactions can reduce nitrate or oxidize ammonia to nitrite. Nitrite is an intermediate species formed during nitrification and denitrification processes. Nitrite can cause serious illness (brown blood disease) in fish, even though they don't exist for very long in the environment. Fig 2.9 depicts the diurnal variation of nitrite along the channel S_1-S_5 in Cochin estuary during three different seasons. The variation of nitrite at S_6 (northern upstream) is represented in Fig 2.10. Nitrite during peak summer monsoon was higher in saline water and lower in freshwater. Accordingly the inlet region showed maximum nitrite levels, whereas the upstream regions S_5 and S_6 showed minimum nitrite during both spring and neap tides.

At the Cochin inlet, nitrite levels were 0.45-0.96µM (surface) and 0.65-2.15µM (bottom) during spring tide and 0.37-0.46µM (surface) and 0.30-1.30µM (bottom) during neap tide. Due to high salinity during spring tide, the nitrite at the minor inlet too showed higher concentration during spring (surface 0.84; bottom 0.93µM) than neap (surface 0.48; bottom0.42µM) tide. High surface nitrite at the upstream S_6 (0.48 µM) and S_4 (0.65 µM) especially during spring indicated their riverine origin.

During post monsoon, the distribution of nitrite was dependent on the dissolved oxygen levels in the water column, when the southern upstream (S_5) had relatively low nitrite than northern upstream (S_6) owing to saturated dissolved oxygen at S_5. The nitrite concentration at S_5 during spring tide was 0.34-0.52µM (surface) and 0.32-0.41µM (bottom), while during neap tide the nitrite was 0.21-0.36µM (surface) and 0.22-0.30µM (bottom). During spring, there was an increase in nitrite (surface 0.41-0.64; bottom 0.52-1.46µM) at the Cochin inlet especially in the bottom (similar to monsoon observations), which was high saline, cool and oxygen deficient, indicating the presence of upwelled waters. However, such an increase was not observed during neap tide (surface 0.23-0.48; bottom 0.08-0.29µM).

During pre-monsoon, even though the water column was homogenous with respect to salinity, there exist vertical gradient in the distribution of nitrite. The surface layer showed higher nitrite than bottom layer in all the stations (except S_4 and S_5) and the lowest nitrite (surface 0.10-0.45; bottom 0.12-0.35µM) was noticed at S_2, where the water column was well oxygenated.

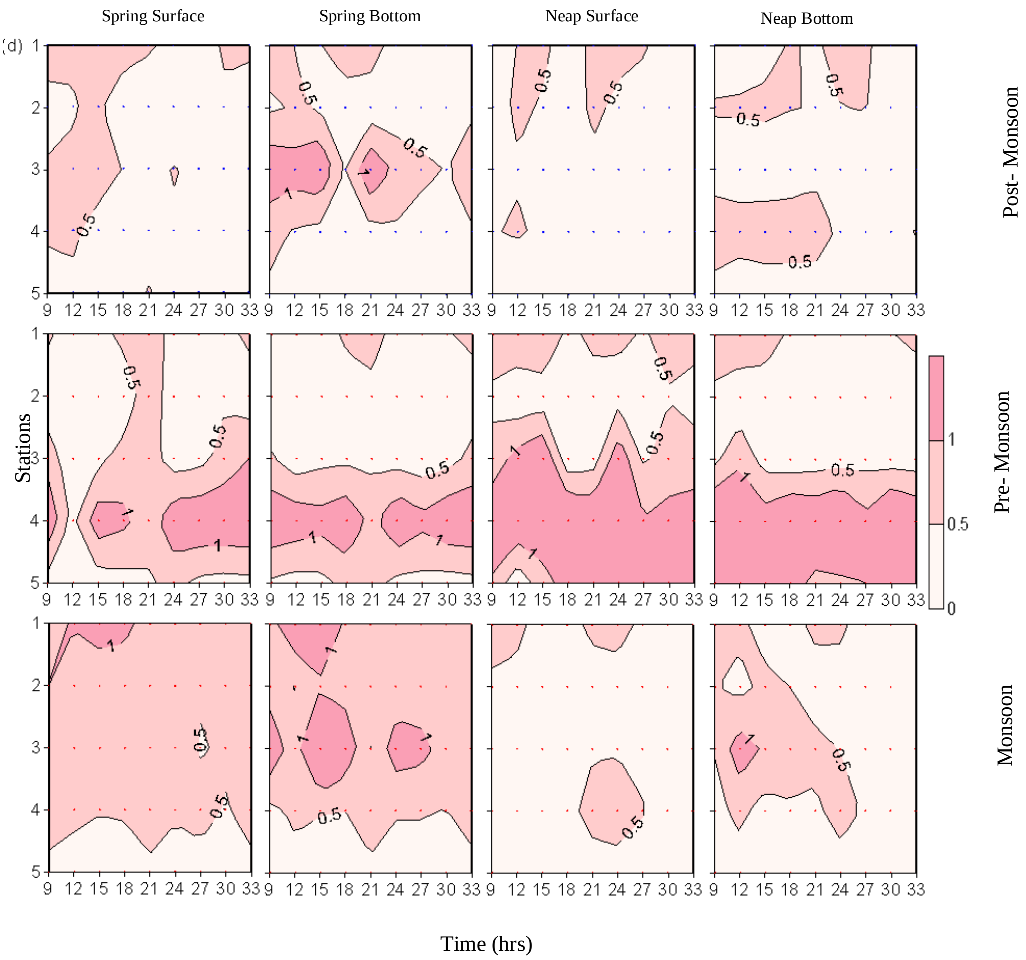

Fig 2.9 : Diurnal variation in nitrite (µM) in Cochin estuary (S_1-S_5) during three seasons The stations S_1 to S_5 are represented by number 1 to 5.

Increase in nitrite levels during monsoon and post monsoon at Cochin inlet was associated with coastal upwelling, whereas it is generally low during pre-monsoon period. The nitrite at Cochin inlet during spring phase varied as 0.12-1.01µM (surface); 0.20-0.64µM (bottom) and during neap phase as 0.14-1.5µM (surface) and 0.17-0.92µM (bottom) throughout pre-monsoon.

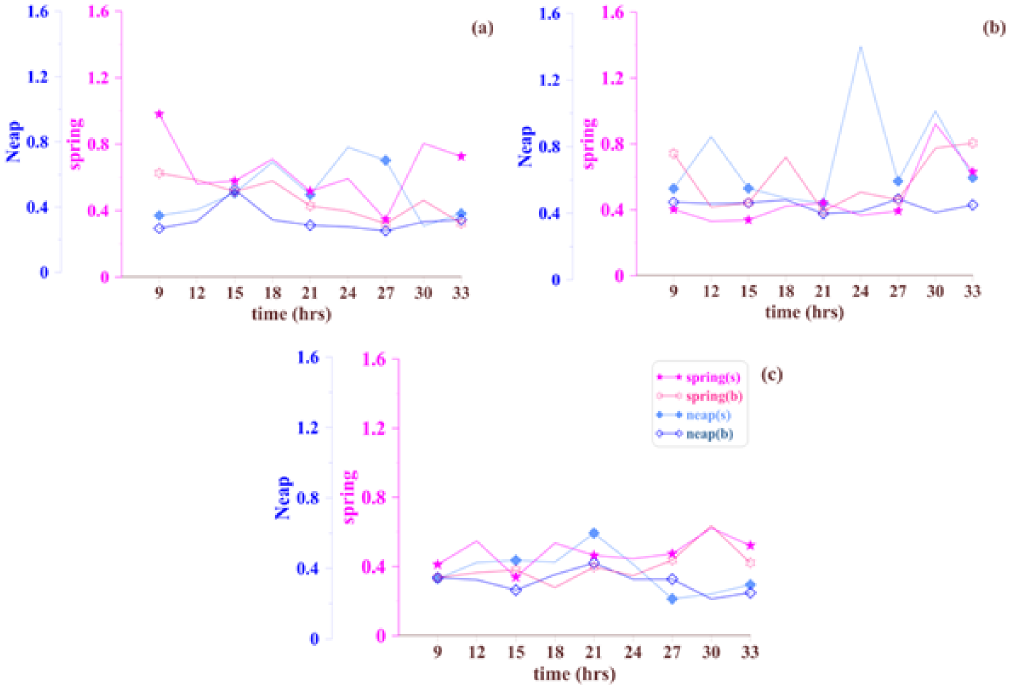

Fig 2.10: Diurnal variation of nitrite at S_6 (northern upstream) during different seasons (a) Post Monsoon, (b) Pre Monsoon, (c) Monsoon

During pre-monsoon, there was a remarkable increase in nitrite towards the southern estuary (S_4) up to 1.47µM during spring tide and 1.84µM during neap tide. This was not due to the changes in salinity. Instead, there are food processing industries surrounding S_4, the sodium nitrite and sodium nitrate used as preservatives (Cammack et al., 1999) may result in this high nitrite. The presence of certain bacterial communities like Ammonia oxidizing bacteria (AOB) and Archea can also enhance ammonia oxidation to increase the nitrite levels (James et al., 2008). Vipindas et al., 2015 observed such bacterial communities and their significant role on ammonia oxidation at S_4 during monsoon. The proximity of station S_4 to the Muvattupuzha river entrance can also be a reason for the nitrite enrichment. An increase in nitrite

(1.58 and 1.93 µM) was also noticed at the S_5 during pre-monsoon (neap) period. As the Thannermukkam bund is closed during this period, the increase in nitrite can be due to its upward intrusion from S_4 to S_5.

2.4.5 Ammonia-N

Ammonia-N can be the next most abundant form of inorganic nitrogen for phytoplankton growth after nitrate (Stephens et al., 1976). Fig 2.11 depicts the diurnal variation of ammonia along the channel S_1-S_5 in Cochin estuary during three different seasons. The diurnal variation of ammonia in S_6, northern upstream is represented in Fig 2.12. During monsoon, ammonia concentration showed a decreasing trend towards upstream with the lowest ammonia level at S_5, southern upstream with an inverse relation with dissolved oxygen. The variation in ammonia at S_5 during monsoon spring tide was 4.75 (S) and 3.98µM (B) respectively and neap tide was 3.79 (S) and 2.34µM (B) respectively (time series average). The ammonia recorded at northern upstream, S_6 was high, possibly due to nonpoint sources of discharge. The ammonia concentration at S_6 during spring was 6.46 µM (S) and 5.76 µM (B) and during neap was 5.9 µM (S) and 5.3 µM (B). The ammonia was maximum near the minor inlet (S_1) during spring tide and at the major inlet (S_3) during neap tide, coinciding with low DO. The ammonia at S_3 was 6.46µM (S) and 5.76µM (B) during spring and 6.9µM (S) and 11.0µM (B) during neap tide. The surplus ammonia in the surface waters of Cochin estuary (except S_3 & S_4 during neap tide) indicates its estuarine origin. Recent studies have shown that nutrient concentrations in the Cochin estuary are often controlled by organic matter decomposition, nitrification, and nitrogen fixation apart from sediment re-suspension (Miranda et al., 2008; Vipindas et al., 2015). In addition to the riverine inputs, there are additional sources of ammonia in to the estuary from several tributaries, agricultural drains and sewage treatment plants.

Similar to monsoon observation, nitrate was the major nitrogen fraction during post monsoon period also, while ammonia was relatively low. During post monsoon spring, minor inlet showed enhanced level of ammonia together with lowest dissolved oxygen while during neap tide the highest ammonia was observed at S_4 when the dissolve oxygen decreased with intrusion of high saline water. Ammonia showed moderately higher values in northern upstream when compared to southern upstream S_5 due to the highly oxygenated condition at S_5. The ammonia at S_4 during spring was 4.38µM (S) and 3.44µM (B), while during neap, it was 15.14µM (S) and 11.23µM (B).

Ammonia concentration was noticeably high in the Cochin estuary during pre-monsoon, with a decreasing trend towards upstream. The maximum concentration was noticed at inlet and Arookutty (south estuary). At the inlet, it was averaged to 22.86µM (S) and 15.49µM (B) during spring tide and 16.7µM (S) and 16.1µM (B) during neap tide. At $S_{4,}$ ammonia averaged to 18.03µM (S) and 11.74µM (B) during spring tide and varied as 3.9-87.6µM (S) and 2.8-23.9µM (B) during neap tide. Ammonia was generally high at the surface in the entire estuary except at S_6, where it was stratified during pre-monsoon, where the average concentration was 6.9µM (S) and 20.2µM (B) during spring and 10.3µM (S) and 16.5µM (B) during neap tide. High ammonia along with oxygen deficiency in bottom of S_6 is probably due to re-mineralization during dry season (Pratihary et al., 2014).

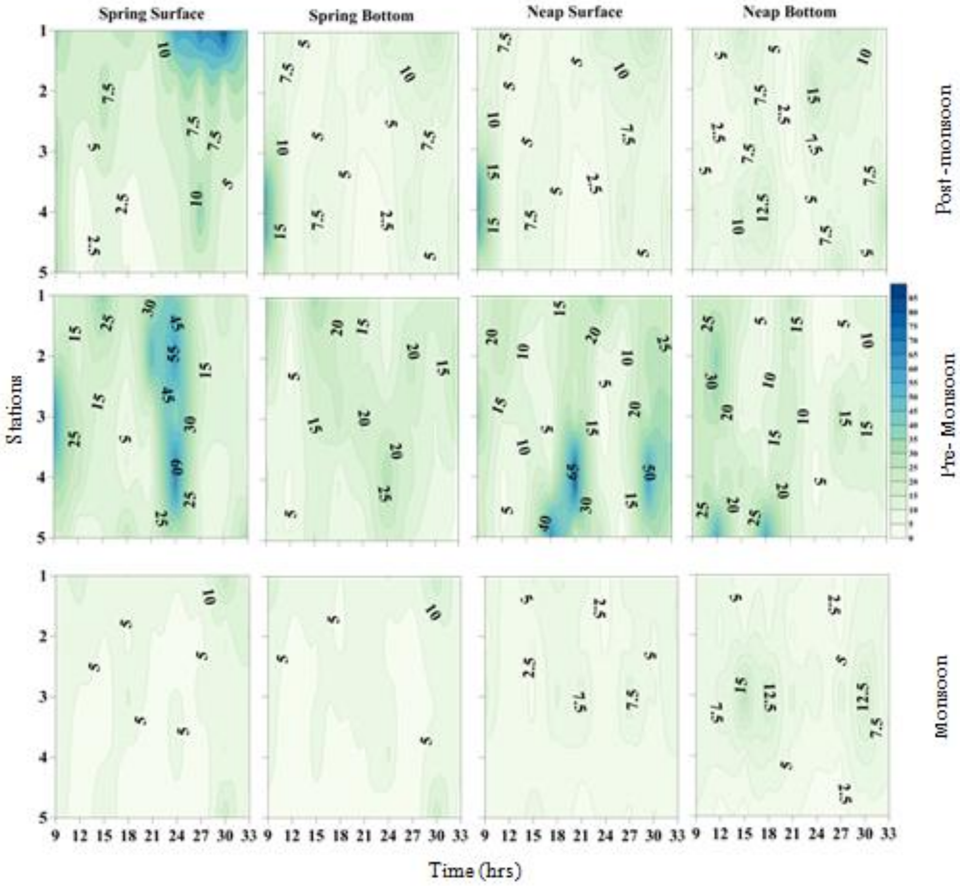

Fig 2.11: Diurnal variation in ammonia (μM) in the Cochin estuary (S_1-S_5) during three seasons. The stations S_1 to S_5 are represented by number 1 to 5.

During pre-monsoon, the southern upstream S_5 showed higher ammonia in surface than northern upstream especially during neap tide. The average ammonia at S_5 during spring tide was 16.4μM (S) and 8.8μM (B) and during neap tide, it was 21.1μM (S) and 18.2μM (B) respectively. Bhavya et al., 2015 have shown that despite a high nitrification and biological assimilation, ammonia levels are consistently high in the Cochin estuary.

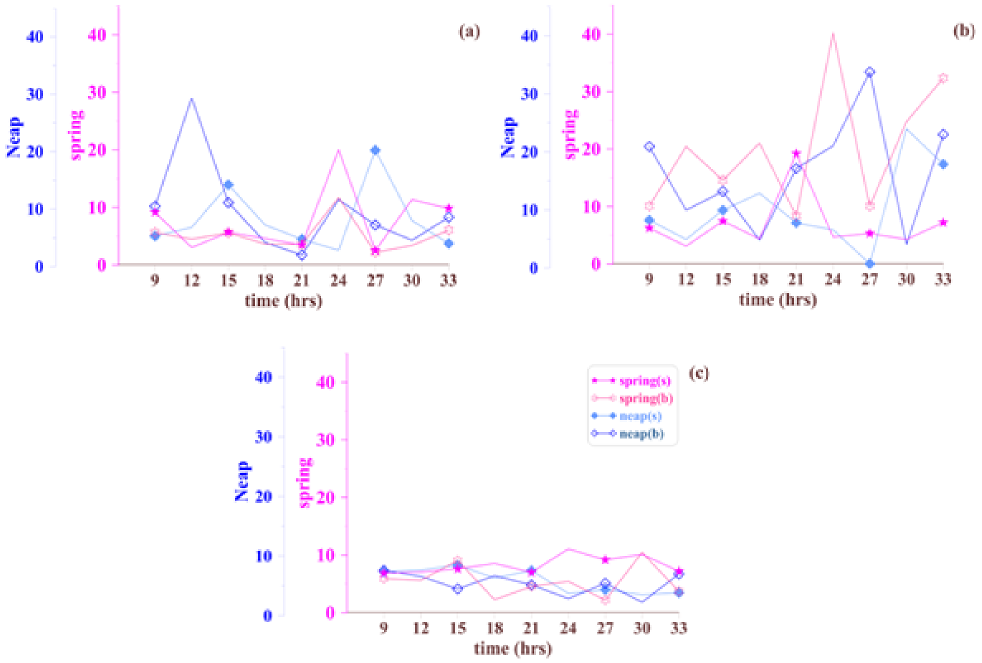

Fig 2.12: Diurnal variation of ammonia at S_6 (northern upstream) during different seasons (a) Post Monsoon, (b) Pre Monsoon, (c) Monsoon.

2.4.6 Silicate-Si

The Si is primarily derived from rock weathering and hydrothermal vents, while its removal is through biogenic processes (Treguer et al., 1995). Silicon is required as a macronutrient by certain groups of plants such as diatoms, which account for 25% of the world's net primary production (Willen, 1991). The cycling of Si is thus, strongly dependent on its assimilation and dissolution of diatoms frustules. Fig 2.13 depicts the diurnal variation of silicate along the channel S_1-S_5 in Cochin estuary during three different seasons. The diurnal variation of silicate in S_6, northern upstream was represented in Fig 2.14. During peak summer monsoon, increased freshwater discharge increased the silicate concentration in the northern estuary (S_1, S_2 and S_6) compared to southern estuary (S_4 and S_5) especially during neap tide despite a high salinity (Fig. 2.2). Silicate observed at $S_{2,}$ stagnant north estuary and S_6 was more or less similar, which was high during spring tide when river discharge was also high. During spring tide, silicate was 114.79-136.01µM (S) and 121.17-136.63µM (B) at S_2, while during neap tide; it was 107.77-132.10µM (S) and 108.72-132.10µM (B). Similarly, at S_6 it was 117.55-133.49µM (S) and 113.76-137.81µM (B) during spring tide, whereas it was 118.33-127.12µM (S) and 111.43-154.71µM (B) during neap tide. At the Cochin inlet, the water column was stratified and the vertical gradient in silicate was also high. Silicate (spring 47.75; neap 56.56µM) was less at the bottom than surface (spring 106.67; neap 113.81µM) and, was higher during ebb than during flood period.

During post monsoon period, the silicate levels were lowered due to reduction in the river discharge. During this period, though river discharge was more during spring, silicate was high during neap phase at S_2, S_5 and S_6. The silicate at S_6 during spring was 109.2µM (S) and 105.63µM (B) while during neap, it was 117.73(S) and 118.92µM (B). At the Cochin inlet, silicate was low in the bottom (spring 41.3; neap 21.6µM) than the surface (spring 86.8; neap 48.2µM). Since the intrusion of salt water during neap period was extended up to $S_{4,}$ there was considerable reduction in silicate levels at the S_4 bottom during neap. The average silicate observed at S_4 during spring tide was 104.5µM (S) and 106.52 µM (B), while during neap tide it was 106.94µM (S) and 79.14 µM (B).

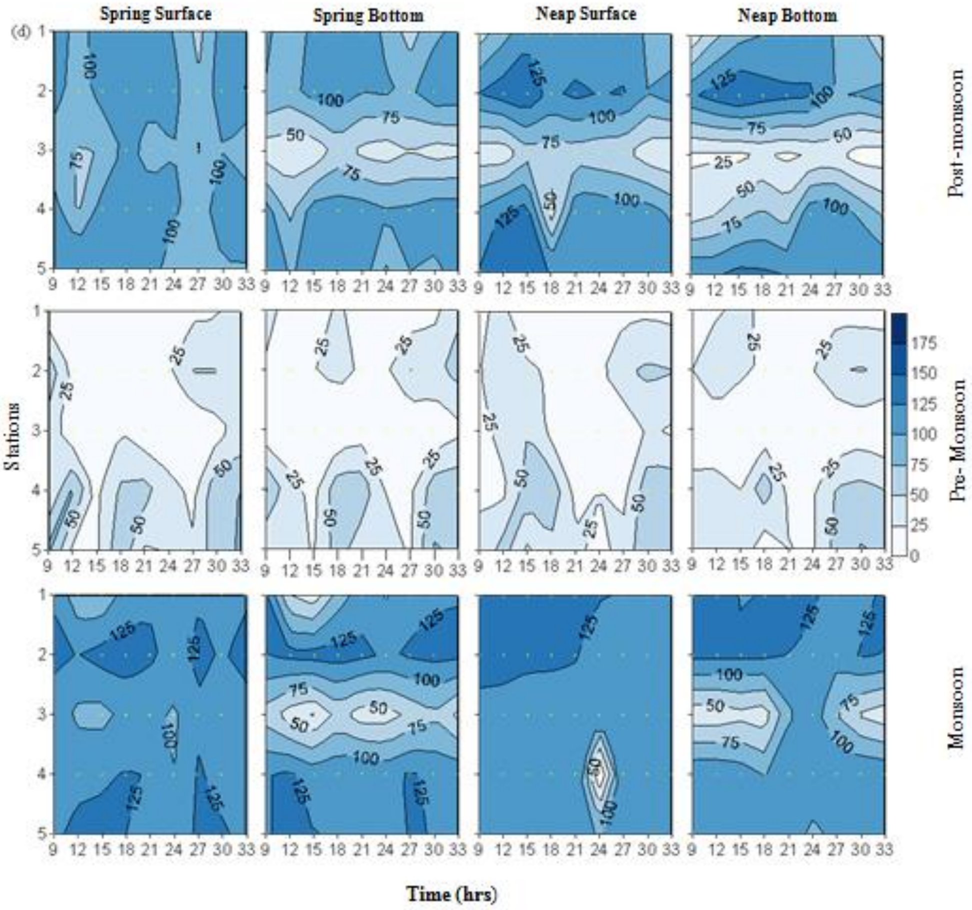

Fig 2.13: Diurnal variation in Silicate (µM) in Cochin estuary during three seasons. The stations S_1 to S_5 are represented by number 1 to 5.

During pre-monsoon, as the tidal activity increased, the salinity at S_1 and S_2 during both tides increased as compared to S_4 and S_5, while the silicate levels decreased. Since the sea water incursion was not strong enough to mask the fresh water flow, silicate concentration at S_6 increased in the surface during spring tide when river discharge increased.

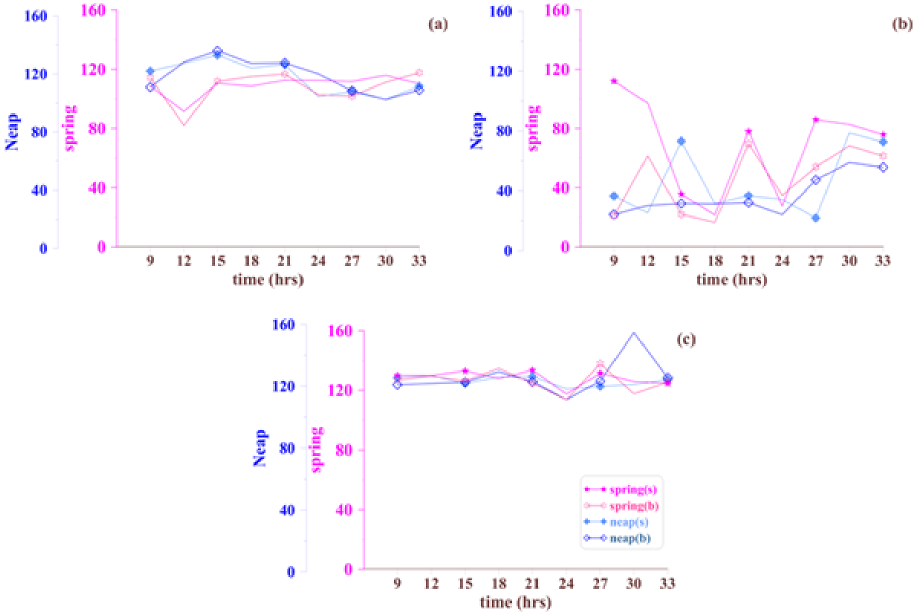

Fig 2.14: Diurnal variation of silicate at S_6 (northern upstream) during different seasons (a) Post Monsoon, (b) Pre Monsoon, (c) Monsoon.

The average silicate levels at S_6 were 68.5µM (S) and 45.5µM (B) during spring while it was 45.6µM (S) and 37.2µM (B) during neap. At the southern upstream (S_5), since the water column was isohaline (~10), the silicate at both surface (41 - 45.9µM) and bottom (40.5 - 42.7µM) were slightly lower than its concentration in the northern upstream (except at bottom during neap phase).

2.4.7 Phosphate-P

Phosphorus is a major nutrient regulating the growth and production of phytoplankton. Natural sources of phosphates include phosphate-containing rocks and solid or liquid wastes. It enters the estuary through fertilizers, industrial effluents and cleaning compounds. Its concentration helps to predict the total biomass of phytoplankton. The form of phosphorus involved in the biogeochemical processes is the phosphates. Estuarine sediments are generally rich in phosphorus which may be liberated to overlying waters under favorable conditions.

Fig 2.15 depicts the diurnal variation of phosphate along the channel S_1-S_5 in Cochin estuary during three different seasons. The diurnal variation of phosphate in S_6, northern upstream was represented in Fig 2.16. A marked spatial variation in phosphate was evident from the observation. During monsoon, the entire estuary showed moderate level of phosphate (spring 0.29-4.83: neap 0.12-4.85µM), the low concentrations towards the upstream (S_5 & S_6). The average phosphate concentration at northern upstream, S_6 was 0.69µM (S) and 0.92µM (B) during spring tide, while it was high 1.15µM (S) and 1.20µM (B) during neap tide. In the south estuary $S_{5,}$ phosphate was consistently low (0.19-0.53µM) irrespective of tidal variation. During monsoon (spring), PO_4 was slightly higher (2.15-3.12µM) at S_2 via external input, while it was high at minor inlet S_1 along with high nitrate and silicate during neap indicating higher river input. It's obvious that phosphate at the major inlet (with pH >7.7) was lower in the bottom (spring 1.50; neap 1.71µM) than at the surface (spring 2.09; neap 2.08µM) due to its sea water origin. As the minor inlet is shallow (~2.5m), the phosphate at bottom (spring 1.97; neap 1.86µM) is higher than at surface (spring 1.50; neap 1.80 µM) due to churning of sediments. During peak monsoon, the discharge through Muvattupuzha River and non-point sources from small tributaries/canals and sewage inputs added more phosphate to S_4 (pH 6.6-7.4) to increase the concentration to 1.56-2.53µM.

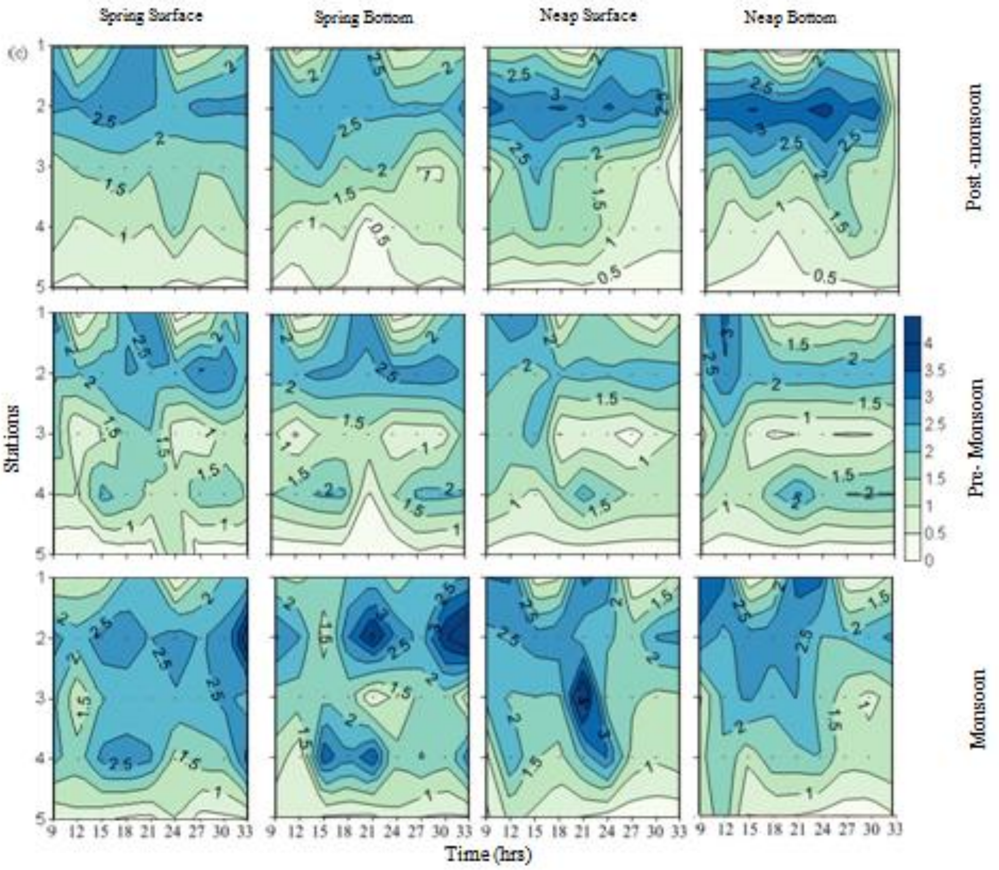

Fig 2.15: Diurnal variation of phosphate(µM) in Cochin estuary during different seasons. The stations S_1 to S_5 are represented by number 1 to 5.

During post monsoon period, the phosphate levels in the estuary varied from 0.18 to 3.2µM during spring and from 0.17 to 3.9µM during neap phase. There was phosphate enrichment at S_2 (3.9µM), S_1 (2.5µM) and S_3 (2.0µM) during neap tide. The variation in the phosphate concentration, especially at S_2 could be due to increased re-suspension or domestic discharge. Desorption of sediment phosphorus at higher salinity has been reported for the Cochin estuary (Rajagopal, 1974; Martin et al., 2008; Gireesh et al., 2013b). There are several aquaculture fields near S_2, where ammonia and phosphorus compounds are used to destroy the predators (Kartha and Karunakaran Nair, 1980). As a result, the N/P ratio in this region was low (<10) compared to its average estuarine value of 25.

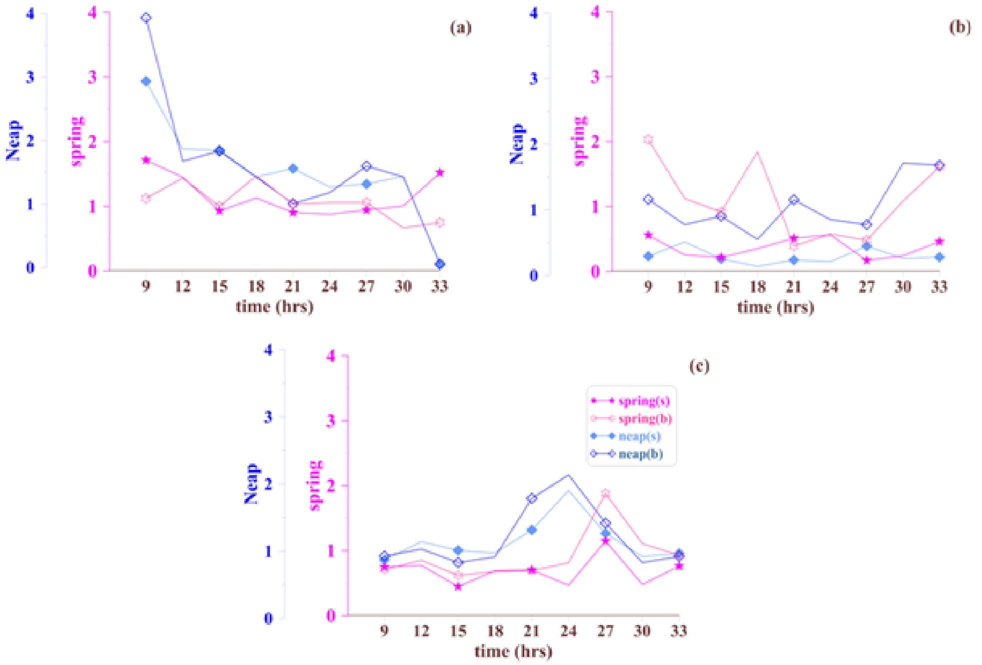

Fig 2.16: Diurnal variation of phosphate at S_6 (northern upstream) during different seasons (a) Post Monsoon, (b) Pre Monsoon, (c) Monsoon.

Phosphate concentration in the estuary is strongly controlled by the pH during pre-monsoon season. It is apparent that phosphate concentration is low at pH < 6.9 (station S_5) due to adsorption to suspended particles. The phosphate concentration at S_5 during spring and neap tides were 0.03-1.48µM and 0.09-0.36µM, respectively. Phosphate was high in waters above pH 7 (S_1, S_2, S_4) following its release from particles into water column.

2.5 NUTRIENT FLUXES

The input and export fluxes of nutrients through Cochin estuary during 2 successive tides of peak summer monsoon are depicted in Fig 2.17.

During peak summer monsoon, the fluxes of all nutrients through southern upstream was high during spring phase corresponding to increased river discharge through southern rivers, however the fluxes of all the nutrients (except NH_4) through northern upstream was high during neap phase. The river discharge through Periyar was more or less similar during spring (196.7m3/s) and neap (196.4m3/s) tides, but there was an increase in the nutrient fluxes across the northern upstream (S_6) during neap phase, due to enrichment of these nutrients (nitrate, nitrite, silicate and phosphate) in the source water. However, the ammonia flux was high during spring tide due to its enriched levels.

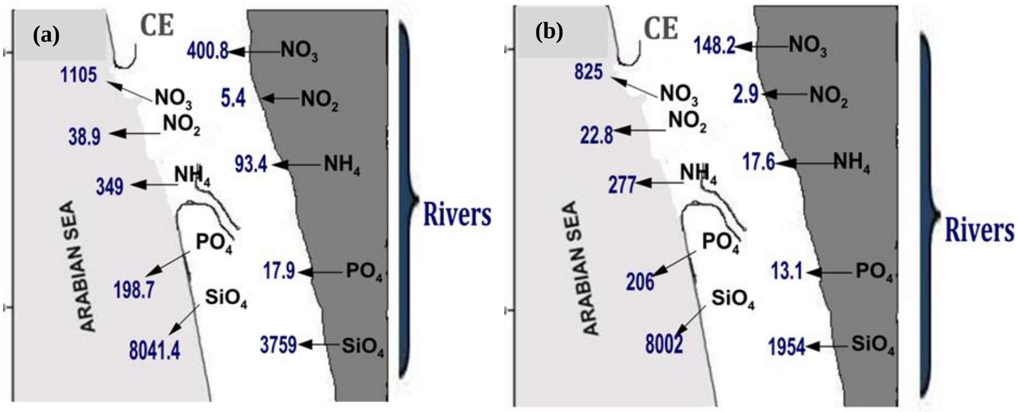

Fig 2.17: Input and export fluxes of nutrients (tons/day) through Cochin estuary during summer monsoon (a) spring tide (b) neap tide.

The flux estimation reveals that the Cochin estuary receives 21.42 tNO_3, 0.39t NO_2, 0.30t PO_4, 96.67t SiO_4 and 7.41t NH_4 from northern upstream each day during spring phase and 29.25t NO_3, 0.48t NO_2, 1.63t PO_4, 140.01t SiO_4 and 5.87t NH_4 per day during neap phase of summer monsoon. The south of the estuary received high freshwater input, which increased the nutrient input during spring phase (379.4t NO_3; 5.06t NO_2; 85.94t NH_4; 17.68t

PO_4 & 3662.94t SiO_4) and neap phase (118.95t NO_3; 2.38t NO_2; 11.70t NH_4; 11.46t PO_4 & 1813.93t SiO_4), which was very high compared to the fluxes from the northern upstream (Table 2.1).

Table 2.1: Nutrient fluxes (td^{-1}) through Cochin estuary during peak summer monsoon (a) spring phase & (b) neap phase

Variables	Input through Periyar (t/d)	Input through southern rivers (t/d)	Net input (t/d)	Export through minor inlet (t/d)	Export through major inlet (t/d)	Net export (t/d)	Net flux (t/d)
(a) spring tide							
NO_3-N	21.4	379.4	400.8	20.6	1085.0	1105.5	704.7
NO_2-N	0.4	5.1	5.4	0.4	38.5	38.9	33.4
NH_4-N	7.4	85.9	93.4	10.1	339.2	349.3	255.9
DIN	29.2	470.4	499.6	31.0	1462.6	1493.6	994.0
PO_4	0.3	17.7	18.0	4.3	194.4	198.7	180.7
SIO_4	96.7	3662.9	3759.6	198.7	7842.6	8041.4	4281.8
(b) Neap tide							
NO3-N	29.2	118.9	148.2	11.6	812.9	824.5	676.3
NO2-N	0.5	2.4	2.9	0.3	22.5	22.8	20.0
NH4-N	5.9	11.7	17.6	2.5	274.8	277.3	259.7
DIN	35.6	133.0	168.6	14.5	1110.1	1124.6	956.0
PO4	1.6	11.5	13.1	3.9	202.5	206.4	193.3
SIO4	140.0	1813.9	1953.9	105.6	7896.5	8002.1	6048.2

Negative sign for input and export fluxes denotes landward fluxes and positive sign denotes seaward fluxes.
Negative sign for net flux represents net removal and positive sign represents net addition of nutrients other than riverine.

During spring tide, as the freshwater discharge into the estuary (through 6 rivers) was high, more freshwater reached the inlet and the estuary flushes out more nutrients during spring phase (except PO_4 & SiO_4). The export fluxes through the Cochin inlet during spring and neap tides was (1085 & 812.9)t NO_3, (38.5 & 22.5)t NO_2, (339.2 & 274.8)t NH_4, (194.4 & 202.5)t

PO_4 and (7842.6 & 7896.5)t SiO_4 per day. The corresponding fluxes through minor inlet (S_1) were relatively low (20.56 & 11.63)t NO_3, (0.41 & 0.31)t NO_2, (10.05 & 2.52)t NH_4, (4.29 & 3.88)t PO_4, (198.73 & 105.62)t SiO_4 per day.. The net fluxes through Cochin estuary was calculated as the difference in the input and export fluxes (input-export). It should be noted that during monsoon period, the estuary exported 704.7, 33.43, 255.9, 180.73 and 4281.8 tons of NO_3, NO_2, NH_4, PO_4 and SiO_4 respectively per day during spring tide and 676.3, 19.95, 259.7, 193.31 and 6048.15 tons of NO_3, NO_2, NH_4, PO_4 and SiO_4 per day during neap tide. The total export of nutrients is greater than the river input, indicating the internal processes (nonpoint sources) to be quite significant in the estuary during monsoon period.

Despite a higher input of nutrients during post monsoon, the export of nutrients from the Cochin estuary was high during monsoon, possibly due the increased monsoonal flushing. The nutrient inputs from southern rivers were higher than from the northern river (River Periyar). The input and export fluxes of nutrients through Cochin estuary during post monsoon are depicted in Fig 2.18. During post monsoon spring, the Cochin estuary received 444, 7.7, 64.6, 22.2 and 4149.9tons of NO_3, NO_2, NH_4, PO_4 and SiO_4 and exported 485, 16.6, 90.4, 85.5 and 3922 tons of NO_3, NO_2, NH_4, PO_4 and SiO_4 per day (Table 2.2). Similarly, during neap tide, the input and export fluxes varied from 383 to 468t DIN, 11 to 97t PO_4 and 3109 to 2476t SiO_4. To sum up, there was a net export of nutrients (except SiO_4) during post monsoon, while SiO_4 was retained in the estuary.

It is evident that between successive spring and neap tides, there was an increase in the net fluxes (Input-Export) of phosphate 63.3 to 86.6t, ammonia 25.8 to 43.1t and DIN 76.4 to 85.8t except for nitrate 41.7 to 35.8t, whereas silicate showed substantial removal during spring (-227t) and neap (-633t) phases.

Table 2.2: Nutrient fluxes (t/d) through Cochin estuary during post monsoon during (a) spring phase (b) neap phase

Variables	Input through Periyar (t/d)	Input through southern rivers (t/d)	Net input (t/d)	Export through minor inlet (t/d)	Export through major inlet (t/d)	Net export (t/d)	Net flux (t/d)
(a) Spring							
NO_3-N	74	370	444	26	459	485	41.7
NO_2N	1.64	6.08	7.7	0.61	16	16.6	8.9
NH_4-N	15.5	49.11	64.6	5	85.37	90.4	25.8
PO_4	7	15.18	22.2	5	81	85.5	63
SiO_4	636.1	3513	4149	173	3749.8	3923	-227
(b) Neap							
NO_3-N	55	22	280.6	8.28	308.12	316.4	35.8
NO_2-N	1.06	3.1	4.14	0.26	10.8	11.1	6.9
NH_4-N	24.6	73.1	97.7	6.5	134.3	140.8	43.1
PO_4	3.9	7.2	11.1	1.04	96.7	97.7	86.6
SiO_4	298.8	2810.8	3109	78.5	2398.1	2476	-633

Negative sign for input and export fluxes denotes landward fluxes and positive sign denotes seaward fluxes

Negative sign for net flux represents net removal and positive sign represents net addition of nutrients other than riverine.

During spring phase, the net nitrate flux was high due to well stratified condition following high river flow. However, higher fluxes of PO_4 and NH_4 during neap phase when the freshwater flow diminished could be due to the high concentration of these nutrients in the estuary. The water column during neap phase was vertically mixed at the Cochin inlet, which increased the export of phosphate and ammonia.

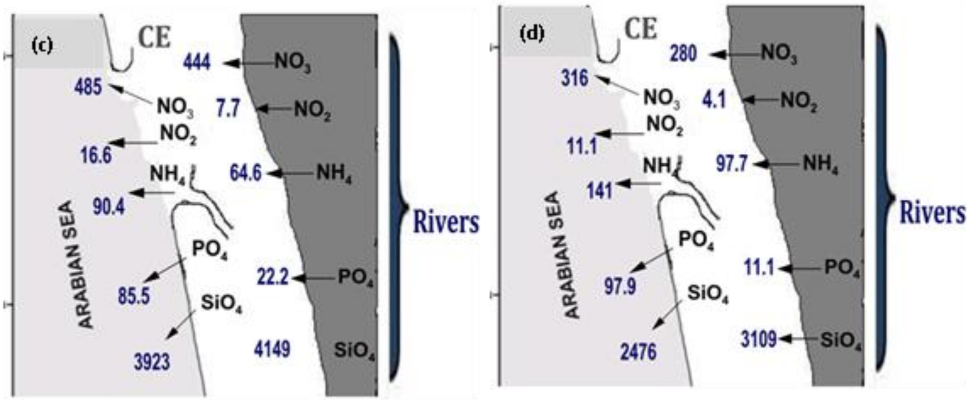

Fig 2.18: Input and export fluxes of nutrients (tons/day) through Cochin estuary during post monsoon (c) spring phase (d) neap phase.

The input and export fluxes of nutrients during the pre-monsoon are depicted in Fig 2.19. The input of nutrients through rivers was relatively low due to reduced freshwater flow. The nutrient input during spring phase was slightly higher than during neap phase as freshwater input during spring period was relatively higher. The concentration of nutrients at S_6 was higher than at S_5 during this period. As the tides were towards upstream during neap, the input fluxes of inorganic nitrogen (DIN) and silicate from the north estuary was considerably low compared to its fluxes from the south estuary (Table 2.3). Input of nitrate, nitrite, ammonia and silicate was 7.40, 0.21, 7.85 and 29.77 tons from the north estuary and 14.35, 0.41, 13.50 and 134.44 tons from the south estuary during spring tide. The phosphate flux was higher from the north than south due to its higher concentration in the north. Approximately 1.13t of phosphate has entered the estuary from north estuary, while its input from the south estuary was negligible during pre-monsoon spring.

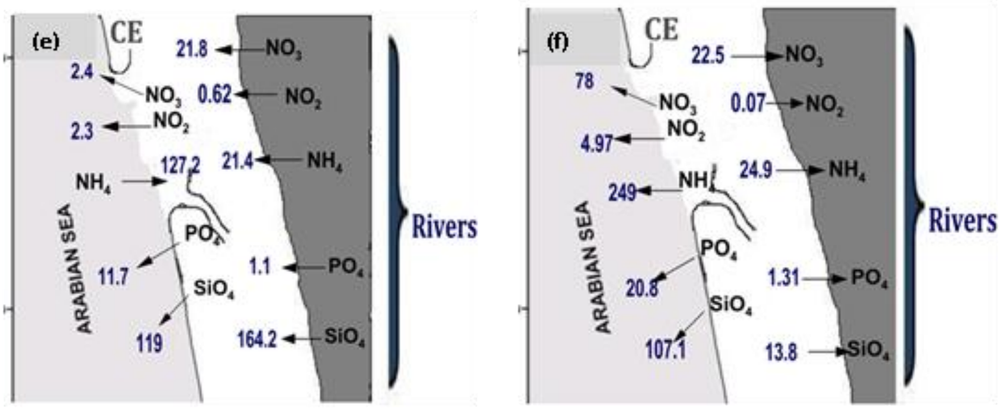

Figure 2.19: Input and export fluxes of nutrients (tons/day) through Cochin estuary during pre-monsoon (e) spring phase (f) neap phase.

Even though freshwater discharge was relatively high during pre-monsoon spring than neap, the nutrient delivery was less due to increased tidal activity and landward flow at the Cochin inlet to reduce the nutrient export. However, the export of nitrate (2.5t), nitrite (2.2t), and silicate (93.4t) through Cochin inlet was several times higher than their respective fluxes through the minor inlet (0.12t NO_3, 0.11t NO_2 & 25.38t SiO_4) during spring phase. The input of NO_3 and SiO_4 during pre-monsoon spring exceeded their export fluxes, indicating their estuarine removal (19.35t NO_3, and 45.42t SiO_4). .Nitrate is normally consumed by phytoplankton, while the removal of silicate can be through biological uptake as well as adsorption on to suspended particles (Balachandran et al., 1999). However, the export fluxes of NO_2 and PO_4 during pre-monsoon spring was greater than their input fluxes resulting in a net export of 1.64t NO_2 and 10.67t PO_4. The net export of phosphate is due to desorption of phosphorus at high pH and salinity (Chambers et al., 1995). The high pH probably favors the sorption of Si to and release of P from sediment, as both reactions were competing for the same anion exchange sites at the inlet (Koski et al., 2001). Thus, SiO_4 is retained in the estuary due to its burial in the sediment. The magnitude of P release also depends on the amount of Fe and Al oxides in the sediment. The enrichment of nitrite in the south estuary resulted in its net export.

Table 2.3: Nutrient fluxes (t/d) through Cochin estuary during pre-monsoon: (a) Spring tide (b) neap tide.

Variables	Input through Periyar (t/d)	Input through southern rivers (t/d)	Net input (t/d)	Export through minor inlet (t/d)	Export through major inlet (t/d)	Net export (t/d)	Net flux (t/d)
(a) Spring tide							
NO3-N	7.4	14.35	21.75	-0.12	2.5	2.39	-19.35
NO2-N	0.21	0.41	0.62	0.11	2.2	2.26	1.64
NH4-N	7.85	13.5	21.35	5.66	-132.9	-127.24	*148.58
DIN	15.46	28.25	43.71	5.65	-128.3	-122.65	*166.36
PO4	1.13	-0.07	1.05	1.67	10.1	11.72	10.67
SIO4	29.77	134.44	164.21	25.38	93.4	118.79	-45.42
(b) Neap tide							
NO3-N	-21.56	-0.96	-22.51	-3.1	81.13	78.03	100.55
NO2-N	-0.62	0.55	-0.07	0.09	4.88	4.97	5.04
NH4-N	-13.65	-11.2	-24.85	3.31	245.68	248.99	273.84
DIN	-35.83	-11.6	-47.43	0.3	331	331.3	378.73
PO4	-1.37	0.06	-1.31	0.69	20.06	20.75	22.05
SIO4	-76.54	62.79	-13.75	-0.97	108.07	107.1	120.85

Negative sign for input and export fluxes denotes landward fluxes and positive sign denotes seaward fluxes

Negative sign for net flux represents net removal and positive sign represents net addition of nutrients other than riverine.* denotes additional input from the adjacent coast.

At the Cochin inlet, the landward (negative) fluxes of NH_4 indicate a daily net import of 148.6t NH_4 in the estuary. High concentrations of NH_4 during flood period were responsible for the negative fluxes during spring. The source of ammonia in the coastal waters may be the re-mineralization in the sediment (Dunn et al., 2008). Studies have shown that the nutrient requirement for phytoplankton production over the western Indian inner shelf is met by benthic regeneration of ammonia (Naqvi et al., 2006; Pratihary et al., 2014). This ammonia-rich water has likely adverted in to the estuary due to strong flood currents (Vinita et al., 2015).

During pre-monsoon (neap), the river flow was considerably reduced and the fluxes of nutrients through northern rivers were negligible and directed landward. However there was riverine input of nitrite, silicate and phosphate in to the estuary through the south estuary during this period. Since the tidal activity was slightly lowered during neap there was a net export of all the nutrients at the major inlet. The net export during neap was 100.5t NO_3, 5.04t NO_2, 273.8t NH_4, 22.05t PO_4 and 120.85t SiO_4 per day. The maximum fluxes were for NH_4 and minimum for NO_2. The residual fluxes at Cochin inlet showed an ebb dominance, as the ebb currents could transport nutrients into the sea even during pre-monsoon (Vinita et al., 2015b).

2.5.1 Nutrient fluxes - a comparison with other estuaries

A comparison is made here on the net nutrient fluxes for Cochin estuary with other Indian estuaries such as Chaliyar, Tapi, Hoogly and Meghna (Table 2.4). Flux studies in Chaliyar estuary reported a net transport of nitrogen into the sea during wet and into the river during dry period (Xavier et al., 1993). The Meghna estuary exhibited a net addition of nutrients (Uddin et al., 2014), while Tapi estuary showed a net removal of P and N (Bapardekar et al., 2004) and Hoogly estuary showed a net removal of SiO_4 (Mukhopadhyay et al., 2006). Cochin estuary showed a net addition of nutrients during wet and a net removal (SiO_4 and NO_3) during dry periods. The N fluxes of our system were very high compared to the fluxes through other estuaries. However, the N and P fluxes during monsoon were comparable with that of the Hoogly estuary. The N fluxes during pre-monsoon were higher than for the Meghna estuary while it was comparable during monsoon and post monsoon periods. The P fluxes from Cochin estuary was lower than that reported for Meghna estuary.

Table 2.4: Non-conservative/net fluxes (± Δ)td^{-1}for different estuaries in India.

Indian estuaries	Δ P	Δ SiO_4	Δ NO_3	Δ NO_2	Δ NH_4	Δ DIN	Location	Reference
Tapi	-17.3					-63.7	Madypradesh	Bapardekar et al., 2004
Hoogly	10.7	-84.9				67.7	West Bengal	Mukhopadhyay et al., 2006
Meghna (Pre)	337.0					28.5	Bangladesh	Uddin et al., 2014
Meghna (Mon)	690.3					79.7	,,	,,
Meghna (Post)	3370.9					1026.6	,,	,,
Chaliyar			-0.1			-0.2	Kerala	Xavier et al., 1993
CE (Pre: spring)	10.7	-45.4	-19.4	1.6	-148.6	-166.4	Kerala	Present study
CE (Pre: Neap)	22.1	120.9	100.6	5.0	273.8	378.7	,,	,,
CE (Mon: spring)	63.0	-227.0	41.7	8.9	25.8	76.0	,,	,,
CE (Mon: Neap)	86.6	-633.0	35.8	6.9	43.1	85.0	,,	,,
CE (Post: spring)	180.7	4281.8	704.7	33.4	255.9	994.0	,,	,,
CE (Post: Neap)	193.3	6048.2	676.3	20.0	259.7	956.0	,,	,,

CE – Cochin estuary

2.6 SUMMARY AND CONCLUSION

This is the first attempt to quantify the fluxes of nutrients from the Cochin estuary into the sea. The fresh water flow and tidal activity are found to regulate the distribution of salinity and nutrients in the Cochin estuary. There was stratification in the lower estuary during summer monsoon and post monsoon periods, whereas it was transformed into a well-mixed condition during pre-monsoon. The seawater incursion into the estuary was limited to the lower estuary during monsoon (spring tide), while it reached upto Arookutty (22 km south of the inlet) during post monsoon (lowered freshwater flow). During pre-monsoon, the entire estuary changed to homogenous condition with complete vertical mixing. The influence of freshwater discharge was well reflected in the salinity structure during the spring-neap phases.

Depletion in dissolved oxygen in the north estuary (S_6) during pre-monsoon was due to heterotrophic re-mineralization, while upwelling was responsible for the low DO at the inlet during monsoon and post monsoon periods. The intrusion of oxygen deficient waters coupled with heterotrophic re-mineralization has reduced the DO at S_4. An increase in dissolved oxygen was observed towards southern upstream (Thanneermukkam).

The most abundant inorganic form of nitrogen in the Cochin estuary, nitrate, was high at S_6 (Varapuzha). During pre-monsoon, ammonia was abundant at certain locations like Nedungad, Cochin inlet and Thanneermukkam. At Nedungad, ammonia was relatively high due to greater uptake of nitrate by phytoplankton. Nitrite was high in oxygen deficient waters, which decreased towards upstream. During low discharge period, bacteria mediated nitrification increased the nitrite levels in the south estuary.

The estuary showed high ammonia in the surface indicating its fresh water contribution. It was generally high during ebb tide and low during flood tide at the inlet, however during pre-monsoon neap; it was high during flood tide. The concentration of ammonia generally increased when dissolved oxygen decreased and vice versa. Thus, the lowest ammonia was recorded at southern upstream containing saturated dissolved oxygen. Higher ammonia along with the oxygen deficiency at Varapuzha (bottom) during dry season may be due to heterotrophic re-mineralization. At Nedungad (S_2), DO was saturated and ammonia was high indicating a maximum uptake of nitrate by phytoplankton. The high chlorophyll*a* coinciding with low nitrate are indications of productive waters at S_2.

The entire estuary showed moderate levels of phosphate, while south estuary showed minimum levels, which also showed high photosynthetic activity. Adsorption of P to suspended particles is likely in this region due to slightly acidic waters ($pH < 6.9$). The phosphate was maximum at Nedungad (S_2), possibly due to external inputs. In general, the phosphate distribution in the Cochin estuary is mostly controlled by the tidal activity, pH, river discharge and external inputs (sewage, agricultural activity and industrial effluents). The adsorption and desorption of P follows a buffering mechanism to regulate the phosphate concentrations in estuaries (Tallberg et al., 2000).

The major source of silicate in the estuary was the freshwater input. Silicate concentration was high during spring than neap period and showed an inverse trend with salinity. Silicate was slightly higher in the northern upstream than the southern upstream.

The transport of nutrients was generally directed seaward except for pre-monsoon (spring), when they were landward due to increased tidal forcing. The input of nutrients from the south estuary was several times higher than their respective fluxes from the north estuary, especially during post monsoon period. However, there was an import of NH_4 during pre-monsoon (spring) from the adjacent coastal region. The export was maximum during monsoon following increased freshwater flow. The export of nutrients during monsoon could also be due to the addition of nutrients other than rivers. The SiO_4 flux was maximum during monsoon, though it was substantially removed during estuarine mixing. There was net export of all the nutrients (except SiO_4) during post monsoon with maximum net flux for PO_4. While SiO_4

retained within the estuary. The adsorption of SiO_4 on to particles at higher pH at the inlet can be the reason for net removal during post monsoon. During pre-monsoon, the estuary showed a net export during neap because the net water flow was into the sea. However during spring phase, the estuary showed a net addition for NO_2 and PO_4 and a net removal for NO_3 and SiO_4. The maximum addition of PO_4 in the estuary occurs during post and pre-monsoon periods. The high pH might promote the sorption of Si to and release of P from sediment leading to a net burial of Si and release of phosphate in the estuary during post and pre monsoon period. The removal of NO_3 during pre-monsoon spring was related to uptake by planktons (high chlorophyll *a*). It is apparent that the intra-tidal and spring-neap variations in the nutrients were well reflected in the net transport of nutrients through the Cochin inlet.

There was a reduction in the net fluxes of nutrients from spring to neap phases of monsoon due to variations in the river discharge. However, the net fluxes of phosphate and ammonia during post monsoon were high during neap compared to the spring period, because there was an increase in their ambient concentrations during the former period. The flux of all nutrients decreased considerably during pre-monsoon (spring) period, probably due to the relatively low nutrient concentration and the reduction in the flushing characteristics.

The present study shows that Cochin estuary is a source of all nutrients during monsoon and a sink for SiO_4 during post and pre monsoon. The removal (15-20%) of SiO_4 during post-monsoon was coincided by a net addition of N and PO_4. During pre-monsoon spring, 88.9% of NO_3 and 27.6% of SiO_4 was removed from the estuary due to biogeochemical processes. It has been estimated that approximately 148.6tons of NH_4 was retained in the estuary as an additional input from coastal region. In view of this, Cochin estuary is a small source of nutrients to the adjacent coastal region.

The spring neap tidal oscillations play an important role in net transport of materials across the Cochin estuary during pre-monsoon, whereas freshwater discharge plays a major role during monsoon. During post monsoon, both freshwater discharge and tidal activity together controls the net transport. The internal processes such as nitrification, heterotrophic re-mineralization, and adsorption-desorption, stratification etc played important roles in the organic enrichment in the Cochin estuary (Gupta et al., 2009; Shoji et al., 2008; Gireesh et al., 2013a). The organic matter influences the metabolic functions and nutrient transports of estuaries. The upwelling and benthic regeneration are other important processes in the inlet region. Present study shows that despite a moderate utilization of nutrients, substantial amount of nutrients are exported from the Cochin estuary, especially during peak summer monsoon. The nutrients were generally high during this period due to intense rain fall and river flow. The six rivers are generally connected to numerous channels in the estuary, which gather more nutrients on their course. However, the high run off maintains a better flushing of the estuary to regulate the nutrient balance and safe guard the estuary from wide spread eutrophication.

The present estimates of nutrient fluxes from Cochin estuary was higher than some estuaries (Chaliyar and Tapi estuary), but comparable with that of Hoogly and Meghna estuaries. The P fluxes observed for Cochin estuary is extremely lower than that reported for Meghna estuary and comparable to that reported for Hoogly river estuary.

The significance of the study is that the export fluxes from the Cochin estuary could be a major factor sustaining the spectacular monsoon fishery along the southwest coast of India. The Cochin estuary seems to be a source of nutrients to the adjacent coastal areas, as evidenced by the increased productivity and frequent occurrences of blooms in the adjacent coastal areas, even during dry season (Madhupratap et al., 1987; D'Silva et al., 2012). The eutrophication in coastal waters to a certain extent increase the fishery production however as a consequence of monsoon upwelling, when the hypoxia intensify over the western India shelf, the pelagic and benthic fishes tend to the surface layers to avoid oxygen deficient waters. Thus controlling nutrient input from estuary is of important for achieving a healthy coastal environment.

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Chapter 3

FRACTIONATION OF TRACE METALS IN SEDIMENT

Contents

3.1 INTRODUCTION

Over the past five decades, there has been a rapid increase in the human settlement along the coastal regions globally. As a consequence, many coastal and estuarine systems have been severely affected by encroachment and environmental deterioration. Trace metal contamination was one of the important factors that have lead to widespread environmental contamination (Nriagu and Pacyna, 1988). The behavior of trace metals in aquatic medium depends on the environmental conditions, which in turn, activate their speciation and reactivity (Bruland and Lohan, 2003). It is already established that sediments are the ultimate sink of all trace metals entering an aquatic system and is a reliable indicator of natural process and anthropogenic activities (Forstner, 1981; Szefer, 2002). Therefore, quantification of trace metal input is an essential requirement for environmental monitoring.

Sediment is a complex heterogenous matrix comprising minerals and organic matter. The minerals present are usually weathering rock fragments and secondary minerals such as phyllosilicates or clay minerals, oxides of Fe, Al, and Mn and sometimes carbonates (usually $CaCO_3$). The organic matter may comprise of living organisms (mesofauna and microorganisms), dead plant/plankton materials (litter) and humic substances. The mobility of trace metals in sediments is controlled by the prevailing biogeochemical processes influenced by early digenesis such as sorption, precipitation, dissolution, advection, diffusion, bio-irrigation and bio-turbation etc. The organic matter facilitates early diagenesis (Rullkotter, 2002) and impact chemical speciation of metals by complexation (Luther III et al., 2001; Louis et al., 2009; Dang et al., 2014). At sediment-water interface, reductive dissolution of Fe-Mn oxyhydroxides facilitating remobilization of initially bound trace metals and scavenging of metals by newly formed Fe-Mn oxyhydroxides are the major processes (Gao et al., 2009; Scholz and Neumann, 2007).

Concentration of trace metal in sediment is an indicator of elemental contamination of a region; though it does not help to identify its bioavailability (Sundaray et al., 2011). This is because trace metals exist in different chemical forms within the sediments with different mobility and toxicity. Since the bioavailability of a metal ion depends on its chemical form in aqueous medium (Jain et al., 2004), understanding the mechanism of its geochemical distribution and fractionation is essential to minimize its pollution potential in estuarine and coastal area.

Cochin estuary (CE), located along the south west of India, is composed of a complex system of shallow network of canals spread over more than 256 km^2 (Qasim, 2003). The estuary is micro-tidal (amplitude ~ 1m) and the seasonal salinity distribution is largely influenced by the seawater intrusion and freshwater runoff (Revichandran et al., 2011). Depending upon the degree of mixing between the freshwater and saltwater, there is a progressive seasonal shift in the estuarine hydrography from a stratified (monsoon) to a partially mixed (post-monsoon) and well-mixed (pre-monsoon) conditions (Sankaranarayanan et al., 1986; Shivaprasad et al., 2013). The bathymetry varies considerably from 10-13 m in the shipping channels to approximately 2-7 m in other parts of the estuary (Menon et al., 2000). The region annually receives about 320 cm rain, of which, nearly 75% occurs during June to September.

There are mainly six rivers debouching ~ 2 x $10^9 m^3$ of freshwater into the estuary annually (Srinivas, 2000). Approximately, 33 % of the total fresh water discharge is through the River Periyar, which is the life line of the estuary. The estuary exhibit wide variation in its flushing time from ~ 1-2 days during monsoon to ~ 8-9 days during pre monsoon (Vinita et al., 2015a). The low lying swamps and tidal creeks with patches of mangroves support the breeding and growth of larvae and juveniles of many economically important species in the estuary (Jyothibabu et al., 2006). The estuary is known as a nursery ground of commercially important prawns and fishes (Gopalan et al., 1983). The fields around the estuary are suitable for aquaculture, as they support traditional, seasonal and perennial prawn fishery.

A systematic change over the last five decades like shrinkage of the estuary due to reclamation (Gopalan et al., 1983) and increased discharge of pollutants have made an adverse impact on the environmental degradation of the estuary (Qasim and Madhupratap, 1979; Menon et al., 2000). Approximately 70% of Kerala's industries (fertilizer, pesticide, radio-active mineral processing, chemical and allied industries, petroleum refining and trace metal process and fish processing) are located along the banks of River Periyar.

It is estimated that nearly 0.104Mm^3 of industrial and 260 tons of domestic wastes reach the Periyar River daily from the Kochi industrial belt (Balanchandran et al., 2006). The effluents from these industries contain organics, alcohols, ammonia, nitrates, phosphorous, trace metals such as Cd, Hg, Cr, Zn, Pb, Cu and rare earth element products, suspended solids, radiologicals, chlorides of metals, pesticides etc (Manju and Sujatha, 2012). A long term assessment of trace elements in the northern estuary (Balachandran et al., 2005) remarked an expanse of 18 times in Zn and 9 times in Cd level. There are so many reports showing the enrichment of Pb, Cd and Zn in the estuarine sediments (Balachandran et al., 2002: 2005: 2006; Kumar et al., 2010; Akhil et al, 2014; Manju and Sujatha, 2012; George et al., 2016; Renjith et al., 2016; Salas et al., 2017).

The present study was mainly focused on the Cochin Estuary and the adjoining coastal marine environment (Fig 3.1), which experiences two distinct regimes of alluvial loading: an export of sediment from the estuary during the dynamic season (monsoon) followed by silting environment during the remaining period (Nair et al., 1993). Geochemical studies have also shown that there is a shift in the sediment characteristics from kaolinite dominant rivers and estuary to a fine-grained montmorrilonite on the coastal shelf (Nath et al., 2000). The montmorrilonite are thus, responsible for a greater accumulation of organic matter in the coastal environment due to their large surface area. The organic matter input to the Cochin estuary is primarily from terrigenous and lateral sources during monsoon; though there may be a contribution from the sea during the post and pre-monsoon periods (Gireeshkumar et al., 2013a).

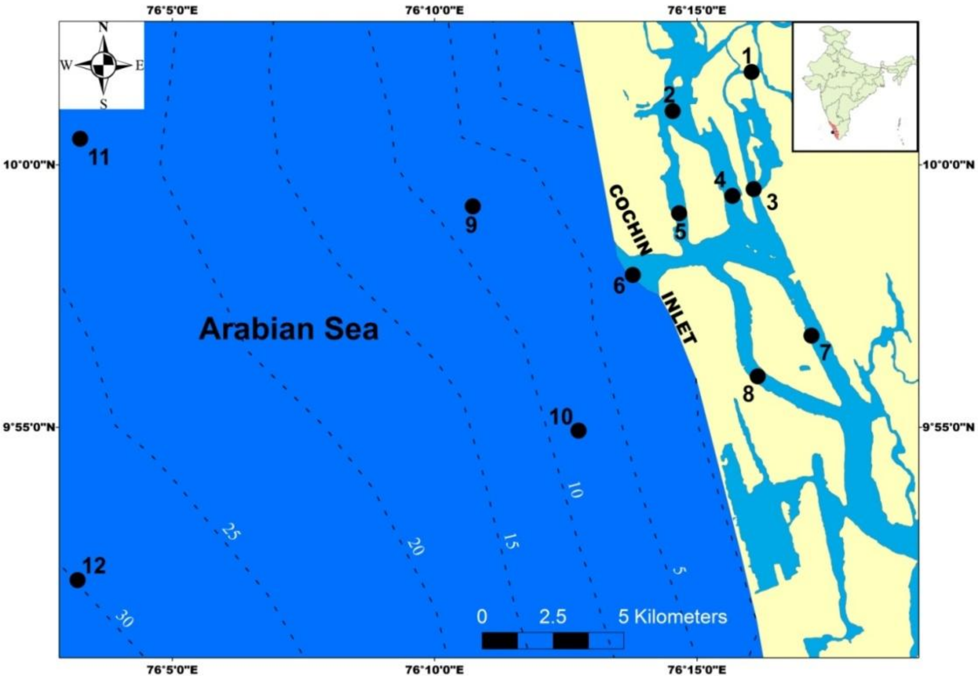

Fig 3.1: Map of the study area showing locations of sampling sites

Trace metal accumulation in the sediments of Cochin estuary is influenced by the intense anthropogenic activities, complex morphology (Manju et al., 2013) and weak flow (Balachandran et al., 2005; Thomson et al., 2002). This has eventually reduced the benthic biodiversity and increased the abundance of less tolerant species in ecologically sensitive areas in the estuary (Udayakumar et al., 2014; Martin et al., 2011). The diversity of the bio-resources in the estuary has a direct bearing on the adjacent coastal ecosystem as well (Priju et al., 2007). There has also been an enrichment of trace metals in coastal sediments during monsoon due to terrestrial loading (Balachandran et al., 2003; Manju et al., 2013; Sreekanth et al., 2015). The present study attempts to quantify the fractions of trace metals in Cochin estuary and its coastal sediments to identify the mechanism of trace metal accumulation and their mobility.

3.2 SAMPLING STRATEGY

The geographic positions of sampling stations are given in Table 3.1. In order to understand trace metal loading to the estuarine regions and its subsequent effect on coastal region, surface sediments were collected from 8 locations in the north and central estuary, in addition to the adjacent coastal stations at a depth of 5.3, 6.8, 27 and 30 m. The coastal stations at ~5 and ~27 m were located north of the Cochin inlet and stations at ~6.5 and ~30 m were located south of the Cochin inlet. The sampling was carried out during October 2011. Water sample from each locations were collected using a 5L Niskin sampler (Hydrobios Kiel). The sample for dissolved oxygen (DO) was collected without air bubbles in a glass bottle, fixed onboard and later analyzed according to Winkler's method (Grasshoff et al., 1983). Nutrients were analysed following standard procedures (Grasshoff et al., 1983). Salinity was measured using a salinometer (DIGI Auto, Model 5, Tsurumi-Seiki). Sediments were collected using a Van-veen stainless steel grab (0.042 m^2), sealed in plastic bottles, kept in ice, transported to the laboratory and stored at -20º C until analysis.

Table 3.1: Station locations in Cochin estuary and adjacent coastal region

SI No	Sampling Locations	St. code	Lat (°N)	Long(°E)
1	Moolampilly	S_1	10.0312	76.2666
2	Vallarpadam north	S_2	10.0174	76.2442
3	Bolghatty	S_3	9.9913	76.2680
4	Vallarpadam-Bolghatty bridge	S_4	9.9891	76.2607
5	Vallarpaadam-Vypeen bridge	S_5	9.9823	76.2445
6	Cochin inlet (10-15m)	S_6	9.9702	76.2415
7	Ernakulam Channel	S_7	9.9454	76.2880
8	Mattanchery channel	S_8	9.9341	76.2688
9	Near shore (5.3m)	S_9	9.9734	76.1870
10	Near shore (6.8m)	S_{10}	9.9293	76.2264
11	Off shore (27m)	S_{11}	10.004	76.0833
12	Offshore (30m)	S_{12}	9.9167	76.0833

3.3 ANALYTICAL METHODOLOGY

3.3.1 General sediment characteristics

The sediment samples were portioned into three for the analysis of total metals, organic carbon and grain size. For grain size analysis, the inorganic carbonates were removed using 10% HCl and organic matter using H_2O_2 (Folk, 1980). For texture analysis, the sediments were washed with distilled water, dried (at 30°C) and treated with sodium hexametaphosphate to disperse the sediments and the particles were separated following the pipette analysis (Krumbein and Pettijohn, 1938). Sediment organic carbon (OC) was analyzed by wet chromic acid oxidation method suggested by El Wakeel and Riley, 1957. The amount of total organic matter (TOM) was computed by multiplying the OC values with 1.80 (Muller et al., 1986).

3.3.2 Trace metal analysis

For the analysis of trace metals, the sediment samples and rock standards (MAG 1) was dried (at 60°C), powdered (mortar and pestle) and acid digested with a mixture of suprapure HF+HNO_3+$HClO_4$ (7:3:1) in Teflon vessels on a hot plate to dryness (Balaram and Rao, 2002).

Table 3.2: Trace metal concentrations (mg/kg) in Standard reference material (MAG 1) and RSD (%) in analysis and are given below.

Sl No	**Element**	**Standard Reference Material (MAG 1)**			**PAAS**
		Certified value (mg/kg)	**Observed value (mg/kg)**	**RSD (%)**	
1	Zn	130 ± 6	130 ± 0.265	0.20	85
2	Mn	710	759 ± 3.563	0.47	850
3	Cr	97 ± 8	97 ± 0.562	0.58	110
4	Ni	53 ± 8	53 ± 0.543	1.02	55
5	Cu	30 ± 3	30 ± 0.071	0.24	50
6	Co	20 ± 1.6	20.4 ± 0.164	0.82	23
7	V	140 ± 6	140 ± 1.389	0.99	150
8	Cd	0.2 ± 0.03	0.17 ± 0.005	2.50	-
9	Sn	3.6	3.8 ± 0.053	1.47	-
10	Pb	24 ± 3	24 ± 0.343	1.43	20
11	Zr	130 ± 13	126 ± 0.512	0.39	210
12	Nb	12	12 ±0.037	0.31	19
13	Hf	3.7 ± 0.5	3.7 ± 0.036	0.97	5

*Standard reference material (MAG 1) was obtained from Geological survey of India (GSI). *PAAS is the Global Shale Value used for normalisation of trace metals.

The residues were re-dissolved in 2% ultrapure HNO_3 (containing 1 ppm Rhodium as internal standard) and analyzed using an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). The Certified Reference Material (MAG 1) was obtained from Geological Survey of India to validate the method (Table 3.2). Precision and accuracy of the analysis was checked by the replicate analysis of the certified reference material (MAG-1) obtained from Geological survey of India. % error of the analysis ranged from 0.2 to 7.40% for MAG-1 reference material. The relative standard deviation, RSD (standard deviation/ mean of triplicate samples) ranged from 0.204 to 2.50% for MAG-1 reference material.

3.3.3 Metal fractionation

Fractionation of sediment metals was achieved through sequential extraction procedure (SEP) suggested by Tessier et al., 1979 (Fig 3.2). In brief, sediment trace metals can be progressively extracted in to different fractions based on their relative mobility in different solvents. The different extracts contain the metals as exchangeable, hydrous oxide bound, organic bound and lattice bound fractions. During the extractions, the metals of anthropogenic origin normally tend to concentrate in the first three fractions, while the metals bound to residual (fourth) fractions are of natural origin or lithogenous. The exchangeable metal fractions (Fr 1) can be removed by changing the ionic strength, which allow leaching of metals sorbed to the surface of sediment. The carbonate bound fractions are susceptible to pH variation and extraction of sediment using1M ammonium acetate (pH 7) can yield the above two fractions. The metals bound to Fe-Mn oxide (Fr 2) can be extracted using 0.5 M $NH_2OH.HCl$. The metals bound to organic phase (Fr 3) can be removed through oxidation for which, H_2O_2 and 3.2M ammonium acetate (acidified to pH 2) can be used. The residual fraction (Fr 4) consists of metals strongly incorporated into the primary and secondary minerals. This fraction is the hardest to remove and requires the use of strong acids ($HF+HNO_3+HClO_4$) to break down the silicate structures. For the present study, all the extraction procedure was performed in a clean environment.

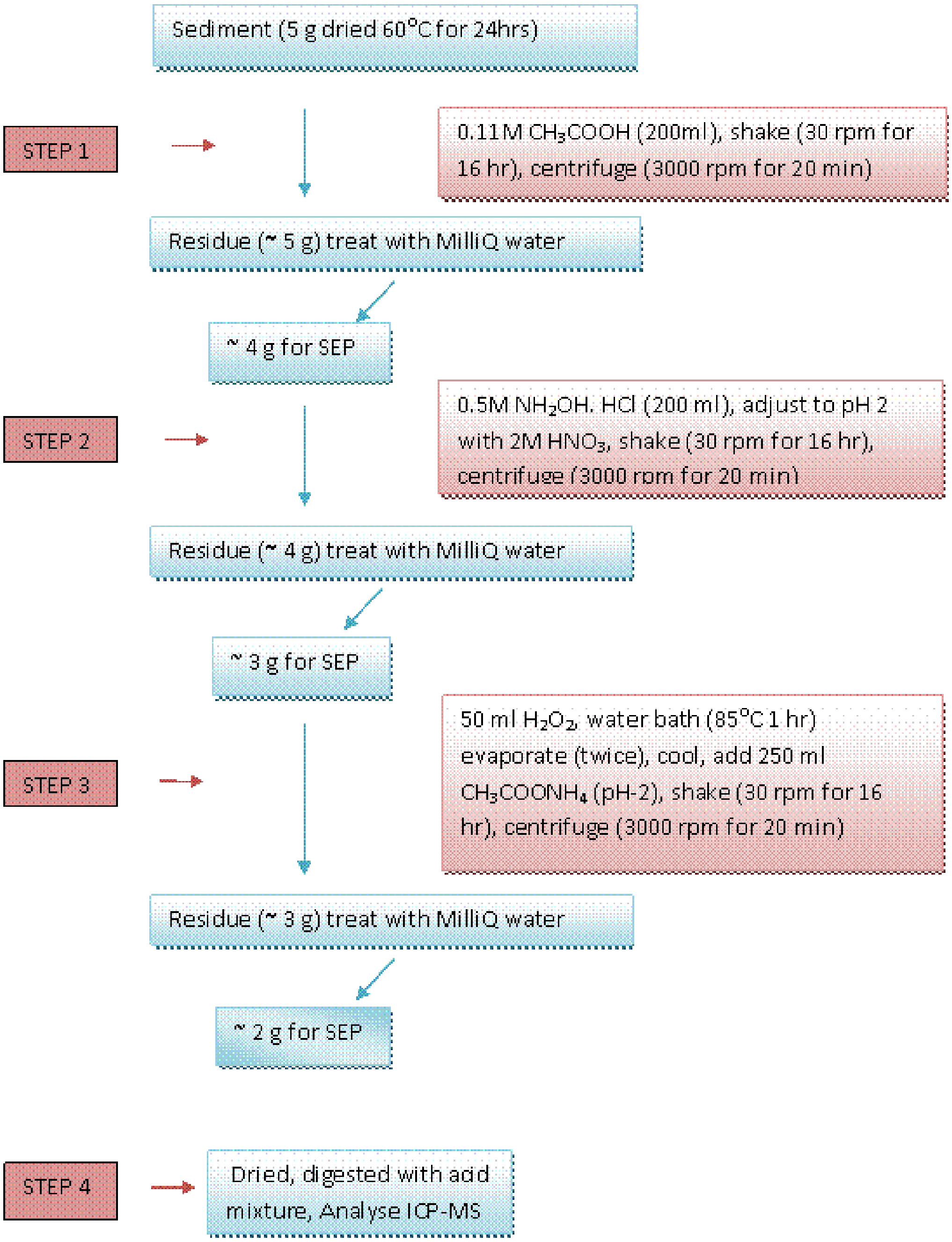

Fig 3.2: Schematic representation of metal fractionation in sediments (Tessier et al., 1979).

3.3.4 Clay mineralogy

Mineralogical composition of the clay fractions (< 2µ) in sediments were analyzed using a XRD. The sample preparations for XRD measurement are depicted in Fig 3.3. The diffractograms were obtained using Cu/40kv/20 ma as X-ray source. The XRD patterns were recorded with intensity (cps) vs 2θ distinguished from 3.0000-35.0000 in continuous scan mode with speed of 1.5000 deg/min. In order to facilitate XRD analysis, sediments (< 2µ) were washed with Milli-Q water to remove salt and confirmed with silver nitrate test for chloride. The samples were washed by dilute HCl to remove inorganic carbon and then treated with 50% H_2O_2 to remove organic carbon. They were finally washed with Milli-Q water to remove the remaining acid, dried (50°C), cooled in desiccators, homogenized to fine powder and mounted on XRD for measurement. The minerals were identified and quantified from X-ray diffractograms (Appendix 2b).

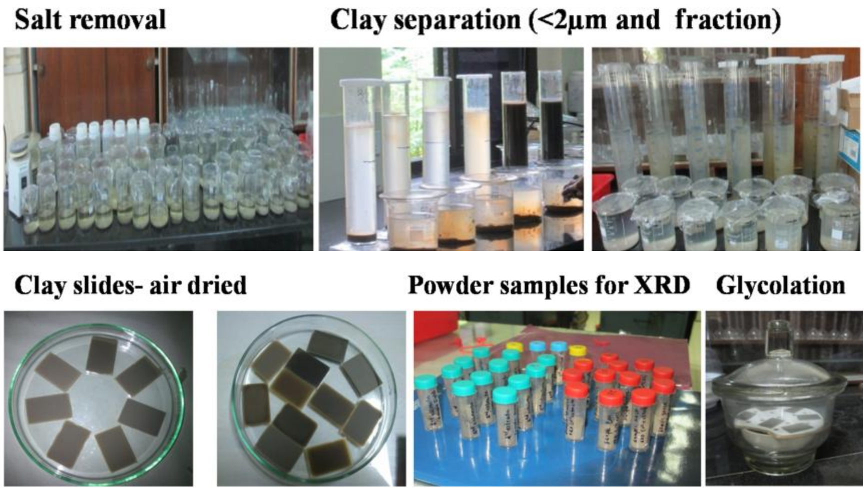

Fig 3.3: The sample preparations for XRD

3.3.5. Data processing

3.3.5.1. Normalisation factor

The significance of normalisation is to check the similarity of pattern for many elements supporting homogeneity (Taylor and McLennan, 1985), which is caused by the mixing of materials derived from different sources, with different age and rock types, during weathering, transport and deposition (Dupre et al., 1996; Nath et al., 2000). The elemental concentrations are normalized with those of Post Archean Australian Shale reference material (PAAS) for plotting shale normalized pattern.

3.3.5.2. Risk Assessment code

Based on the Tessier fractionation, the risk assessment code (RAC) was used to evaluate the potential risk due to each metal. The RAC assessment was expressed as the percent of Fr 1 in the total metal. The criteria governing NF and the RAC are summarized in Table 3.3.

Table 3.3: Criteria for the pollution: Normalisation Factor (NF) and Risk Assessment Code (RAC).

Normalisation Factor (NF)			**Risk Assessment Code (RAC)**		
NF	**Class**	**Pollution status**	**Fr.1 (%)**	**Class**	**Risk**
< **1**	0	Low	< **1**	1	No risk
1 - 3	1	Moderate	**1-10**	2	Low risk
3 - 6	2	Severe	**11-30**	3	Moderate risk
> **6**	3	Extreme	**31-50**	4	High risk
			> **50**	5	Very high risk

3.3.5.3 Canadian sediment quality guidelines for the protection of aquatic life

As the sediment quality guidelines are not available for Indian ecosystems, Canadian sediment quality guidelines were used as a tool to compare with the functioning of healthy aquatic ecosystems (CCME, 2001). These criteria are based on several field research studies demonstrating the interaction between chemicals and aquatic organisms to establish a cause and effect relationship for that particular organism. Comparison of measured concentrations of various contaminants following the above guidelines will provide a probable degree of contamination and its impact on the ecology (Table 3.4). The guidelines are based on the two stages, threshold effect levels (TEL) and probable effect levels (PEL). The TEL and PEL are used to identify the following three ranges of chemical concentrations with regard to biological effects. It is likely that the TEL will be adopted as the interim marine sediment quality guidelines ISQGs (CCME, 2001):

- < TEL - Minimal effect range within which adverse effects rarely occur.
- TEL to PEL - Possible effect range within which adverse effects occasionally occur.
- > PEL - Probable effect range within which adverse effects frequently occur.

3.4 RESULTS

3.4.1 General characteristics of sediment in the study domain

3.4.1.1 Sediment texture

Textural parameters showed a significant spatial variation throughout the study domain (Fig 3.4). This was evidenced by the variation in the sand (1.56-70.38%), silt (5.04-45.98%) and clay (22.6-61.06%) fractions in the sediments. Among the 8 stations in the estuary, the sand content was highest at S_5. Silt was greater at S_4 while clay showed high values at S_8.

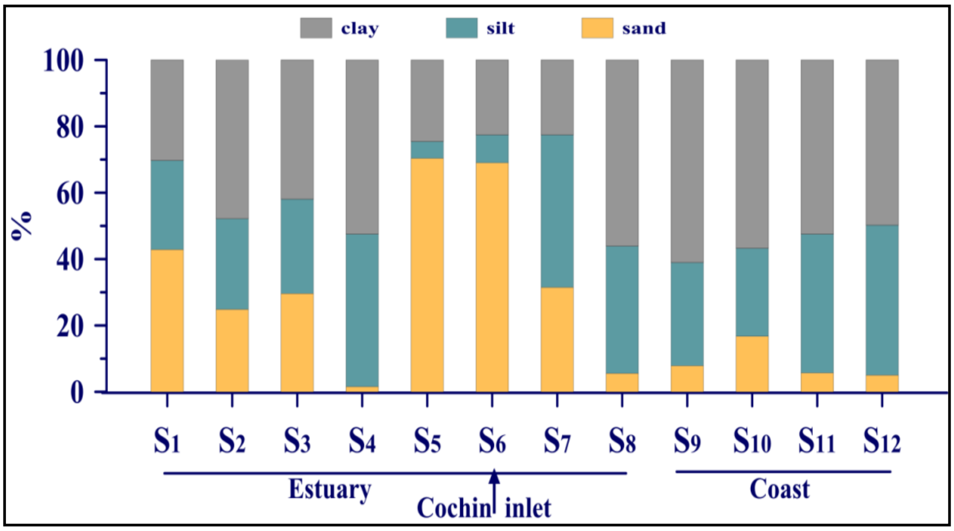

Fig 3.4: Sand, silt and clay fractions (%) in the sediments of Cochin estuary and adjacent coastal region during October 2011.

The estuary was dominated by clayey-sand and silty-clay texture with a progressive increase in the fine fractions from upper to the central estuary, which is in support with earlier studies (Reddy et al., 1992, Nath et al., 2000; Renjith et al., 2016). The sandy nature at S_5 (central estuary) was noteworthy.

Similar distribution during earlier studies during monsoon suggests that there is a possible down estuarine bed load movement (Menon et al., 2000). From our study, the Mattanchery channel (silty-clay) seems to be more clayey compared to Ernakulam channel (sandy-silt). The bar mouth and surrounding regions were sandy and low in clay and silt, possibly due to stronger flushing. The coastal sediments were dominated by silty-clay fraction (Fig 3.4). The near shore areas (~5m, ~7 m) showed higher clay content than offshore regions (~30 m).

3.4.1.2 Clay minerals

Clay minerals are a group of important hydrous aluminium phyllosilicates with a layer (sheet like) structure and very small particle size. They may contain significant amount of iron, alkali metals, or alkaline earths. Clay mineral constitutes a major fraction of sediments and their reactivity regulates the overall physic-chemical environment (Whitehouse et al., 1960). The clay mineral composition depends on the regional climate, provenance, rock type etc. The composition of clay minerals is an indicator of the sediment dispersal pattern in various environments (Grim, 1968). Information on clay minerals is essential to identify the origin, early diagenesis, chemical weathering and depositional behavior of the region.

The XRD diffratograms of the sediments from the estuarine and coastal stations clearly show prominent peaks corresponding to the minerals kaolinite and smectite whereas the peaks corresponding to illite, chlorite, gibbsite and quartz were less prominent (Fig 3.5). Thus, kaolinite was found to be the dominant clay mineral in the estuary and coastal region except at S_2, S_9 and S_{11}, where smectite was the dominant fraction (Appendix 2b). These minerals generally reflect the terrestrial origin and subsequent weathering of laterites. The laterite and red soils of the drainage basins are the major source of kaolinite, while black and peat soils over the hinterland are the source of smectite and illite (Rao et al., 1995). Previous studies have reported a gradual decrease in the kaolinite content concomitant to an increase in smectite towards the north of Cochin estuary. As smectite was mostly associated with fine grained sediments, the dominance of this fraction in the estuarine stations (S_2) may be attributed to the severe flow restrictions in the region (Balachandran et al., 2006). Greater surface area and smaller size of smectite allows strong bonding with organic matter, which undergo flocculation over a wide range of salinity (Degens and Ittekkot, 1984). Increased flocculation in the flow restricted northern region has been reported in CE (Balachandran et al., 2005). Since the salinity in this station varied narrowly, the flocculation was for a major reason for the dominance of smectite in this region. The high concentrations of smectite and strontium (Sr^{87}/Sr^{86}) ratio in the upstream of Mandovi and Zuari estuary are attributed to the extreme chemical alteration (Rao et al., 2015).

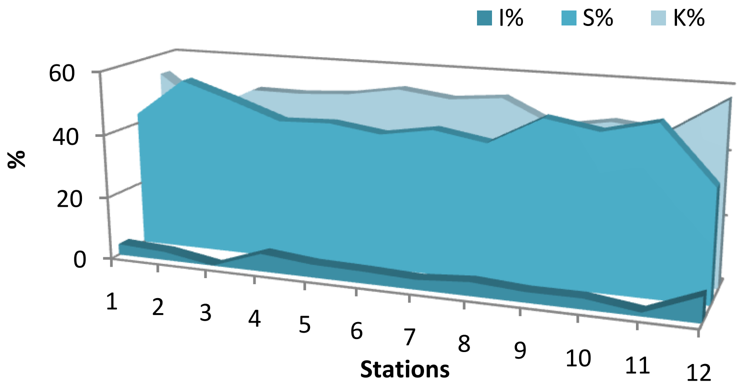

Fig 3.5: Clay minerals (%) in the sediments of Cochin estuary and adjacent coastal region (S_1-S_{12}) during October 2011

In the inner shelf (30 m), the sediment showed higher kaolinite content than the near shore region. One of the earlier studies has suggested that deposition of kaolinite along the inner shelf sediments might have taken place due to the lowering of sea level during the Halocene period (Reddy et al., 1992). However, in the absence of any marked variations in the source material (Reddy et al., 1992; Nath et al., 2000) the spatial variation in the abundance of kaolinite and smectite in the estuary and adjacent coastal stations can be assumed to be due to their transport differentiation and flocculation in the estuary.

3.4.1.3 Sediment organic carbon

Organic carbon content in the sediment varied from 6.53 to 36.52mg/g (dry weight, Fig 3.6). It was relatively high along the coastal stations (24.22 to 36.62mg/g) compared to the estuarine stations (12.7 to 25.81mg/g). This is because the sediment texture can significantly influence the accumulation of organic carbon.

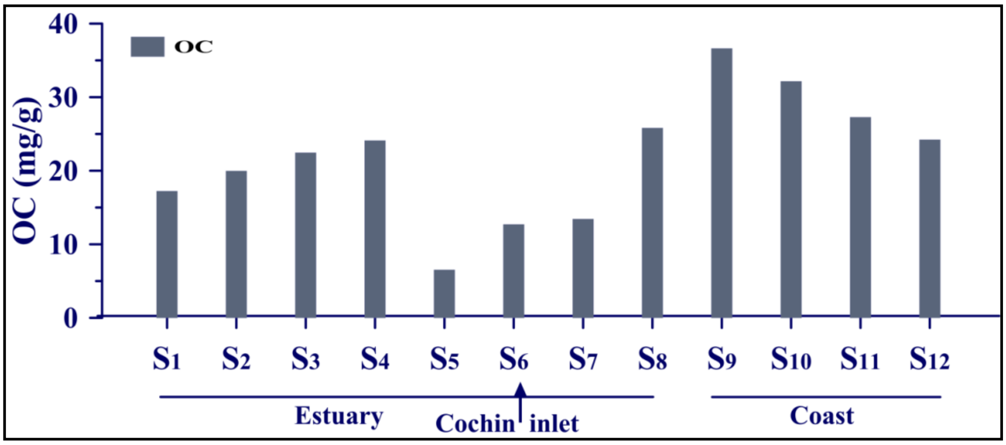

Fig 3.6: Organic carbon (mg/g) in the sediments of Cochin estuary and adjacent coastal region during October 2011.

It was observed that silty-clay sediments along stations S_2, S_4, S_8, S_9, S_{10}, S_{11} and S_{12} have high organic carbon while stations with sandy sediments (S_5 and S_6) showed low organic carbon. The organic carbon in the near shore sediments was much higher compared to that in offshore sediments, which may be due to higher productivity along the inner shelf. There are several reports showing higher productivity in the near shore area (Balachandran et al., 2008b; Madhu et al., 2011).

3.4.2 Distribution of trace metals and transition elements

The concentration of trace metals in estuarine sediments varied as Zn (112.5 - 435.7)mg/kg; Cr (84.2 - 183)mg/kg; Mn (298.5 - 1285)mg/kg; Pb (16.7 - 41.9)mg/kg; Cd (0.10 - 2.42)mg/kg; Ni (15.54 - 102.9)mg/kg; Co (8.13 - 21.66)mg/kg; Sn (4.35 - 7.54)mg/kg; Cu (27.23 - 65.7)mg/kg and V (45.6 - 152.1)mg/kg. The results show that Mn is the most abundant metal and Cd as the least abundant trace metal in estuarine sediment, with their maximum concentrations towards the north estuary stations (S_1, S_2, S_3) and minimum near the Cochin inlet (S_5, S_6). The transition elements also varied as: Zr (47.8 - 106.3)mg/kg; Hf (1.27 - 3.03)mg/kg and Nb (4.9 - 15.8)mg/kg.

The concentrations of trace metals in the coastal sediments were as follows: Zn (245.3 - 316.4) mg/kg; Cr (124.9 - 184.5) mg/kg; Mn (261.8-393) mg/kg; Pb (23.9 - 25.6) mg/kg; Cd (0.16 - 0.19) mg/kg; Ni (67.7 - 95.4) mg/kg; Co (15.2 -17.2) mg/kg; Sn (4.4 - 9.9)mg/kg; Cu (48.9 - 64.22) mg/kg and V (107 - 121.6)mg/kg. The trace metals showed near shore enrichment and a decrease towards deeper station (30 m), supporting the earlier reports (Laluraj, 2009). The transition elements (Zr, Hf and Nb) in coastal sediments also varied from (92.4 - 107.7)mg/kg; (2.7 - 3.03)mg/kg and (11.2 - 13.8)mg/kg respectively.

3.4.3. Sediment Quality Guidelines and evaluation of pollution criteria

Geochemical normalization of an element is estimated as the ratio of concentration of the element in the sample to the concentration of the same element in the global shale or the primitive mantle of the earth (Nath et al., 2000). The pollution status of an environment can be evaluated based on the normalisation factors. Thus, the normalisation factor (NF) less than 1 refers to low contamination, NF < 3 refers to moderate contamination, NF > 3 indicates severe contamination and NF > 6 indicates extreme contamination. The shale normalized value of elements in both estuarine and coastal sediments are depicted in Fig 3.7.

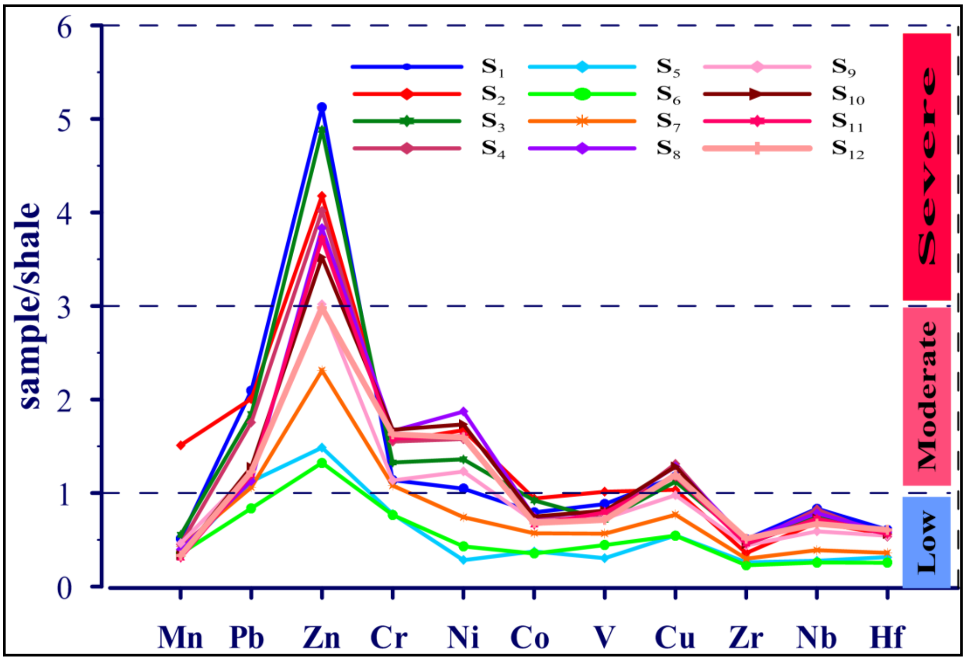

Fig 3.7: Shale normalized pattern of trace metals showing the level of contamination in Cochin estuary and adjacent coastal region during October 2011

Based on the Fig 3.7, it can be seen that Zn is moderately contaminated near the Cochin inlet (S_6, S_5, S_7), whereas it is severely contaminated at all other estuarine and coastal stations. Mn and V showed moderate contamination at S_2 while all other stations showed low contamination. Pb (except S_6) and Cr (except S_5, S_6) showed moderate contamination for both estuarine and coastal stations. Ni and Cu showed moderate contamination for all the stations except S_5, S_6 and S_7, whereas Co, Zr, Nb and Hf showed low contamination for both estuarine and coastal stations.

The results of the trace metal contents in sediments from the present study were checked for their quality using standard sediment quality guidelines (Table 3.4). The concentration of Zn in S_5 and S_6 with sandy texture was < TEL shows that an adverse effect can rarely occur in these regions. The Zn at S_7, S_9 and S_{12} were in the range TEL - PEL indicating that adverse effect can occur in these regions occasionally, whereas the stations S_1, S_2, S_3, S_4, S_8, S_{10} and S_{11} were showing values > PEL, which is an indication that these regions are prone to frequent adverse effect due to trace metal pollution.

Table 3.4: Sediment quality guidelines for the protection of aquatic life based on the Canadian Council of Ministers of the Environment (CCME)

Elements	Observed value	TEL	PEL	ERL	ERM
Cu	27.2 - 65.7	18.7	110	34	270
Zn	112.5 - 435.7	124	270	150	410
Cr	84.2 - 184.5	52.3	160	81	370
Cd	0.10 -2.42	0.68	4.2	1.2	9.6
Pb	16.7-41.9	30.2	110	46.7	218
Ni	15.54-102.9	15.9	43	20.9	51.6
Mn	261.8 - 1285	460	na	na	na

*na = no available data; ERL= effect low range; ERM = effect medium range; TEL = threshold effect level; PEL = probable effect level.

The concentrations of Pb in S_1, S_2, S_3 and S_4 covering northern and central estuary are between TEL and PEL indicating the adverse effect due to this metal to be occasional. Other stations with low Pb content indicate less contamination. Cr concentration at all stations were > TEL, while it was > PEL at stations S_2, S_4, S_8 and S_{10} ,S_{11} and S_{12} showing that adverse effects due to Cr can occur frequently in these regions. The Cd was > TEL at S_1, S_3 and S_4, indicating that the adverse effect of Cd contamination can occur intermittently in these regions. The Ni in sediment S_5 was below TEL while all other stations showed values higher than TEL and above PEL in most of the stations (except S_5, S_6 and S_7). The Cu concentration in the studied region was between TEL and PEL highlighting the possibility of occasional adverse effects. The Mn showed concentration higher than TEL in north estuary S_1, S_2 and S_3, while all other stations contained Mn < TEL indicating that the chances of any adverse effect are very rare in these stations.

3.4.4 Fractionation of metals

3.4.4.1 Zinc

Distribution of Zinc in different fractions of estuarine and coastal sediments is presented in Fig 3.8. The organic phase contained the lowest fraction (Fr 3) of Zn (0.08 - 4.07% of total concentration) in both estuarine and coastal sediments except at S_7 and $S_{8,}$ where Fr 3 forms the major non residual binding phase. However, Fr 3 (0.8 - 17.6mg/kg) showed an increase with the increasing Zn loading in estuarine sediments (r^2 =0.81, Table 3.5). Instead, the association of Zn with Fe/Mn oxy hydroxide (Fr 2) was significant (~0.8 to 29.8mg/kg, Fig 3.8). It was also seen that Fr 2, the concentration of Zn in Fe/Mn oxy hydroxide fraction (0.3 to 8.62 % of total Zn) gradually increased with the increasing Zn loading in the estuarine sediments (r^2 = 0.88, Table

3.5), while such a linear trend was not observed for the coastal sediments (r^2 = 0.24, Table 3.6). This indicates that Fe/Mn oxy hydroxide phase could be a major binding phase for Zn deposition in the estuarine sediments.

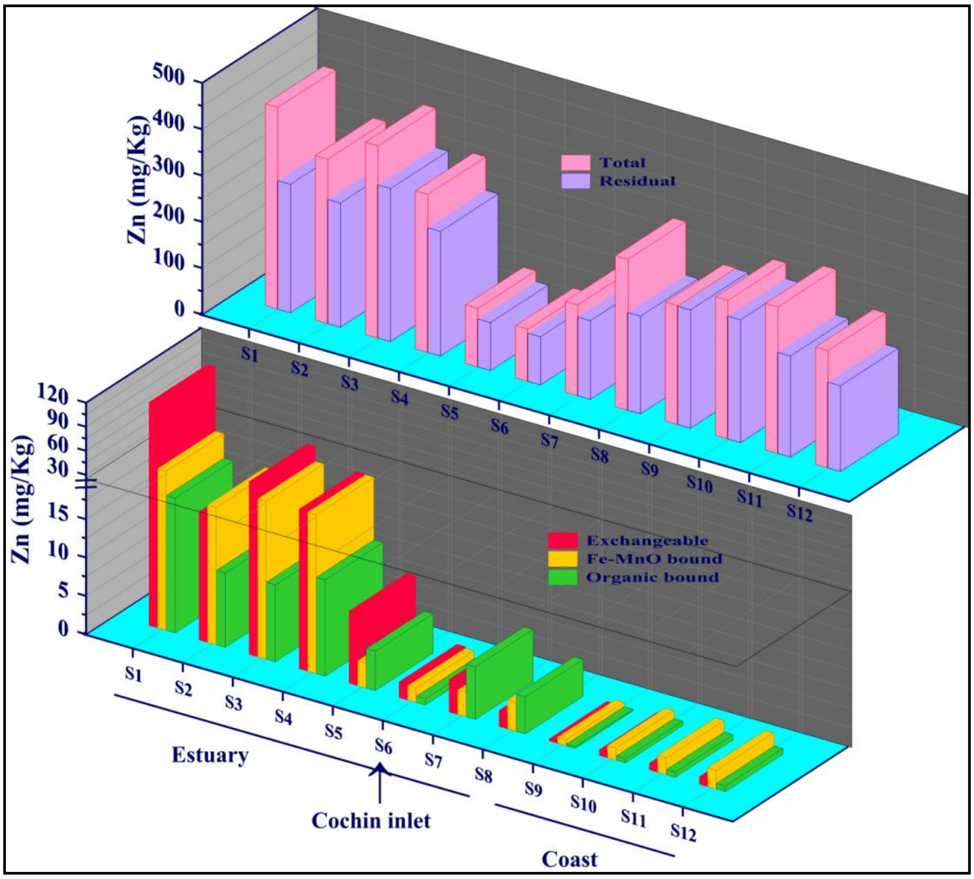

Fig 3.8: Total Zn and its four different fractions in the sediments of Cochin estuary and adjacent coastal region on October 2011.

The highest fractions of non-residual Zn (0.6 to 25.1% of the total Zn) were found to associate with exchangeable and carbonate/bicarbonate phases (Fr 1) in the estuarine sediments (except S_7 & S_8). This fraction also increased towards the north estuary to peak at S_1. However, most of the non-residual Zn was associated with Fe/Mn oxy hydroxide phase (Fr 2) towards the coastal environment. Fr 1 (2.1-109.6mg/kg) also did not increase with the increasing Zn loading, indicating that adequate Fe-Mn oxide binding sites were already available for its association in the sediment. The residual fraction (Fr 4) was the major fraction of the total Zn (~103.4 to 330.5 mg/kg, Figure 3.8) in both the environments. The Zn concentration in residual fraction was even higher than its concentrations in the adjacent source rocks of Granulitic terrain (Nath et al., 2000).

3.4.4.2 Chromium

Distributions of Cr in different fractions in the estuarine and coastal sediments (Fig 3.9) showed exchangeable and carbonate/bicarbonate phases (Fr 1) as the poorest fractions (0.1-1.5% of total Cr). Table 3.7 shows that the absolute concentration of Cr (0.08 to 2.53mg/kg) in Fr 1 did not gradually increase with the increasing Cr loading in the estuarine sediments (similar to Zn) (r^2 =0.14) whereas Fr 1 showed a gradual increase with increasing Cr loading towards the coast (r^2 = 0.75, Table 3.8). Concentration of Cr in Fr 2 (Fe/Mn oxy hydroxide) was higher than Fr 1 and ranged from 1.1 to 3.02 % of total Cr in sediments. Table 3.7 shows that Fr 2 (1.68 - 3.64mg/kg) did not gradually increase with the increasing Cr loading in estuarine sediments (r^2 =0.25) however Fr 2 gradually decreased with the increasing Cr loading in the coastal sediments (r^2= -0.61; Table 3.8). This is probably because Cr forms thermodynamically weak complexes with Fr 1 and Fr 2.

The highest factions of non-residual Cr were found to associate with organic binding phases (Fr 3) and found to be the preeminent non residual binding phase for Cr (1.31 to 17.4%) in the entire domain. Fr 3 (2.17-21.92 mg/kg) showed a gradual increase with increase in total Cr in the sediments

($r^2_{estuary}$= 0.75; r^2_{coast} = 0.57). The Cr in Fr 3 showed strong linear correlation with organic matter (r^2 =0.72) in the estuary and a weak correlation in the coast (r^2 = -0.28).

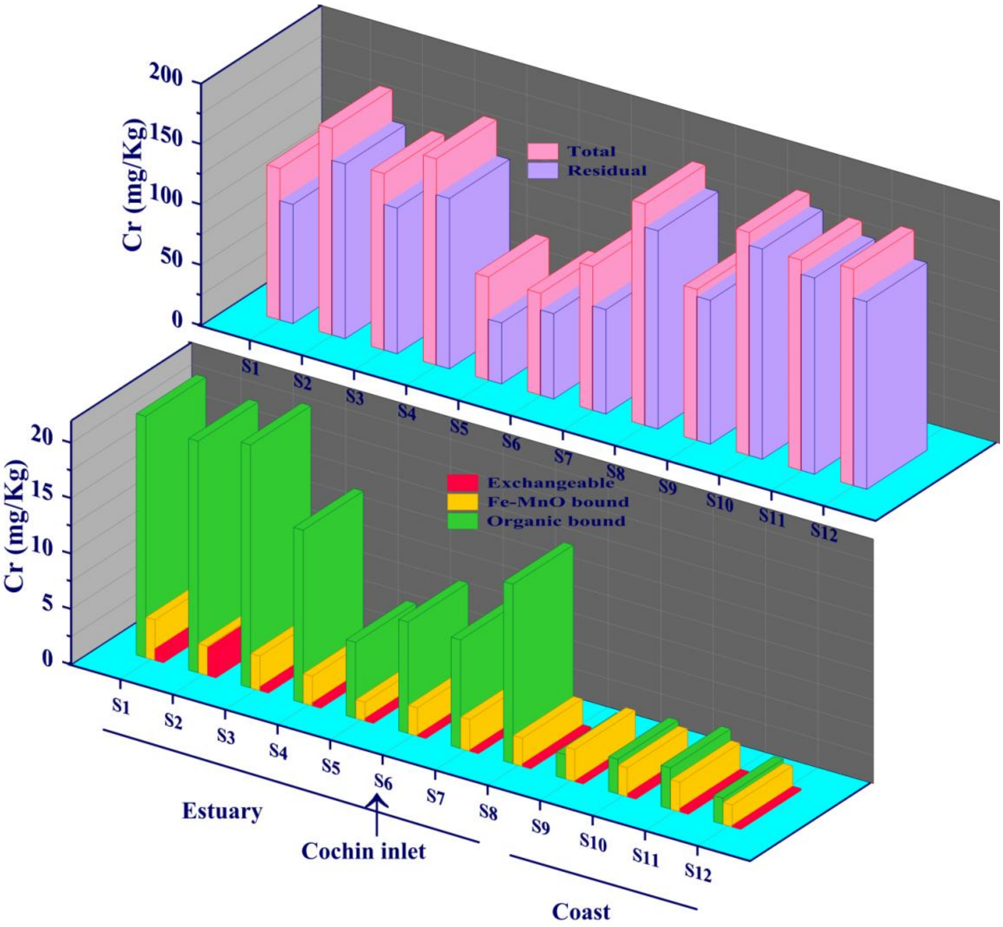

Fig 3.9: Total Cr and its four different fractions in the sediments of Cochin estuary and adjacent coastal region on October 2011.

The geochemical fractionation study generally reveals that a major part of Cr in the sediments is present as lithogenous (Fr 4) fraction (50.0-173.9mg/kg) derived from the crustal sources of felsic composition. It is observed that the concentrations of Cr in the residual fraction gradually increased with the increasing total Cr loading (Table 3.7 & Table 3.8) in sediments.

3.4.4.3 Cadmium

Cadmium showed wide variation in its affinity towards different fractions (Fig 3.10). The dominant fraction (6.8-49% of total Cd) was associated with exchangeable and carbonate/bicarbonate phases (Fr 1) at S_1 (north estuary) and S_5 (central estuary). This fraction is highly toxic, since a change in the environmental conditions (ionic concentration, pH) will make it available to organisms. When with the salinity increases, this fraction will be released to the water. Similarly, when the pH decreases also, this fraction will be released to water column and become available to biota. Cd bound to Fr 1 in S_2 and S_4 were higher than residual fraction.

Fe/Mn oxy hydroxide (Fr 2) was the dominant non-residual fraction of Cd (8.2 to 40.4% of total Cd) associated with the sediments at $S_{2,}$ $S_{3,}$ S_4 and S_7 (north and central estuary). The concentration of Cd in Fr 1 (0.01 to 0.97mg/kg) and Fr 2 (0.01 to 0.87mg/kg) gradually increase with the increasing Cd loading in sediments. The lowest fraction of the total concentration of Cd (vary from 2.9 to 25.46 % of the total Cd) was present as organic binding phases (Fr 3) except at coastal region south of inlet (S_{12}) where Fr 3 forms the major binding phase (42.9%). The absolute concentration of Cd in Fr 3 showed a gradual increase with increase in total Cd in sediments ($r^2_{estuary}$=0.84; r^2_{coast}= 0.73) (Table 3.7 & Table 3.8).

The major part of the total Cd in the sediments of S_3, S_6, $S_{7,}$ S_8, S_9, S_{10} and S_{11} was present within the structure of the sediments (Fr 4) (0.04 to

1.16mg/kg) and suggests that Cd entered through anthopogenic input get deposited and incorporated into the crystal lattice of minerals in these sediments.

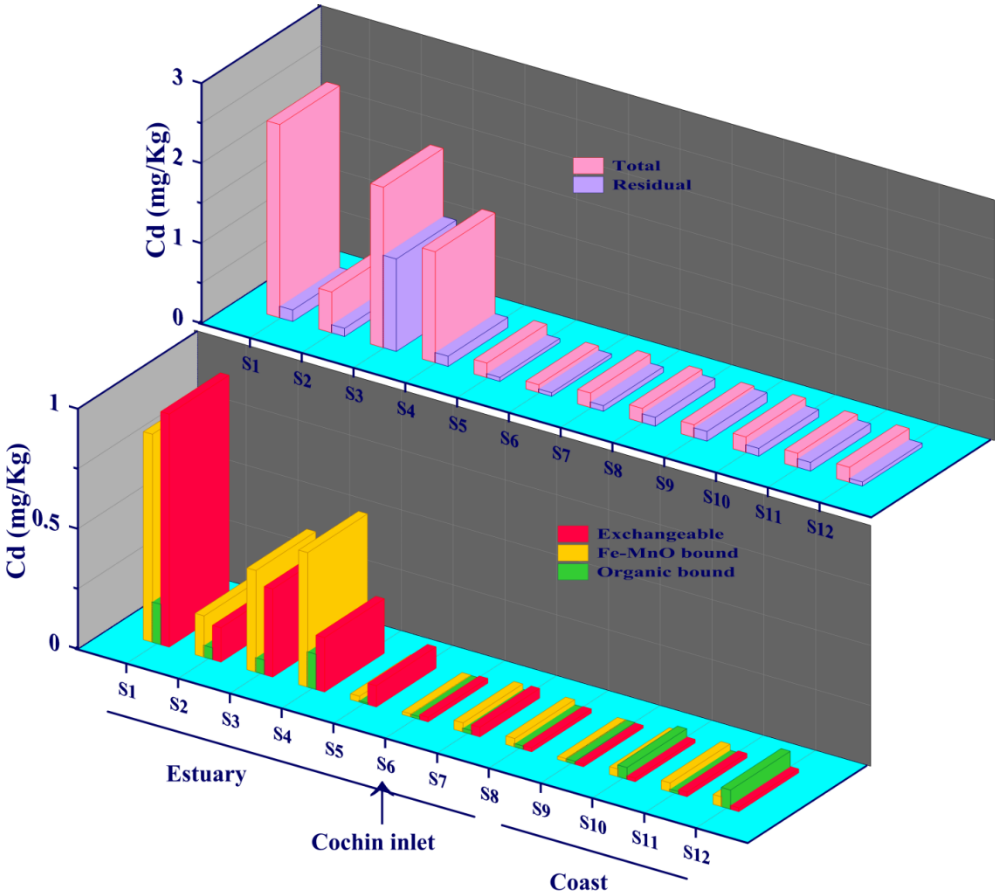

Fig 3.10: Total Cd and its four different fractions in the sediments of Cochin estuary and adjacent coastal stations on October 2011.

3.4.4.4 Lead

Distribution of Pb in different fraction of sediments is presented in (Fig 3.11). It is observed that the lowest concentration of Pb (~0.5 to 6.0% of total Pb) was present as soluble, exchangeable and carbonate/bicarbonate bound fraction (Fr 1). The results from the present study show that Pb in Fr 1 (0.1 to 2.4mg/kg) did not increase with increasing Pb concentration in sediments

(Table 3.5 & 3.6). The organic bound fraction (Fr 3) was higher than Fr 1 and varied from ~ 3.8 to 17.8% of total Pb.

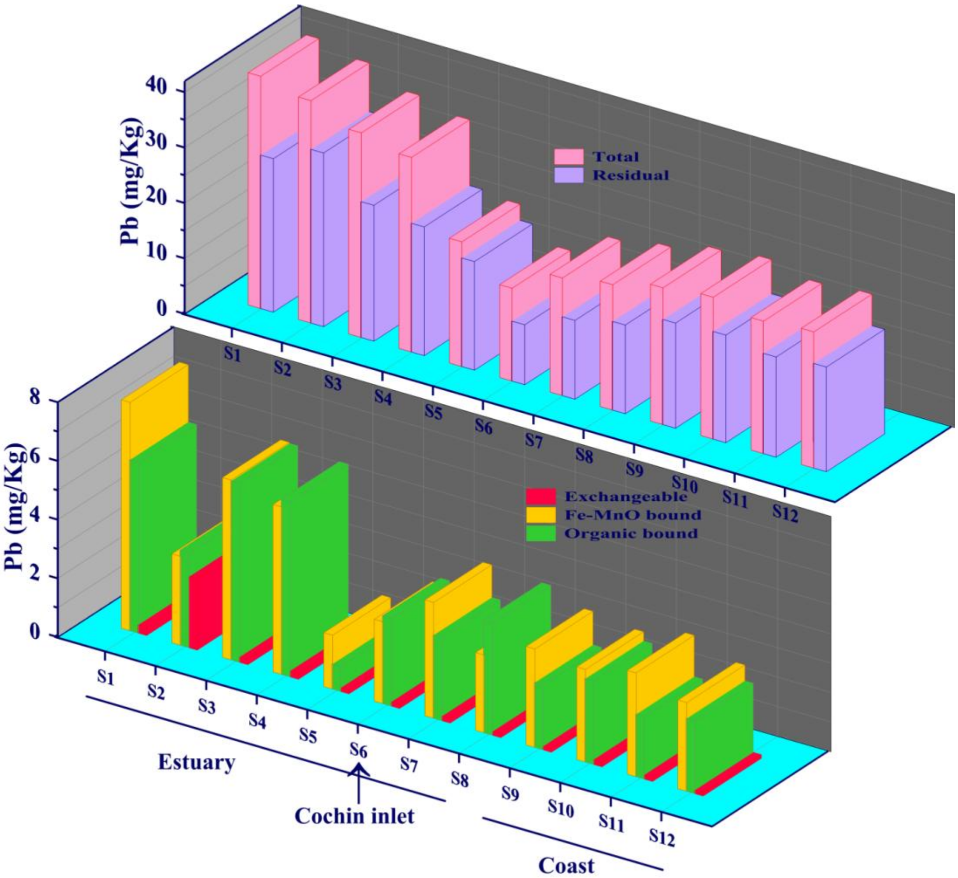

Fig 3.11: Total Pb and its four different fractions in the sediments of Cochin estuary and adjacent coastal stations on October 2011

Organic binding phase was the major non residual fraction of Pb in the estuarine stations S_2, S_3, S_4, S_6 and S_8 with high organic matter. Pb in Fr.3 showed a gradual increase with increasing organic matter in estuarine sediments (r^2 =0.78, Table 3.5). However Fr 3 (0.9 to 6.1 mg/kg) did not show any increase with increasing total Pb loading in the sediments. Concentration of Fr 2 was higher than the Fr 1 and varied from ~ 7.6 to 18.6% of total Pb.

Metals bound to Fe-Mn oxyhydrodide was the (1.8 to 7.8mg/kg) was most dominant in the estuarine stations $S_{1,}$ S_5 and S_7 and coastal stations S_9, S_{10}, S_{11}, S_{12}. Even though organic matter was higher in coastal sediments than estuarine sediments, Pb was preferentially associated with Fe/Mn oxy hydroxide phase than organic bound phase in the coastal sediments. The residual fraction of Pb (Fr. 4, 10.8 to 31.3 mg/kg) linearly increased with total Pb in sediments ($r^2_{\text{estuary}} = 0.95$; $r^2_{\text{coast}} = 0.96$, Table 3.5 & 3.6).

3.4.4.5 Nickel

Distribution of Ni in different binding phases of the studied sediments is presented in Fig 3.12. The relative affinity of Ni for different non-residual binding phases in the sediments was in the order of organic carbon binding phase > Fe/Mn oxyhydroxide phase > exchangeable carbonate/bicarbonate phases. Ni in Fr 1, Fr 2 and Fr 3 varied as 0.73 to 2.19mg/kg; 0.44 to 3.28mg/kg and 0.91 to 10.5mg/kg respectively. It is observed that Ni in Fr 3 gradually increased with increase in Ni loading (r^2=0.84) in estuarine sediments (Table 3.7). However, Ni in Fr 2 gradually increased with increase in Ni loading (r^2=0.98) in coastal sediments (Table 3.8) as it forms stable association with Fe/Mnoxyhydroxide phase in coastal sediments.

Most of the non residual fraction of Ni was bound to organic phase indicates that Ni forms thermodynamically stable complexes with organic matter in estuarine and coastal sediments. However the weak correlation of Ni in Fr 3 with organic matter in coastal sediments can be due to the difference in the nature of organic matter present. The association of Ni with sulphides can also make the difference as metal bound to sulphides were also extracted with Fr 3. A major part of the total Ni in the sediments was present within the structure of the sediments (Fr.4) (10.9 to 92.1mg/kg). The concentration of Ni (in the residual fraction) gradually increased with the total Ni concentrations in the sediments ($r^2_{estuary}$= 0.99; r^2_{coast}= 0.99) (Table 3.7 & Table 3.8).

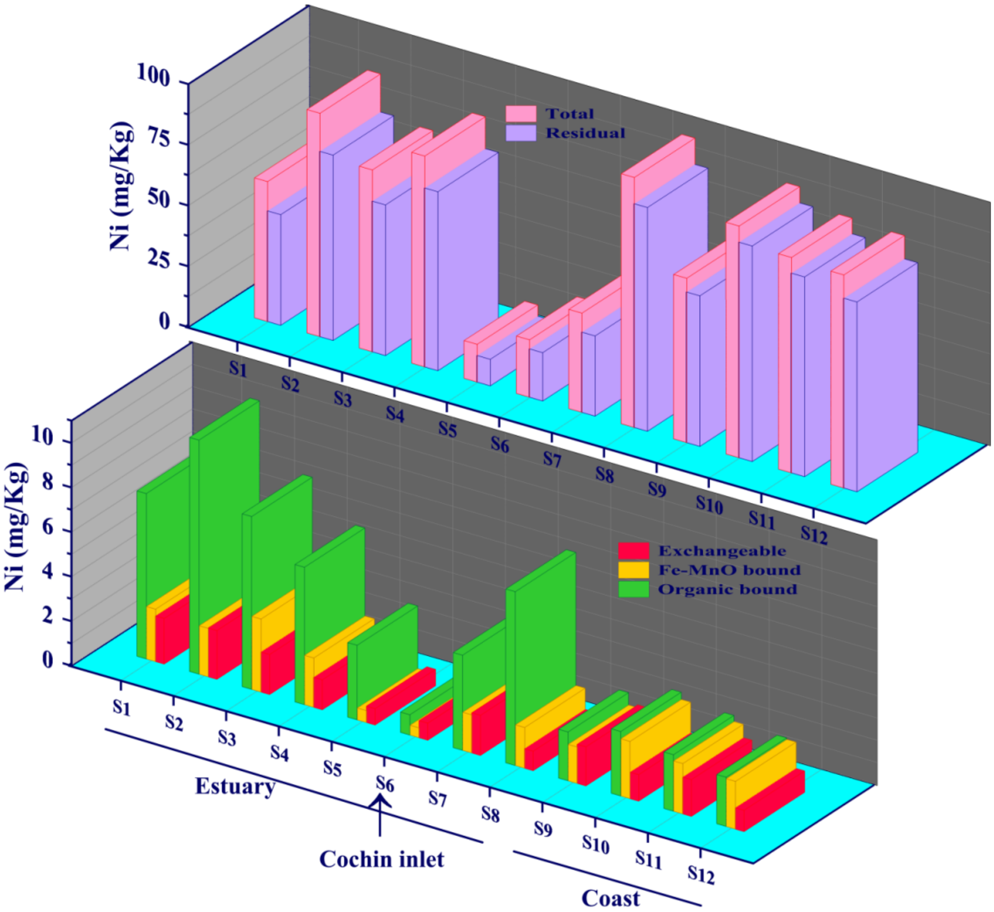

Fig 3.12: Total Ni and its four different fractions in the sediments of Cochin estuary and adjacent coastal stations on October 2011

3.4.4.6 Copper

Distribution of Cu in different binding phases of the studied sediments is presented in Fig 3.13. Concentration of Cu as Fe/Mn oxyhydroxide phase (Fr 2) and water-soluble, exchangeable, and carbonate/bicarbonate complexes

(Fr 1) were low and found to vary from (0.01 to 0.25%) and (0.0 to 0.6%) of the total Cu in the sediments. The Fr 1 was entirely absent in coastal sediments. The highest fractions of non-residual Cu (~0.03 to 4.1% of the total Cu) were found to associate with organic binding phases in the sediments (Fr 3) (Fig 3.13).

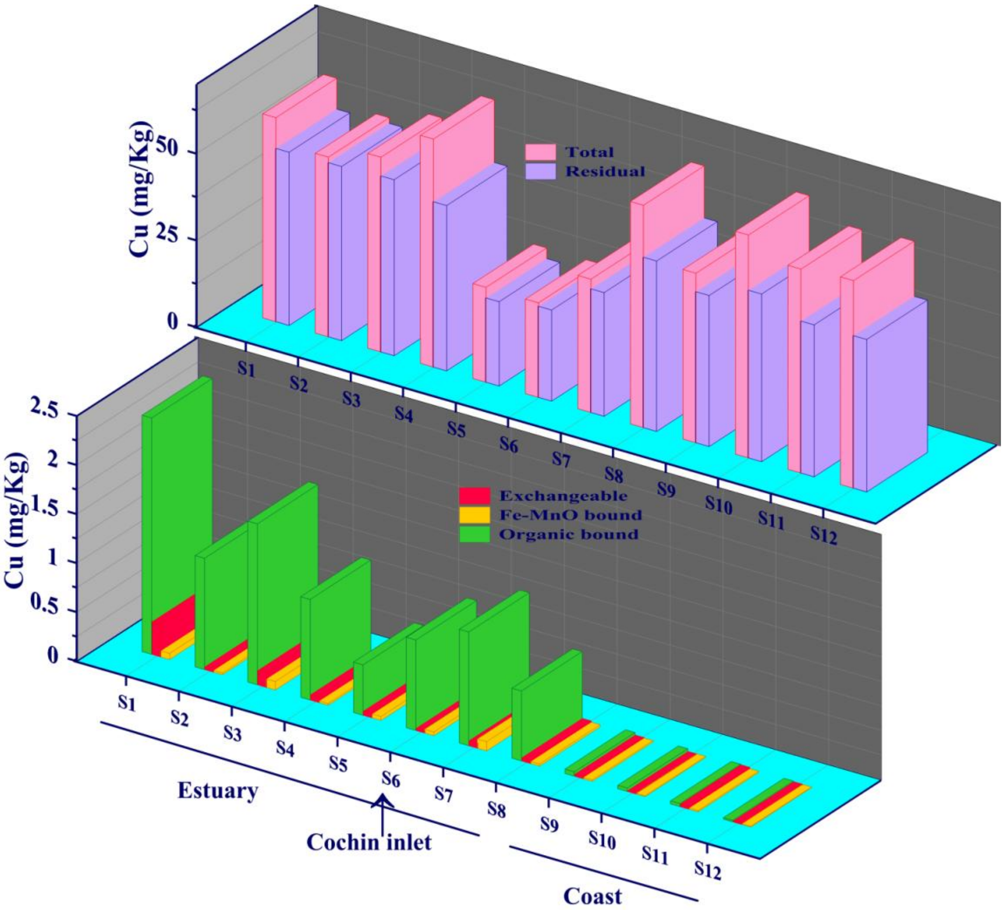

Fig 3.13: Total Cu and its four different fractions in the sediments of Cochin estuary and adjacent coastal stations on October 2011

The concentration of Cu in Fr 3 (~0.02 to2.41 mg/kg) did not showed an increase with the increasing Cu loading in the sediments. The association of Cu with organic matter, Fr 3 increased with organic matter in coastal sediments, however such a linear inter relation was not observed in estuarine sediments (Table 3.9 & Table 3.10). The relative affinity of Cu for different non-residual binding phases in the sediments was in the order of organic carbon binding phase > exchangeable carbonate/bicarbonate phases > Fe/Mn oxyhydroxide phase. Major fractions of the total Cu (~24.3 to 50.7mg/kg) were present within the structure of the sediments (Fr.4). Figure 3.13 shows the variation of residual fraction with changing total Cu content in the sediments. The range of Cu concentrations in residual fraction of the sediment was in close correspondence with the geology of the adjacent source rock (granulitic terrain) (Nath et al., 2000).

3.4.4.7 Manganese

Distribution of Mn in different binding phases of the sediments is shown in Fig 3.14. The relative affinity of Mn for different non-residual binding phases in the sediments was in the order of exchangeable carbonate/bicarbonate phases > Fe/Mn oxyhydroxide phase > organic carbon binding phase except in S_2, where Fe-Mn oxyhydroxide phase found to be the preeminent binding phase in the sediments. The concentrations of organic phase of Mn (Fr 3) were low and found to vary from 2.01 to 7.6% of the total Mn content in the studied sediments. The fraction of total Mn associated with Fe/Mn oxyhydroxide binding phase (Fr.2) and exchangeable carbonate/bicarbonate phases (Fr. 1) was found to vary from 2.04 to 18.8% and 5.2 to 19.4% of total Mn in sediments.

Major portion of Mn in sediments was found to associate with the residual fraction (Fr 4) of sediments (56.03 to 84.6%). The absolute concentrations of Mn in Fr 4 vary from 189.8 to 720mg/kg. Mn concentration in Fr 1 (15.5 to 203.5 mg/kg), Fr.2 (6.1 to 233.6mg/kg) and Fr 3 (6 to

52.7mg/kg) were found to increase gradually with the increasing total Mn content in the estuarine sediments (r^2 0.96; $r^2$0.97; $r^2$0.88) (Table 3.5 & Table 3.6). However in coastal sediments Mn in Fr 1 and Fr 4 gradually increased with increased Mn loading in sediments.

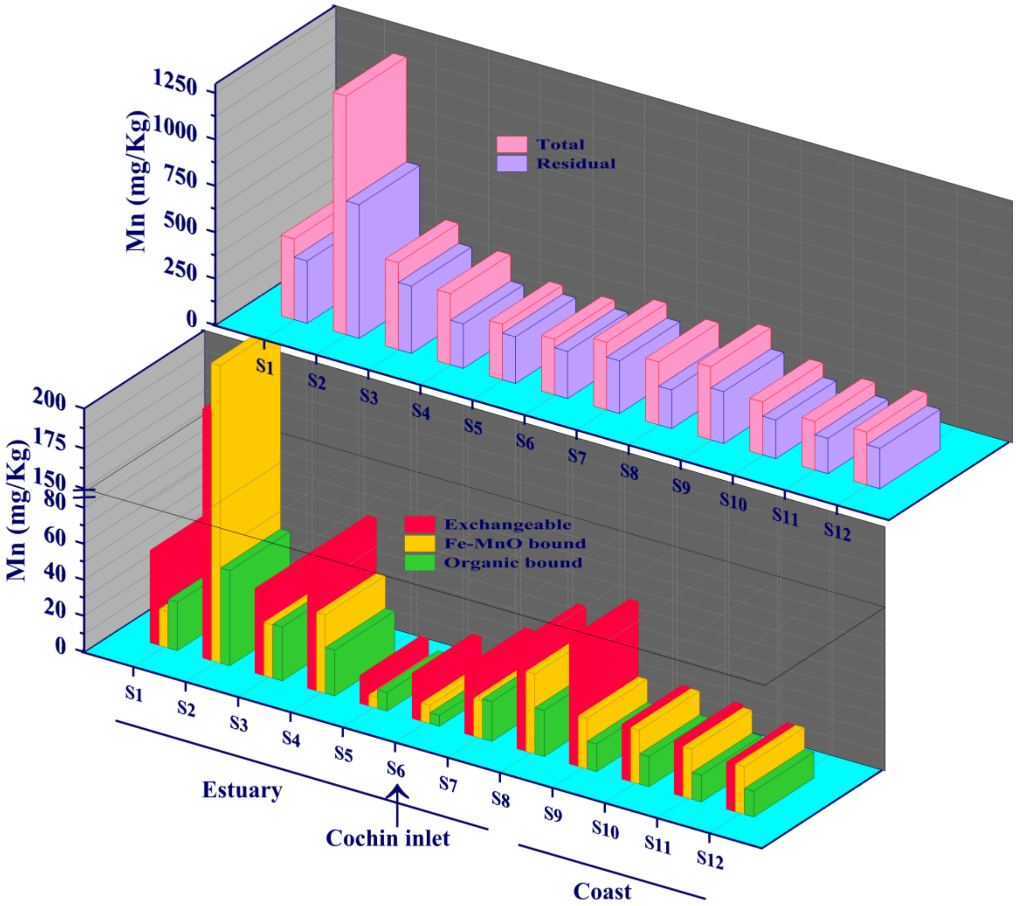

Fig 3.14: Total Mn and its four different fractions in the sediments of Cochin estuary and adjacent coastal stations on October 2011.

3.4.4.8 Vanadium

The relative affinity of V for different non-residual binding phases in the sediments was in the order of Fe/Mn oxyhydroxide phase > organic carbon binding phase > exchangeable carbonate/bicarbonate phases except in sediments of S_2, where exchangeable, carbonate/bicarbonate phases (Fr 1) was the dominant non residual binding phase of vanadium (Fig 3.15). Vanadium in Fr 1, Fr 2 and Fr 3 was found to vary from 0.2 to 12.1mg/kg, 6.4 to 15.9mg/kg and 0.8 to 6.1mg/kg respectively. A major portion of Vanadium in sediments (38 to 123.9 mg/kg) was found to associate with sediment residual fraction which account for 73.9 to 91.8 % of total V in the sediments.

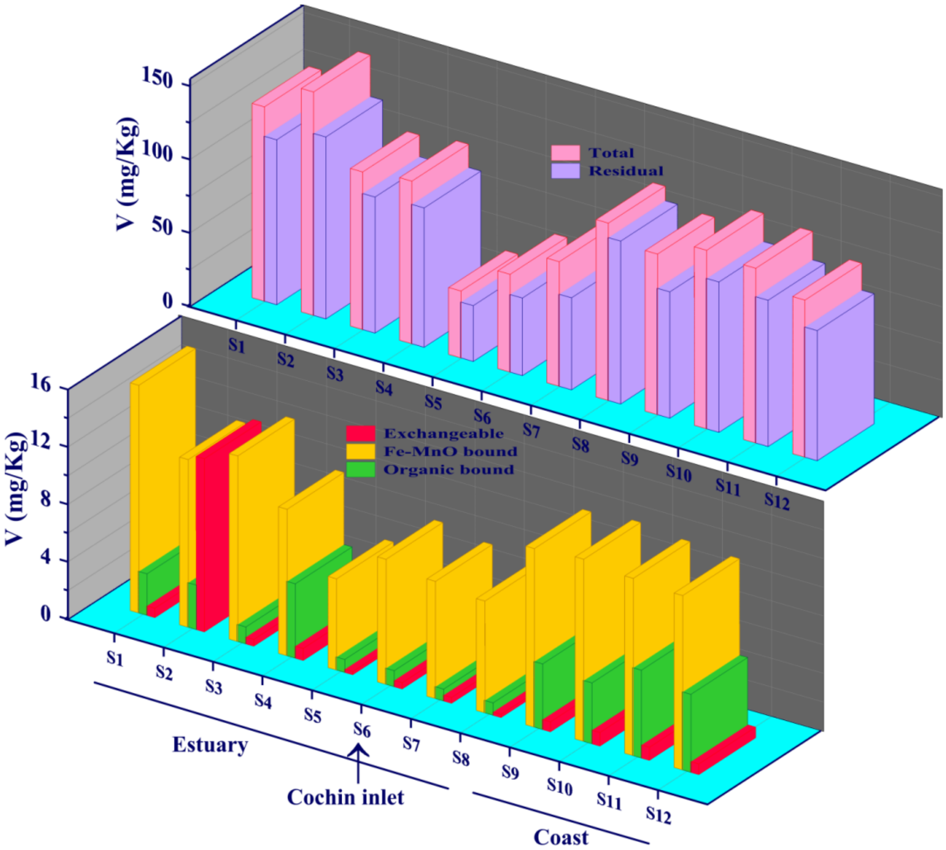

Fig 3.15: Total V and its four different fractions in the sediments of Cochin estuary and adjacent coastal stations on October 2011.

3.4.4.9 Tin

Distribution of Sn in different binding phases of the studied sediments is presented in Fig 3.16. It shows that the lowest fractions of the total concentration of Sn (vary from ~0.0 to 18.7% of the total Sn) were present as water soluble, exchangeable, and carbonate/bicarbonate-Sn complexes (Fr 1) in the sediments. However at S_{12}, Fr 1 was the dominant non-residual fraction of Sn.

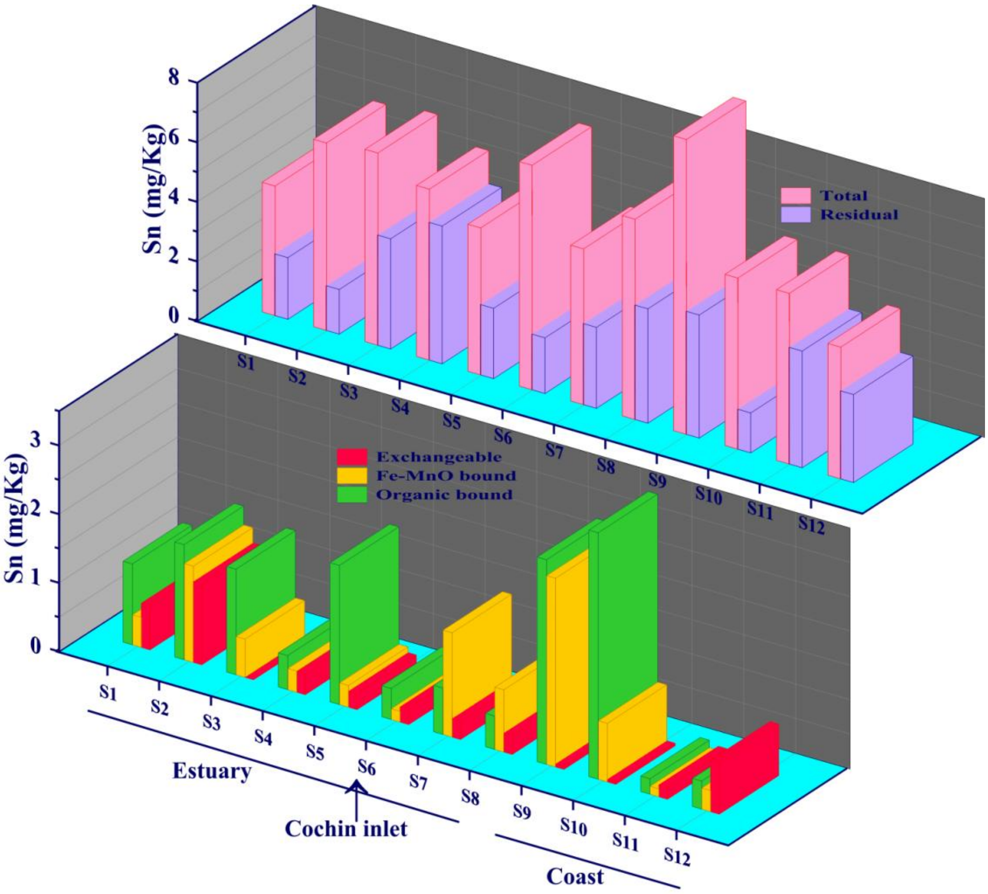

Fig 3.16: Total Sn and its four different fractions in the sediments of Cochin estuary and adjacent coastal stations on October 2011.

The Sn in Fe-Mn oxyhydroxide binding phase (Fr 2) was higher than in Fr 1 and varies from 2.01 to 29.05% of total Sn in the sediment. The absolute concentration of Sn in Fr 1 (non-detectable to 1.18mg/kg) and Fr.2 (0.11 to 2.75mg/kg) did not showed a gradual increase with increasing Sn loadings in sediments. This indicates Sn forms thermodynamically weaker association in Fr 1 and Fr 2 than other binding sites in sediments. The highest fractions of non-residual Sn were found to associate with organic binding phases (3.9 to 62.5% of total Sn) in the sediments (Fr 3) and probably the finest binding phase for Sn in the studied sediments. However the absolute concentration of Sn did not showed significant correlation with organic matter in sediments. This showed that nature of organic matter is a great factor influencing the binding of Sn to organic phases. Major part of the Sn in the sediments (23.3 to 80.6 % of total Sn) was present in the residual fraction except in S_2 and $S_{10,}$ where most of the Sn was in organic binding phase.

3.4.4.10 Cobalt

Distribution of Co in different binding phases of the studied sediments is presented in Fig 3.17. The relative affinity of Co for different non-residual binding phases in the sediments was in the order of organic binding phase (Fr 3) > Fe/Mn oxyhydroxide phase (Fr.2) > exchangeable carbonate/bicarbonate phases (Fr 1) except in S_9, where Fr.1 was the major non residual binding phase.

The concentration of Co in Fr 1, Fr 2 and Fr 3 varied as (0.53 to 1.84)mg/kg, (0.34 to 1.95)mg/kg and (0.65 to 2.95)mg/kg respectively and this together accounts for only 13 to 27.2% of total Co. Major part of the total Co in the sediments was associated with residual fraction (Fr.4) in all the sediments and varied from 6.51 to 16.36mg/kg.

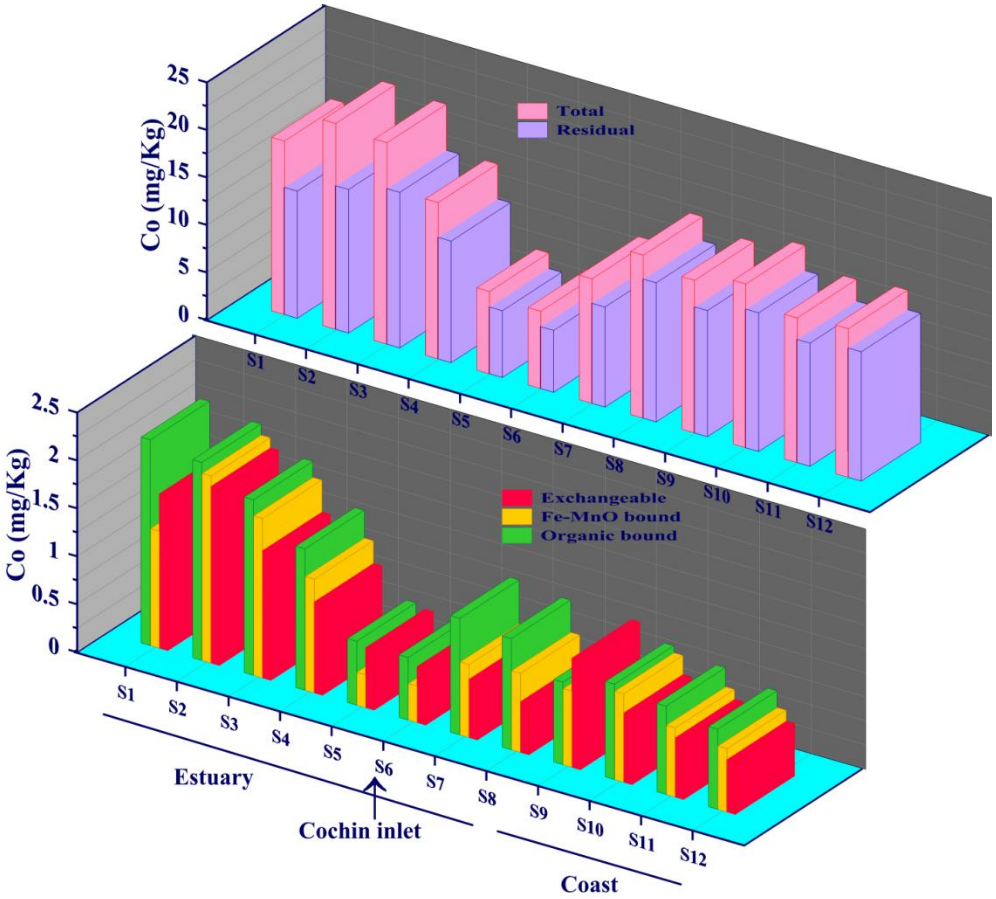

Fig 3.17: Total Co and its four different fractions in the sediments of Cochin estuary and adjacent coastal stations on October 2011

3.4.4.11 Zirconium, Niobium and Hafnium

The relative affinity of Zr, Nb, and Hf for different non-residual binding phases in the sediments was in the order of organic matter binding phase > Fe/Mn oxyhydroxide phase > exchangeable carbonate/bicarbonate phases. However the order slightly changed for Hf in coastal sediments with more affinity towards Fe/Mn oxyhydroxide phases (Fig 3.18 - Fig 3.20). For Nb, affinity towards different binding phases varied spatially. Major part of the Zr (70.7 to 99.7 % of total Zr) , Nb (80.2 to 98.2 % of total Nb) and Hf

(66.8 to 99.2 % of total Zr) in the sediments were present in the residual fraction which was in close correspondence to the geology of the adjacent source rock and are stable in the sedimentary environment.

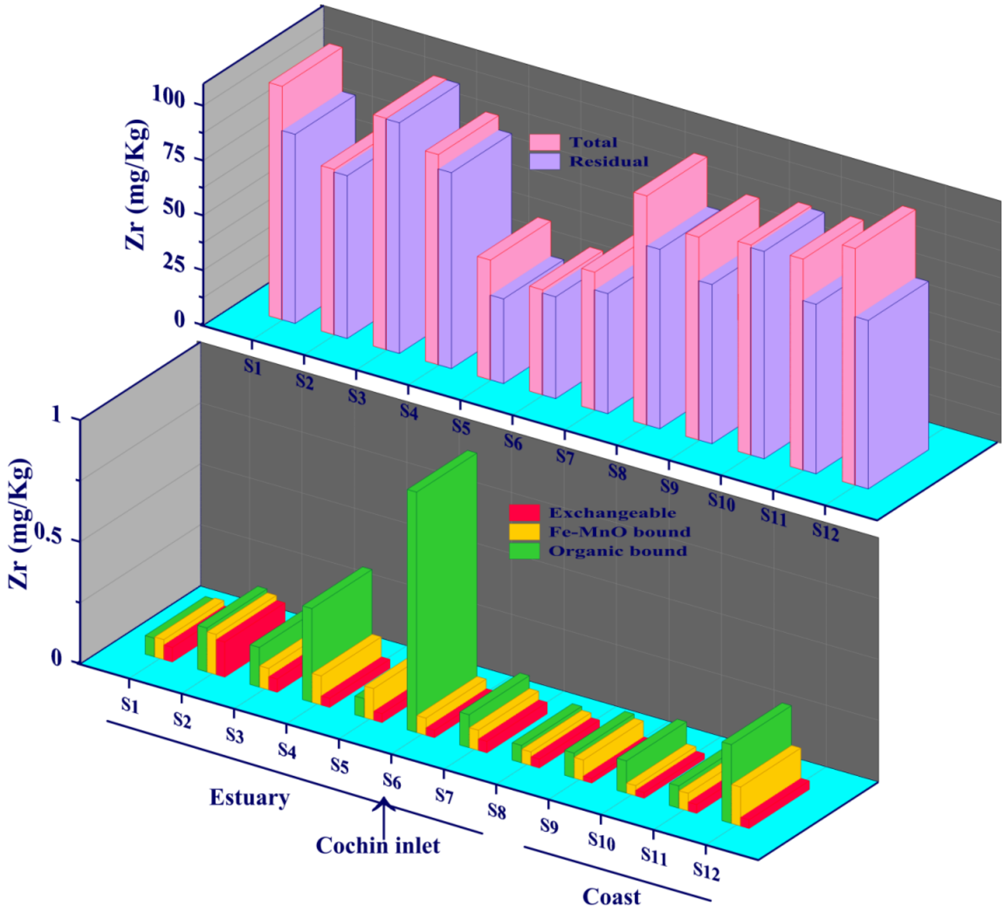

Fig 3.18: Total Zr and its four different fractions in the sediments of Cochin estuary and adjacent coastal stations on October 2011

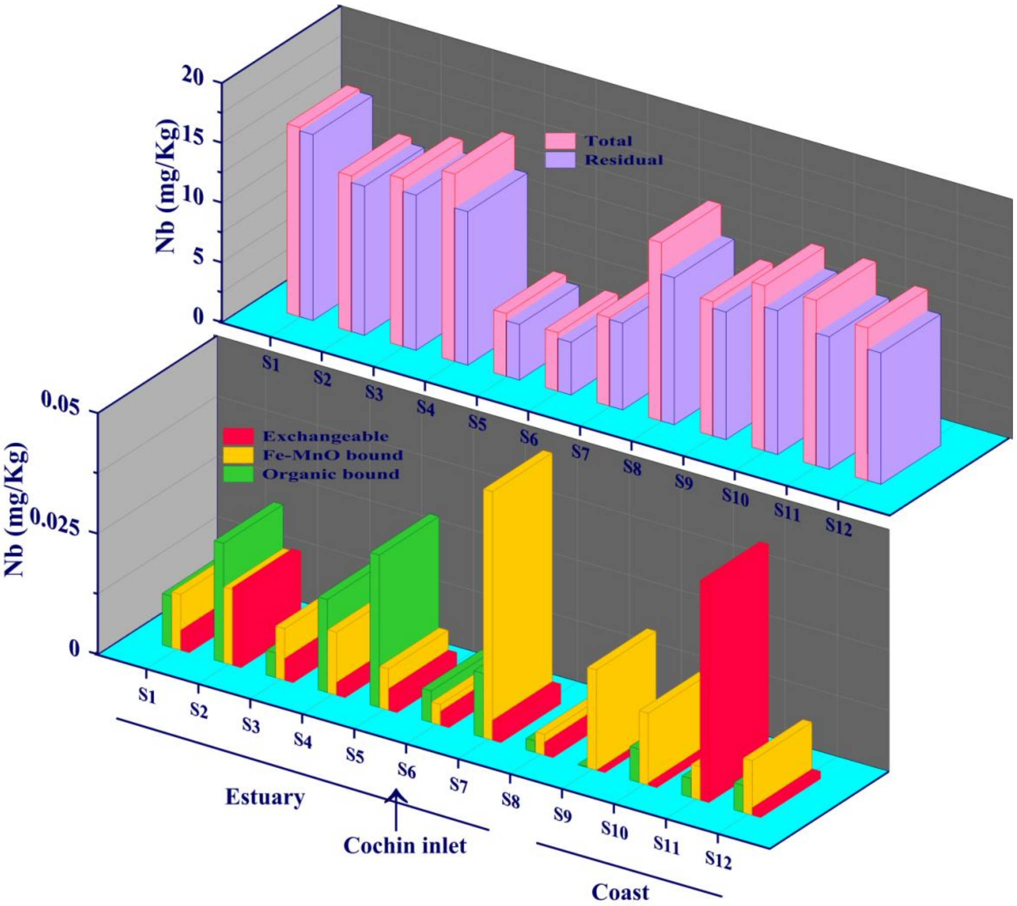

Fig 3.19: Total Nb and its four different fractions in the sediments of Cochin estuary and adjacent coastal stations on October 2011.

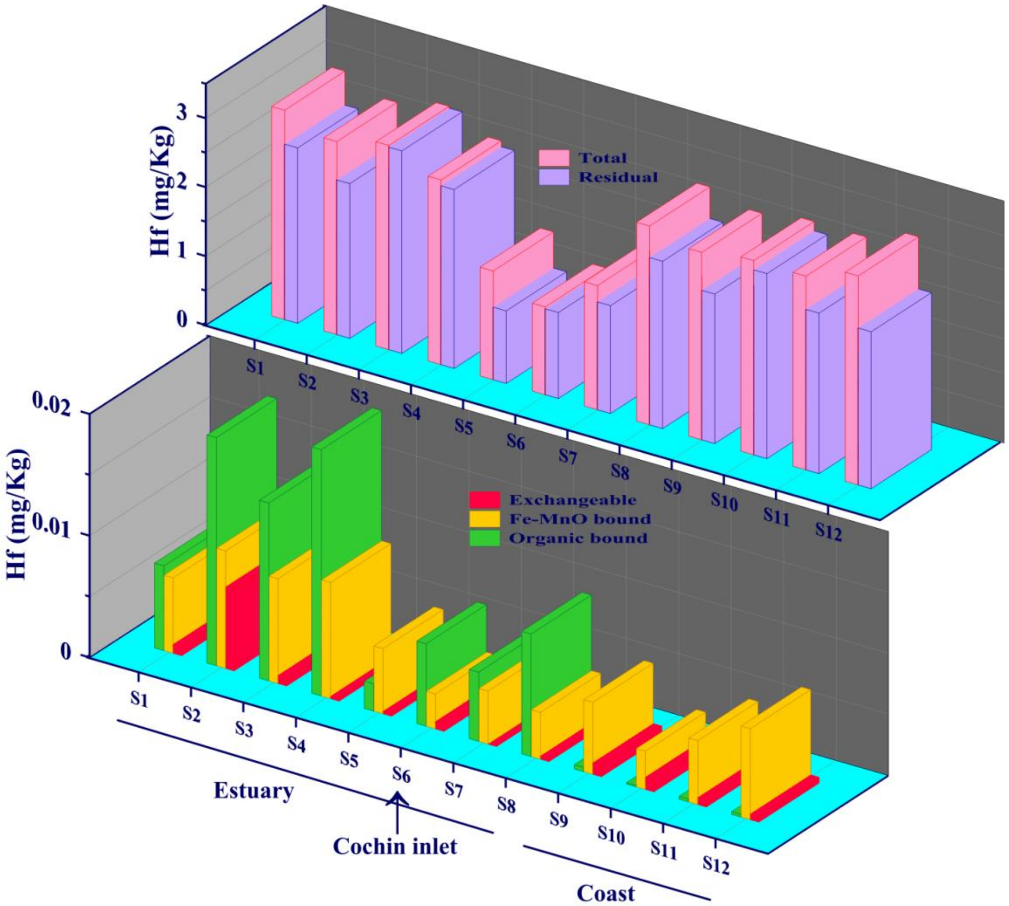

Fig 3.20: Total Hf and its four different fractions in the sediments of Cochin estuary and adjacent coastal stations on October 2011

Table 3.5 Correlation matrix (Pearson) among the different fractions of trace metal (Mn, Pb and Zn), sediment texture and organic carbon in estuarine sediments

Variable	Mn1	Mn2	Mn3	Mn4	TMn	Pb1	Pb2	Pb3	Pb4	TPb	Zn1	Zn2	Zn3	Zn4	TZn	Sand	Silt	Clay	OC
Mn1	**1.00**																		
Mn2	**0.99**	**1.00**																	
Mn3	**0.91**	**0.87**	**1.00**																
Mn4	-0.43	-0.47	-0.13	**1.00**															
TMn	**0.96**	**0.98**	**0.88**	-0.30	**1.00**														
Pb1	**0.96**	**0.98**	**0.82**	-0.41	**0.99**	**1.00**													
Pb2	-0.05	-0.18	0.23	**0.73**	-0.07	-0.17	**1.00**												
Pb3	0.10	-0.04	0.34	0.50	0.00	-0.11	**0.88**	**1.00**											
Pb4	0.68	0.62	**0.79**	0.16	0.70	0.64	0.48	0.43	**1.00**										
TPb	0.57	0.48	**0.75**	0.33	0.57	0.48	**0.71**	0.67	**0.95**	**1.00**									
Zn1	-0.01	-0.12	0.21	0.67	0.01	-0.06	**0.89**	0.66	0.60	**0.74**	**1.00**								
Zn2	0.30	0.17	0.49	0.49	0.25	0.15	**0.86**	**0.86**	**0.77**	**0.91**	**0.77**	**1.00**							
Zn3	0.27	0.15	0.50	0.45	0.24	0.16	**0.86**	0.70	**0.78**	**0.89**	**0.87**	**0.88**	**1.00**						
Zn4	0.46	0.36	**0.73**	0.40	0.41	0.29	**0.74**	**0.85**	**0.75**	**0.88**	0.60	**0.88**	**0.76**	**1.00**					
TZn	0.43	0.32	0.71	0.36	0.37	0.26	**0.74**	**0.83**	**0.75**	**0.88**	0.69	**0.84**	**0.81**	**0.96**	**1.00**				
Sand	-0.43	-0.33	-0.59	0.22	-0.22	-0.16	-0.28	-0.57	-0.29	-0.39	-0.02	-0.41	-0.38	-0.66	-0.64	**1.00**			
Silt	0.22	0.12	0.43	-0.03	0.05	-0.01	0.38	0.52	0.11	0.26	0.05	0.32	0.40	0.53	0.49	**-0.89**	**1.00**		
Clay	0.54	0.47	0.60	-0.37	0.35	0.31	0.10	0.48	0.42	0.43	-0.02	0.40	0.25	0.62	0.63	**-0.86**	0.52	**1.00**	
OC	0.41	0.31	0.56	-0.08	0.23	0.15	0.38	**0.74**	0.33	0.46	0.16	0.52	0.35	**0.76**	**0.76**	**-0.89**	0.67	**0.90**	**1.00**

Values in bold are different from 0 with a significance level alpha>0.05   XLSTAT 2014

Table 3.6 Correlation matrix (Pearson) for trace metal (Mn, Pb and Zn) in different fractions, sediment texture and organic carbon in coastal sediments

Variable	Mn1	Mn2	Mn3	Mn4	TMn	Pb1	Pb2	Pb3	Pb4	TPb	Zn1	Zn2	Zn3	Zn4	TZn	Sand	Silt	Clay	OC
Mn1	**1.00**																		
Mn2	0.08	**1.00**																	
Mn3	0.08	**0.98**	**1.00**																
Mn4	0.94	-0.05	0.01	**1.00**															
TMn	**0.98**	0.04	0.07	**0.99**	**1.00**														
Pb1	-0.41	0.87	0.83	-0.54	-0.47	**1.00**													
Pb2	0.31	0.12	-0.05	-0.02	0.10	0.08	**1.00**												
Pb3	-0.40	0.56	0.67	-0.23	-0.26	0.61	-0.73	**1.00**											
Pb4	0.16	0.51	0.65	0.36	0.32	0.27	-0.71	0.83	**1.00**										
TPb	0.02	0.69	0.81	0.16	0.14	0.53	-0.61	0.91	**0.96**	**1.00**									
Zn1	**-0.96**	-0.36	-0.35	-0.86	-0.92	0.14	-0.35	0.23	-0.27	-0.20	**1.00**								
Zn2	-0.91	-0.49	-0.49	-0.82	-0.88	0.01	-0.25	0.07	-0.41	-0.35	**0.99**	**1.00**							
Zn3	**-0.96**	-0.34	-0.34	-0.88	-0.93	0.16	-0.30	0.21	-0.31	-0.22	**1.00**	**0.99**	**1.00**						
Zn4	0.51	0.90	0.88	0.36	0.46	0.57	0.26	0.30	0.50	0.60	-0.73	-0.82	-0.72	**1.00**					
TZn	-0.46	0.51	0.38	-0.73	-0.62	0.77	0.57	0.02	-0.40	-0.13	0.27	0.24	0.32	0.25	**1.00**				
Sand	-0.06	0.94	**0.98**	-0.08	-0.03	0.84	-0.24	0.81	0.73	0.89	-0.20	-0.36	-0.20	0.77	0.32	**1.00**			
Silt	-0.44	-0.90	-0.93	-0.37	-0.44	-0.58	-0.02	-0.49	-0.69	-0.77	0.66	0.78	0.66	**-0.97**	-0.12	-0.86	**1.00**		
Clay	0.86	0.59	0.58	0.75	0.82	0.11	0.29	-0.01	0.42	0.40	**-0.96**	**-0.99**	**-0.96**	0.88	-0.13	0.44	-0.83	**1.00**	
OC	0.84	0.60	0.60	0.73	0.81	0.14	0.29	0.00	0.43	0.41	**-0.96**	**-0.99**	**-0.96**	0.89	-0.11	0.46	-0.85	**1.00**	**1.00**

Table 3.7 Correlation matrix (Pearson) for trace metal (Cd, Cr and Ni) in different fractions, sediment texture and organic carbon in estuarine sediments

Variable	Cd1	Cd2	Cd3	Cd4	TCd	Cr1	Cr2	Cr3	Cr4	TCr	Ni1	Ni2	Ni3	Ni4	TNi	Sand	Silt	Clay	OC
Cd1	**1.00**																		
Cd2	**0.91**	**1.00**																	
Cd3	**0.81**	**0.96**	**1.00**																
Cd4	0.23	0.27	0.09	**1.00**															
TCd	**0.89**	**0.95**	**0.84**	0.56	**1.00**														
Cr1	0.24	0.19	0.22	-0.09	0.14	**1.00**													
Cr2	**0.75**	**0.73**	0.65	0.36	**0.76**	0.20	**1.00**												
Cr3	0.63	0.67	0.59	0.52	**0.74**	0.58	**0.73**	**1.00**											
Cr4	0.00	0.20	0.27	0.18	0.19	0.36	0.29	0.66	**1.00**										
TCr	0.02	0.24	0.31	0.18	0.21	0.38	0.27	0.65	**0.98**	**1.00**									
Ni1	0.55	0.54	0.49	0.29	0.56	0.66	**0.71**	**0.71**	0.30	0.36	**1.00**								
Ni2	0.50	0.62	0.54	0.69	**0.74**	0.30	0.70	**0.86**	0.64	0.68	**0.73**	**1.00**							
Ni3	0.34	0.39	0.37	0.30	0.42	0.71	0.40	**0.84**	**0.78**	**0.83**	0.67	**0.78**	**1.00**						
Ni4	0.03	0.23	0.29	0.21	0.22	0.36	0.30	0.68	**1.00**	**0.99**	0.31	0.67	**0.81**	**1.00**					
TNi	0.08	0.28	0.33	0.23	0.27	0.40	0.33	**0.72**	**0.99**	**0.99**	0.37	0.70	**0.84**	**1.00**	**1.00**				
Sand	0.02	-0.26	-0.35	-0.14	-0.21	-0.14	-0.30	-0.50	**-0.91**	**-0.95**	-0.32	-0.66	-0.67	**-0.91**	**-0.91**	**1.00**			
Silt	0.03	0.25	0.34	0.06	0.19	-0.02	0.43	0.32	0.66	**0.72**	0.43	0.60	0.45	0.65	0.65	**-0.89**	**1.00**		
Clay	-0.06	0.19	0.26	0.19	0.17	0.29	0.08	0.57	**0.95**	**0.95**	0.12	0.55	**0.73**	**0.96**	**0.95**	**-0.86**	0.52	**1.00**	
OC	0.12	0.35	0.39	0.35	0.37	0.17	0.44	**0.71**	**0.95**	**0.92**	0.28	**0.73**	0.69	**0.95**	**0.95**	**-0.89**	0.67	**0.90**	**1.00**

Table 3.8 Correlation matrix (Pearson) for trace metal (Cd, Cr and Ni) in different fractions, sediment texture and organic carbon in coastal sediments

Variable	**Cd1**	**Cd2**	**Cd3**	**Cd4**	**TCd**	**Cr1**	**Cr2**	**Cr3**	**Cr4**	**TCr**	**Ni1**	**Ni2**	**Ni3**	**Ni4**	**TNi**	**Sand**	**Silt**	**Clay**	**OC**
Cd1	**1.00**																		
Cd2	0.90	**1.00**																	
Cd3	0.17	0.59	**1.00**																
Cd4	-0.37	-0.72	-0.95	**1.00**															
TCd	0.57	0.80	0.73	-0.66	**1.00**														
Cr1	0.81	0.63	-0.10	0.05	0.58	**1.00**													
Cr2	-0.43	-0.76	-0.91	**1.00**	-0.64	0.01	**1.00**												
Cr3	0.77	0.49	-0.34	0.25	0.34	**0.97**	0.20	**1.00**											
Cr4	0.77	0.82	0.40	-0.38	0.91	0.87	-0.39	0.71	**1.00**										
TCr	0.80	0.92	0.58	-0.60	0.95	0.75	-0.61	0.57	**0.97**	**1.00**									
Ni1	-0.29	-0.67	**-0.98**	0.91	-0.85	-0.08	0.88	0.17	-0.56	-0.72	**1.00**								
Ni2	0.66	0.72	0.38	-0.31	0.91	0.84	-0.31	0.68	**0.99**	0.93	-0.55	**1.00**							
Ni3	0.34	0.28	-0.03	0.19	0.62	0.79	0.20	0.70	0.78	0.60	-0.16	0.86	**1.00**						
Ni4	0.74	0.78	0.37	-0.33	0.90	0.87	-0.34	0.71	**1.00**	0.95	-0.54	**0.99**	0.82	**1.00**					
TNi	0.76	0.84	0.48	-0.46	0.94	0.82	-0.47	0.64	**1.00**	**0.98**	-0.64	**0.98**	0.74	**0.99**	**1.00**				
Sand	-0.23	-0.14	0.07	0.23	0.44	0.30	0.29	0.18	0.42	0.25	-0.18	0.56	0.82	0.47	0.40	**1.00**			
Silt	0.61	0.62	0.29	-0.58	0.07	0.04	-0.65	0.06	0.07	0.27	-0.23	-0.09	-0.53	0.01	0.10	-0.86	**1.00**		
Clay	-0.84	-0.94	-0.59	0.79	-0.60	-0.41	0.84	-0.30	-0.58	-0.75	0.62	-0.46	0.05	-0.53	-0.62	0.44	-0.83	**1.00**	
OC	-0.83	-0.94	-0.59	0.79	-0.59	-0.39	0.84	-0.28	-0.56	-0.73	0.61	-0.44	0.07	-0.51	-0.60	0.46	-0.85	**1.00**	**1.00**

Table 3.9 Correlation matrix (Pearson) for trace metal (Sn, V and Cu) in different fractions, sediment texture and organic carbon in estuarine sediments

Variable	**Sn1**	**Sn2**	**Sn3**	**Sn4**	**TSn**	**V1**	**V2**	**V3**	**V4**	**TV**	**Cu1**	**Cu2**	**Cu3**	**Cu4**	**TCu**	**Sand**	**Silt**	**Clay**	**OC**
Sn1	**1.00**																		
Sn2	0.46	**1.00**																	
Sn3	0.28	0.04	**1.00**																
Sn4	-0.57	-0.19	-0.40	**1.00**															
TSn	-0.16	-0.06	-0.38	0.08	**1.00**														
V1	**0.88**	0.53	0.38	-0.48	0.14	**1.00**													
V2	0.37	-0.06	0.16	-0.12	-0.26	0.22	**1.00**												
V3	0.43	-0.15	-0.12	0.26	-0.21	0.32	0.44	**1.00**											
V4	0.58	0.33	-0.05	0.14	0.02	0.51	0.65	0.49	**1.00**										
TV	0.66	0.42	-0.03	0.04	-0.01	0.59	0.68	0.51	**0.99**	**1.00**									
Cu1	0.09	-0.23	0.17	-0.10	-0.58	-0.21	**0.83**	0.18	0.35	0.34	**1.00**								
Cu2	-0.40	0.22	0.11	-0.05	-0.31	-0.38	0.24	-0.45	-0.26	-0.20	0.41	**1.00**							
Cu3	0.21	-0.04	0.08	-0.14	-0.41	-0.01	**0.94**	0.26	0.47	0.51	**0.93**	0.48	**1.00**						
Cu4	0.35	0.29	-0.05	0.37	-0.05	0.32	0.68	0.48	**0.94**	**0.92**	0.41	-0.05	0.54	**1.00**					
TCu	0.18	0.11	-0.23	0.60	-0.07	0.10	0.52	0.56	**0.86**	**0.80**	0.35	-0.19	0.40	**0.94**	**1.00**				
Sand	-0.13	-0.39	0.38	-0.69	-0.07	-0.17	-0.17	-0.48	**-0.71**	-0.68	0.07	0.21	-0.05	**-0.79**	**-0.88**	**1.00**			
Silt	0.03	0.52	-0.50	0.61	-0.13	-0.01	0.15	0.38	0.50	0.52	0.02	0.14	0.17	0.63	0.70	**-0.89**	**1.00**		
Clay	0.21	0.14	-0.15	0.59	0.28	0.32	0.14	0.47	**0.75**	0.68	-0.15	-0.54	-0.09	**0.76**	**0.84**	**-0.86**	0.52	**1.00**	
OC	0.09	0.15	-0.38	0.62	0.32	0.15	0.37	0.43	**0.81**	**0.75**	0.07	-0.25	0.20	**0.87**	**0.92**	**-0.89**	0.67	**0.90**	**1.00**

Table 3.10 Correlation matrix (Pearson) for trace metal (Sn, V and Cu) in different fractions, sediment texture and organic carbon in coastal sediments

Variable	**Sn1**	**Sn2**	**Sn3**	**Sn4**	**TSn**	**V1**	**V2**	**V3**	**V4**	**TV**	**Cu1**	**Cu2**	**Cu3**	**Cu4**	**TCu**	**Sand**	**Silt**	**Clay**	**OC**
Sn1	**1.00**																		
Sn2	-0.50	**1.00**																	
Sn3	-0.68	0.66	**1.00**																
Sn4	0.02	0.31	-0.46	**1.00**															
TSn	-0.63	**0.95**	0.55	0.50	**1.00**														
V1	-0.38	-0.58	0.09	-0.58	-0.48	**1.00**													
V2	-0.84	0.30	0.85	-0.55	0.29	0.58	**1.00**												
V3	0.44	-0.63	**-0.96**	0.54	-0.43	0.06	-0.70	**1.00**											
V4	-0.40	-0.57	0.10	-0.58	-0.46	**1.00**	0.59	0.05	**1.00**										
TV	-0.63	-0.34	0.27	-0.48	-0.21	**0.96**	0.74	-0.07	**0.96**	**1.00**									
Cu1	-0.30	0.05	-0.43	0.83	0.34	-0.03	-0.22	0.64	-0.02	0.09	**1.00**								
Cu2	-0.54	0.60	0.05	0.83	0.81	-0.34	0.01	0.15	-0.32	-0.10	0.83	**1.00**							
Cu3	-0.93	0.77	0.69	0.22	0.87	0.00	0.67	-0.48	0.03	0.29	0.36	0.73	**1.00**						
Cu4	-0.36	-0.15	0.64	-0.94	-0.27	0.70	0.80	-0.63	0.70	0.68	-0.65	-0.59	0.10	**1.00**					
TCu	0.21	-0.80	-0.10	-0.81	-0.87	0.78	0.22	0.06	0.77	0.58	-0.50	-0.84	-0.55	0.70	**1.00**				
Sand	-0.57	0.13	0.83	-0.82	0.02	0.59	0.92	-0.78	0.59	0.65	-0.56	-0.36	0.37	**0.96**	0.47	**1.00**			
Silt	0.80	-0.59	**-0.98**	0.45	-0.53	-0.25	-0.93	0.88	-0.27	-0.45	0.31	-0.11	-0.75	-0.68	0.04	-0.86	**1.00**		
Clay	-0.80	0.91	0.84	0.10	0.91	-0.19	0.65	-0.72	-0.17	0.08	0.07	0.58	0.94	0.16	-0.58	0.44	-0.83	**1.00**	
OC	-0.81	0.90	0.85	0.08	0.90	-0.17	0.67	-0.72	-0.14	0.11	0.06	0.57	0.94	0.18	-0.56	0.46	-0.85	**1.00**	**1.00**

3.5 DISCUSSION

3.5.1 Distribution of trace metals

There are numerous data sets available regarding the trace metal enrichment and their ecological implications in surface sediments of the Cochin estuary (Balachandran et al., 2005, 2006; Maheswari et al., 2006; Mohan et al., 2012; Deepulal et al., 2012; Selvam et al., 2012; Ramasamy et al., 2012; Martin et al., 2012; George et al., 2016) and its impact on the coastal environment (Nath et al., 2000; Balachandran et al., 2003, 2006; Laluraj, 2009; Sudhananth et al., 2011; Udayakumar et al., 2014; Sreekanth et al., 2015). The concentrations of various fractions of trace metals in sediments in the Cochin estuary and adjacent coastal region measured during the present study are comparable with the aforesaid literatures.

The trace metals were low in the sandy sediments at station 5 and 6. Stations with clayey texture showed high metal accumulation which was maximum at S_1 and S_2. The existence of a tidally energetic condition at station 5 and 6 probably did not allow flocculation of fine particles over the sandy sediments, which led to a lower trace metal deposition. On the other hand, despite a relatively low clay and organic carbon at S_1, the high concentration of trace metals in sediments could be due to the flow-restrictions in the region and high loading through the River Periyar. The weak flushing resulted in entrapment of fine particles and trace metals in sediments in the northern estuary (Balachandran et al., 2005). Moreover, % of smectite was higher in this region (S_1), which can hold more trace metals due to its high cation exchange capacity (80-120) and large surface area. The enrichment of metals in the coastal region (S_9, S_{10}, S_{11}, and S_{12}) generally indicates that export fluxes from the Cochin Estuary are quite significant at times. Most of the trace metals (Zn, Mn, Cr, Ni, Cd, Pb, Cu and Sn) in sediments (except station 5 and 6) showed values exceeding the standard sediment quality guidelines (SQG). The normalisation of metals with crustal abundance showed moderate to severe contamination for Zn and moderate contamination for other metals (Mn, Cr, Ni, Cu, Sn, Pb) indicating their anthropogenic input into the estuary. High enrichment factor for Zn, Cd, Cu, Pb and Fe in the north estuary was reported earlier (Balachandran et al., 2005). Zn and Cd observed during the present study were lower than their reported values, while the concentrations of Cu and Pb were slightly high. Estuarine and coastal sediments in general, showed a long-term accumulation of trace metals in sediments. In many cases, it was observed that anthropogenic inputs exceeded the natural weathering processes.

3.5.2 Fractionation of trace metals

The results obtained from the sediment fractionation showed that among the trace metals studied, all the metals were largely associated with the residual phase, although they are available in other fractions. The exchangeable and carbonate/bicarbonate fractions are the important non-residual binding phases for some trace metals (Zn, Cd and Mn). An increase in the labile fraction of Cd and Mn with the increase in total Cd and Mn loading would exacerbate the potential toxicity of these metals in the estuarine and coastal environment. The risk assessment studies (RAC) also support this view indicating a medium risk for Zn and Mn against a high risk for Cd in the estuary. The concentration of Cd in the exchangeable fraction is in good agreement with the results of previous studies in CE (Mohan et al., 2012, Manju, 2014; Renjith et al., 2016).

The organic phase was found to be a major binding phase of Pb, Cr, Ni and Sn in the estuarine sediments. The estuarine sediments enriched in organic matter could make stable bonds with these metals. However, there was a difference in the metal-organic complexes formed in the estuary and coastal sediments. High organic matter in coastal sediments is not an effective scavenger of most of the heavy metals studied however high affinity of vanadium towards the organic matter favored their stable binding in coastal sediments. It has been observed that marine derived organic matter in this coastal region has relatively less complexing capacity towards Ni, Cu, and Pb (Chakraborty et al., 2016). The results from the present study substantiate this, as the organic fractions of these metals have showed a decreasing trend towards the coastal sediments.

There are many studies showing the thermodynamic stability of Cu-organic complexes in sediments (Nair et al., 1992; Prasad et al., 2006; Mohan et al., 2012; Manju, 2014; Renjith et al., 2016). Cu in estuarine sediments can forms thermodynamically stronger complexes with the organic phase due to its high ionic potential and exchange rate (Chakraborty et al., 2016). The present study showed a different trend, as the major portion of Cu was residual and only a small portion was associated with organic phase. Cu in organic binding phase showed an increase with increased Cu loading in sediments however, there was poor correlation with organic carbon has been attributed to the variation in the binding capacity of organic compounds (Zhang et al., 2015). The natural organic compounds present in the environment are (1) amino-compounds (amino acid, protein, peptide, ammonia, etc), (2) carbohydrates (cellulose, amino- sugar, etc.), (3) lipids, isoprenoids and steroids (fat, fatty acid, alcohol etc.), (4) heterocyclic compounds, (5) phenol, quinone and humic compounds and (6) hydrocarbons (Jianfeg et al., 1984., Renjith et al., 2013; Manju and Sujatha, 2012; Gireesh Kumar et al., 2013, Sarkar et al., 2016). The composition, structure, reducing and adsorbing capacities and, the metamorphic forms of organic matter may affect the association of the metal on to the sediment. An earlier study has point out that mineralization under oxidizing conditions may release trace metals attached to the organic matter to the overlying water column (Jain et al., 2004). The labile organic matter undergoes mineralisation faster than the refractive organic matter (Gireeshkumar et al., 2013a). However, humic substances and other high molecular weight compounds take longer time for mineralization (Klucakova et al., 2017). Thus, the humic-bound metals are relatively stable in sediments. Thus, the nature of organic matter has an important role in the fractionation of trace metals in sediments. Moreover, the oxidized fraction comprises trace metals bound to the sulfides. One important pathway of metal immobilization is through sulfate reduction to form sulfide-rich sediments. Many of the trace metals are found to form insoluble metal sulfides that result in their low bio-availability (Sundelin and Erikkson, 2001).

It was observed that Fe-Mn oxy hydroxide is an efficient scavenger of metals like Zn, Ni, Pb, Cd, Mn and V in both the estuarine and coastal environments. The metals bound to Fe-Mn oxy hydroxide phases are found to be increasing with increasing metal loadings in the sediments. This can be due to the increased concentration of Fe-Mn oxides in this region. Several studies have highlighted the role of Fe-Mn oxides as excellent scavengers of trace metals in sediments (Nair et al., 1992; Balachandran et al., 2006, Shynu et al., 2012; Mohan et al., 2012).

Microbially mediated redox reactions can also partially reduce the insoluble Fe^{+3} and Mn^{+2} oxides and release them into pore water and overlying water (Petersen et al., 1995). Moreover, changes in ionic composition and pH also increase the mobility of metals adsorbed to mineral surfaces. However, high concentrations of metals are not the only requirement for their bioaccumulation, rather, it is purely species specific and dependent on the ecological responses of an organism (Maheswari et al., 1997, 2006; Renjitha et al., 2016).

The residual fractions were found to be the dominant in concentrating most of the trace metals in the estuarine and coastal sediments. Mn and Zn concentrations in the residual fraction were higher than the value reported for adjacent source rock (Nath et al, 2000) and the Standard Sediment Quality Guidelines (SQG). The enrichment of metals in the residual fraction may be due to the transformation of non-residual fractions under favorable condition to mask their adverse impact to biota. Trace metals are naturally persistent and non biodegradable. Therefore, they can only be converted to stable forms of reduced availability (Balachandran et al., 2003; 2006). They suggested that there is an annual transformation in the behavior of elements from an inorganic deposition to organic association followed by sedimentary modifications and normalization along the coastal environment of Cochin. From the present study, it is clear that the nature of binding phase has great impact on the mobility of trace metals in the sediments.

A comparison has been made with fractionation of sediment trace metals by other researchers in Cochin estuary. Table 3.11 shows that there is an increase in the exchangeable Cd (Fr 1) in the estuarine sediments over the years. The concentrations of Mn, Cr, Pb, Ni and Cu in exchangeable/carbonate fractions have decreased over the years, but the % of Zn in Fr.1 was similar to previous reports. The high concentration of organic-bound Cu initially has now decreased substantially through its masking into a stable residual phase. Except for these two aspects, the present results are in good agreement with the earlier studies.

The estuarine sediments are exposed to dynamic environment, where short-term fluctuations in the tides, turbidity, salinity, pH, redox conditions, dissolved oxygen etc. bring out significant alterations in their texture and responses to the environment. A small change in these conditions may severely alter the sediment properties and their bioavailability, which should be considered to minimize the pollution levels and to conserve the estuarine and coastal regions.

3.6 SUMMARY AND CONCLUSION

The texture of the estuarine sediments varied from clayey-sand to silty-clay; while the coastal sediments were mainly silty-clay and the bar mouth and surrounding regions were sandy due to strong flushing. There was a progressive increase in the fine fractions from upper to the central estuary. The near shore areas (~5-6.5 m) showed high clay content and organic enrichment compared to the offshore stations (~30 m). It was observed that the silty-clay sediments preferentially accumulated organic carbon while the sandy sediments were impoverished in organic carbon. Organic carbon was relatively high in the coastal sediments than in estuarine sediments. Higher OC in the near shore sediments than in offshore sediments can due to higher clay content and high productivity along the inner shelf. Kaolinite and smectite were the dominant clay minerals observed in the study region with relatively lower percentage of chlorite, illite, quartz and gibbsite. The trace metals were generally low in the sandy sediments and high in clayey sediments. High metal accumulation was observed in north estuary, where smectite content was also high. The concentrations of most of the trace metals (Zn, Mn, Cr, Ni, Cd, Pb, Cu and Sn) in silty-clay dominant sediments were exceeding the standard sediment quality guidelines. The normalisation of metals with crustal levels showed moderate to severe contamination for Zn and moderate contamination for other metals (Mn, Cr, Ni, Cu, Sn, Pb) indicating their anthropogenic input into the estuary. The present study identified increased anthropogenic input of trace metals into the estuary and its impact on the coastal region. The trace metal composition in sediments of the Cochin estuary and adjacent coastal stations was comparable with the previous studies.

Exchangeable, carbonate/bicarbonates phases were the important non-residual fractions of Zn, Cd and Mn. The enrichment of labile fractions of Cd and Mn with increase in total metal content (Cd_T and Mn_T) indicates that this would exacerbate the potential toxicity of these metal in the estuarine and coastal environment. The health risk assessment studies (RAC) also support this showing a medium risk for Zn and Mn and high risk for Cd in sediments, as it was the most mobile element in the sediments. These studies underline the potential health risk about the habitat in the north estuary due to trace metal pollution.

The organic phase was the major binding phase for Pb, Cr and Ni in the organic-rich estuarine sediments showing its stability in binding metals. The organic enrichment in the estuary was found to play an important role in the immobilization of Pb, Cr and Ni. High organic matter in coastal sediments is not an effective scavenger of most of the trace metals studied however its high affinity towards Vanadium makes it more stable in coastal sediments. Vanadium in estuarine sediments was mostly concentrated in the Fe-Mn oxy hydoxide phase rather than organic phase. Major portion of Cu in the estuarine sediments was as residual form and there was only a weak association with organic phase. The non-residual fractions of most of the trace metals in coastal sediments were preferably associated with Fe-Mn oxy hydroxide fraction. Thus, Fe-Mn oxyhydroxide was found to be a good scavenger of Zn, Ni, Pb, Cd and Mn in both estuarine and coastal environments. It was also observed that the second host for Sn and Pb, varied with respect to the sediment texture and organic content of the sediments.

The residual phase was found to be a prominent host for all metals in estuarine and coastal sediments. The residual fraction represented an essentially non-labile component and thus acts as an important sink for trace metals in sediments. Mn and Zn in residual fraction were higher than the value reported for adjacent source rock and the standard sediment quality guidelines (SQG). The enrichment of metals in the residual fraction may be due to the transformation of non-residual forms to stable residual forms to mask its toxicity to biota. The deposition of trace metals in sediments was found to be due to the combined effect of the transport, dispersal and deposition processes taking place from their sources in the rivers to sinks in the estuary and coastal region. It was observed that the high sorption capacity of clay and organic matter strengthen the metals bound to their lattice. The nature of metal binding phase played an important role in the fate and transport of trace metals in the study region. It is well established that bioavailability of a metal is not only a factor for its bioaccumulation; it actually depends on the species specific physiological and ecological conditions. However, measurement of such metal fractions will be useful to understand the metal release from sediments under different conditions and implement for the natural water management systems.

Table 3.11 Metal fractions in Cochin estuarine sediments – a comparison with previous

Metal	Fr.1 (%)	Fr.2 (%)	Fr.3 (%)	Fr.4 (%)	TM(mg/kg)	Instrumentation	Reference
Zn	2.1 - 11.4	22.2 - 38.8	23 - 54	13 - 52	29.3 - 290.5	FAAS	Rajamani et al, 1994
	0.6 - 33	2.4 - 19.3	6.7 - 43.4	28 - 88.8	135.3 - 258.9	AAS	Nair et al, 1992
	0.6-25.1	1.2 - 8.6	0.7 - 4.1	63.7 - 92.5	112.5 - 435.7	ICP-MS	Present study
Mn	23.6 - 30.2	13.0 - 31.0	14.8 - 38.3	4.8 - 66.5	123.6 - 280.5		Rajamani et al, 1994
	2.7 - 49.5	1.4 - 25.7	10.1 - 40	27.8 - 82.2	7.0 -170		Nair et al, 1992
	5.2 -19.4	2.04 -18.8	2.0 - 7.6	28.5 - 84.6	298.5 - 720	ICP-MS	Present study
Cd	6 - 19.6	bdl - 4.2	8.6 - 44.9	35 - 80.8	0.97 - 9.4		Rajamani et al, 1994
	2.1 - 41.5	1.7 - 26.1	15.2 - 59.5	23.3 - 69.4	0.34 - 8.4		Nair et al, 1992
	9.5 - 48.8	13.2 - 40.4	2.99 -11.6	5.9 - 62.4	0.1 - 2.4	ICP-MS	Present study
Cu	1.1 - 2.5	13.5 - 34.1	34 - 45	22.8 - 40.6	5.5 - 51.3		Rajamani et al, 1994
	0.69 -16.2	0.0 - 4.4	7.6 - 49.2	46.6 - 89.8	1.3 - 50.2		Nair et al, 1992
	0.3 - 3.0	3.5 - 26	16 - 32	-	22.2 - 82.2	GFAAS	Chakraborty et al, 2016
	0.1 - 0.6	0.03 - 0.25	1.1 - 4.1	90.5 - 96.9	27.2 - 65.7	ICP-MS	Present study
Pb	1.81 - 13.4	bdl - 29.1	16.2 - 32.6	32.6 - 75.4	33.2 - 117.1		Rajamani et al, 1994
	1.54 - 23.03	1.1 - 20.9	1.4 - 28.6	52.5 - 92.7	3.5 - 49.9		Nair et al, 1992
	0.3 - 2.0	20- 48	7.0 - 30	-	24.4 - 34.2	GFAAS	Chakraborty et al, 2016
	0.5 - 6.0	7.6 -18.6	3.8 - 17.8	64.6 - 87.1	16.7 - 41.9	ICP-MS	Present study
Ni	0.53 - 8.7	0.42 - 4.99	3.1 - 21.9	71.4 - 92.0	1.86 - 70.6		Nair et al, 1992
	0.8 - 3	4.0 -15.0	22.0 -27.0	-	21.1 - 36.1	GFAAS	Chakraborty et al, 2016
	0.9 - 4.7	1.8 - 4.4	3.9 - 21.5	70.3 - 89.5	15.5 - 102.9	ICP-MS	Present study
Cr	0.16 - 8.5	0.03 - 0.5	2.2 - 27.6	71 - 95.6	4.1 - 99.7		Nair et al, 1992
	0.1 - 1.5	1.4 - 3.02	8.0 - 17.4	59.1 - 89.6	84.2 - 183	ICP-MS	Present study

*bdl- below detection limit; TM- Total metal (mg/kg)

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Chapter 4

RARE EARTH ELEMENTS

4.1 INTRODUCTION

The International Union of Pure and Applied Chemistry (IUPAC) define the rare earth elements (REE) as a collection of seventeen chemical elements in the periodic table that include 15 lanthanides (Lanthanum, Cerium, Praseodymium, Neodymium, Samarium, Europium, Gadolinium, Terbium, Dysprosium, Holmium, Erbium, Thulium, Ytterbium and Lutetium) and two other elements Scandium and Yttrium. Scandium and Yttrium are considered as rare earth elements since they tend to occur in the same ore deposits as the lanthanides and exhibit similar chemical properties. The rare earth elements are often described as ‘light-group rare earth element’ (LREE) or ‘heavy group rare earth element’ (HREE). The definition of a LREE and HREE is based on the electronic configuration of each rare earth element. The LREE are defined as Lanthanum (atomic number 57) through Gadolinium (atomic number 64). The LREE have in common increasing unpaired electrons from 0 to 7. The HREE are defined as Terbium (atomic number 65) through Lutetium (atomic number 71) and also Yttrium (atomic number 39). The HREE differ from the first eight lanthanides in that they have paired electrons (a clockwise and counter clockwise spinning electron). The LREEs have no paired electrons. Yttrium is included in HREE group based on its similar ionic radius and chemical properties. Scandium is also trivalent; however, its other properties are not similar enough to classify it as either LREE or HREE.

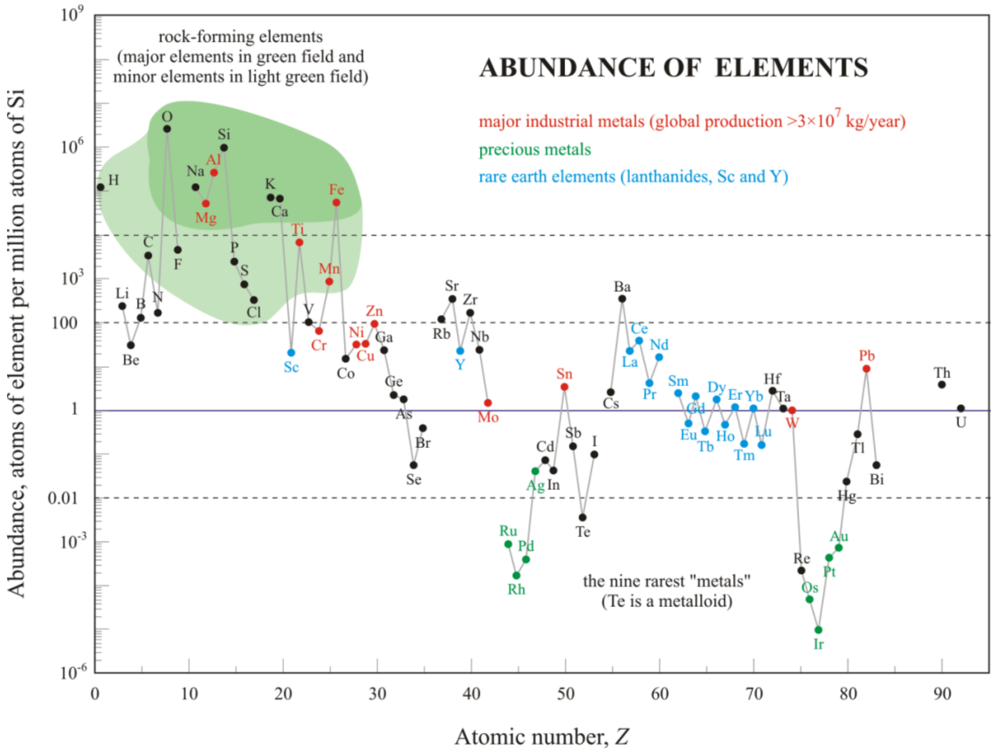

Fig 4.1a: Abundance of Rare Earth Element, Thorium and Uranium per million atoms of silicon (https://en.wikipedia.org/wiki/File:Elemental_abundances.svg).

Despite their name, rare earth elements (with the exception of radioactive promethium) are relatively plentiful in the Earth crust (Fig. 4.1a) The more abundant REE are similar in crustal concentration to common place industrial metals such as chromium, nickel, copper and lead. Even the least abundant REE, thulium is nearly 200 times more common than gold. In contrast to ordinary base and precious metals, REE have very little tendency to become concentrated in exploitable ore deposits. It was due to the scarcity of the mineral that led to the term ‘rare earth’. Thorium and uranium are the two commonly occurring actinides, which have major roles in aquatic biogeochemical processes.

REE are widely used in modern technological devices such as super conductors, magnets, electronic polishers, refining catalysts and hybrid car components (primary batteries). Rare earths are also used as active ions in luminescent materials used in opto electronics (Nd:YAG laser). Erbium-doped fiber amplifiers are significant devices in optical communication systems. Phosphors with rare earth dopants are also widely used in cathode ray tube technology such as television sets; europium as a phosphor dopant made good red phosphors possible. Yttrium iron garnet spheres have been useful as tunable microwave resonators. Rare earth oxides are mixed with tungsten to improve its thermal resistance during welding.

Rare earth elements have become important geochemical tracers to understand the chemical evolution of the earth’s crust (Goldstein and Jacobsen, 1988; McLennan, 1989; Gaillardet, 1995; Dupre et al., 1996). Moreover, REE have been used as analogues for actinide elements for the disposal of radioactive wastes, demonstrating their immobility in weathering environment (Wood, 1990). There are mainly two processes controlling the REE variation in sediments (i) weathering at source and (ii) sedimentological characters in the environment (Nath et al; 1997, 2000, Pattan et al., 2005). The major sources of REE to the ocean are rivers (Goldstein et al., 1988), ocean crust and sediment diagenesis, though it is small relative to the other two

(Elderfield and Sholkovitz, 1987). REE in marine sediments are partitioned into terrestrially derived lithogenous fraction, biogeneous fraction, carbonate fluorapatite, montorillonite, the zeolite, phillipsite, glauconite and Fe/Mn oxide hydride fraction (Piper et al., 2013). Light rare earths (LREE) are either scavenged onto the surface particles such as Mn/Fe oxyhydroxides and clay minerals or precipitated as REE phosphates (Byrne and Kim, 1990). The formations of both promote the enrichment of HREEs in seawater. Certain minerals such as alumino silicates or appatite tend to have high concentration of REE while other minerals have very low concentrations (Graf, 1977).

Several studies have indicated that REE are significantly mobilized during weathering and they behave non-conservatively (Braun et al., 1990; Sholkovitz et al., 1994). River sediments generally have residual and labile fractions. The labile fractions are sensitive to environmental changes such as redox conditions, salinity, chelates, pH, adsorption desorption, complexation, precipitation etc. The provenance and distribution of REEs in Cochin estuary and adjacent coastal region have been studied early (Nath et al., 2000; Siby, 2004; Laluraj 2009; Deepulal et al., 2012). However, very little is known about their fractionation in sediments. Accordingly, the objective of this study is:

❖ To study the distribution and fractionation of rare earths and radioactive uranium and thorium in the sediments of Cochin estuary and adjacent coastal regions to infer their provenance, behaviour and depositional conditions.

4.2 SAMPLING STRATEGY

In order to understand the distribution and fractionation of rare earths, thorium and uranium, the surface sediments were collected from 8 locations from the north and central region of Cochin estuary, in addition to the adjacent coastal stations at a depth of 5, 6.5, 27 and 30m (Fig 4.1b). The coastal stations at ~5 and ~27 m were located north of the Cochin inlet and stations at ~6.5 and ~30 m were located south of the Cochin inlet. The geographic positions of sampling stations are given in Table 4.1. The sampling was carried out during October 2011. Sediments were collected using a Van veen stainless steel grab ($0.042m^2$), sealed in plastic bottles, kept in ice, transported to the laboratory and stored at -20ºC until analysis. Salinity of bottom water measured using CTD are given in Table 4.3.

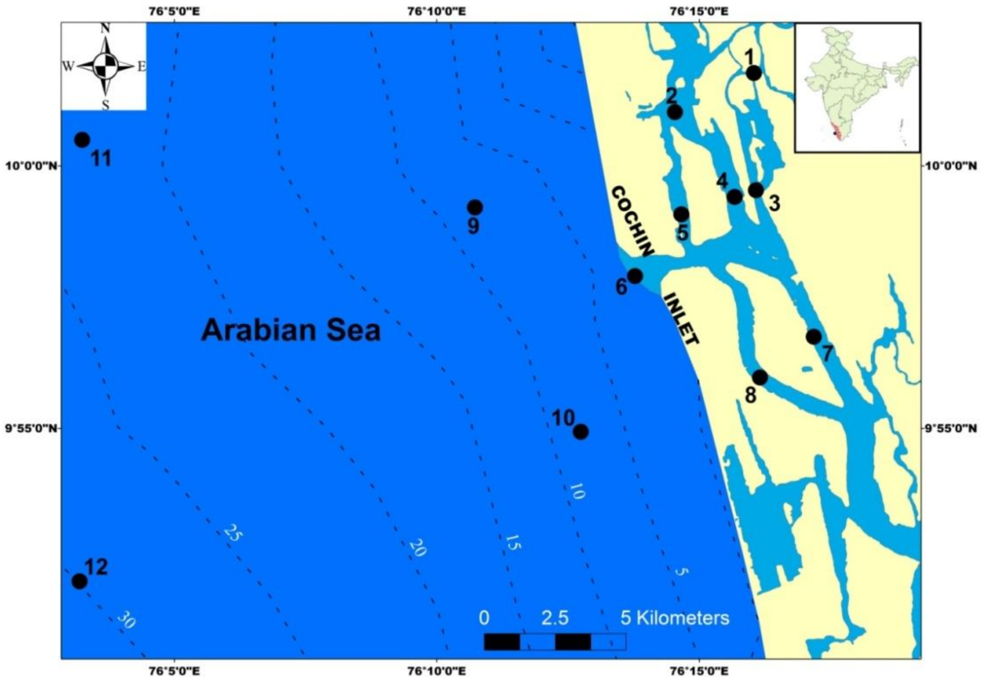

Fig 4.1b**:** Map of the study area showing locations of sampling sites

Table 4.1: Station locations in Cochin estuary and adjacent coastal region

SI No	Sampling Locations	St. code	Lat (°N)	Long(°E)
1	Moolampilly	S_1	10.0312	76.2666
2	Vallarpadam north	S_2	10.0174	76.2442
3	Bolghatty	S_3	9.9913	76.2680
4	Vallarpadam-Bolghatty bridge	S_4	9.9891	76.2607
5	Vallarpaadam-Vypeen bridge	S_5	9.9823	76.2445
6	Cochin inlet (10-15m)	S_6	9.9702	76.2415
7	Ernakulam Channel	S_7	9.9454	76.2880
8	Mattanchery channel	S_8	9.9341	76.2688
9	Near shore (5.3m)	S_9	9.9734	76.1870
10	Near shore (6.8m)	S_{10}	9.9293	76.2264
11	Off shore (27m)	S_{11}	10.0040	76.0833
12	Offshore(30m)	S_{12}	9.9167	76.0833

4.3 ANALYTICAL METHODOLOGY

The sediment samples were portioned into three for the analysis of total metals, organic carbon and grain size. Before the grain size analysis, the inorganic carbonate was removed using 10% HCl and organic matter was removed using H_2O_2 (Folk, 1980). For texture analysis, the sediments were washed with distilled water, dried and treated with sodium hexametaphosphate to disperse the sediments and the particles were separated following the pipette analysis (Krumbein and Petti John, 1938). Shepard nomenclature was used to describe the sediment texture (Shepard, 1954). Sediment organic carbon (OC) was analyzed by wet chromic acid oxidation method suggested by El Wakeel and Riley, 1957. The amount of total organic matter (TOM) was computed by multiplying the OC values with 1.80 (Muller et al., 1986).

Table 4.2: REE, Th and U concentrations (mg/kg) in Standard Reference Material (MAG 1), RSD (%) in analysis and are given below.

SI No	**Element**	**Standard Reference Material (MAG 1)**			**PAAS (mg/kg)**
		Certified value (mg/kg)	**Observed value (mg/kg)**	**RSD (%)**	
1	Sc	17 ± 1	17.2 ± 0.161	0.934	16
2	Y	-	28 ± 0.372	1.328	26
3	**La**	43	43 ± 0.562	1.306	38.20
4	**Ce**	88	88 ± 0.984	1.119	79.60
5	**Pr**	-	9.3 ± 0.012	0.125	8.83
6	**Nd**	38	38 ± 0.349	0.918	33.90
7	**Sm**	7.5	7.5 ± 0.111	1.476	5.55
8	**Eu**	1.6	1.6 ± 0.017	1.074	1.08
9	**Gd**	5.8	5.8 ± 0.036	0.612	4.66
10	**Tb**	0.96	1.0 ± 0.012	1.208	0.77
11	**Dy**	5.2	5.2 ± 0.128	2.463	4.68
12	**Ho**	1	1.0 ± 0.014	1.351	0.99
13	**Er**	3	3.0 ± 0.046	1.521	2.85
14	**Tm**	0.43	0.43 ± 0.000	0.048	0.41
15	**Yb**	2.6	2.6 ± 0.016	0.622	2.82
16	**Lu**	0.4	0.4 ± 0.010	2.535	0.433
17	Th	-	11.9 ± 0.319	2.682	14.6
18	U	-	2.7 ± 0.131	4.852	3.1

*Standard reference material (MAG 1) was obtained from Geological survey of India (GSI). *PAAS is the Global Shale Value used for normalisation of REE.

For the analysis of trace metals, the sediment samples and rock standards (MAG 1) were dried (at 60°C), powdered (mortar and pestle) and acid digested with a mixture of supra pure HF+HNO_3+$HClO_4$ (7:3:1) in teflon vessels on a hot plate (Balaram and Rao, 2002). The residues were re-dissolved in 2% ultrapure HNO_3 (containing 1ppm Rhodium as internal standard) and analyzed using an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). The Certified Reference Material (MAG 1), obtained from Geological Survey of India was used to calibrate the method. Fractionation of sediment metal was achieved through sequential extraction procedure (SEP) suggested by Tessier et al., 1979 (Methodology in detail given in chapter 3). Precision and accuracy of the analysis was checked by the replicate analysis of the certified reference material (MAG-1) obtained from Geological survey of India. % error of the analysis ranged from 0.05 to 5.38% for MAG-1 reference material. The relative standard deviation (standard deviation/ mean of triplicate samples) ranged from 0.048 to 4.8% for MAG-1 reference material (Table 4.2).

4.4 RESULTS

4.4.1 General Characteristics of sediments

The organic carbon and textural pattern of sediments from Cochin estuary and adjacent coastal stations are given in Table 4.3. The organic carbon in the estuarine and coastal stations varied from 6.53 to 25.81mg/g and 24.22 to 36.62mg/g respectively. In the estuary, the organic carbon was low at S_5 and S_6, while all other estuarine stations showed high organic carbon. The coastal sediments showed higher organic carbon than estuarine sediments. The texture of sediments in the estuary varied from sandy-silt to silty-clay whereas in coastal sediments, the texture was silty-clay for all stations (in detail given in chapter 3). The dominant clay minerals identified in the study region was kaolinite and smectite (in detail given in chapter 3).

Table 4.3: Organic Carbon and Textural pattern of estuarine and coastal sediments and salinity in the study region

Stations	**Salinity**	**Organic carbon (mg/g)**	**Sediment Texture**
S_1	4.68	17.22	Clayey sand
S_2	5.44	19.97	Silty clay
S_3	9.13	22.45	Sandy clay
S_4	9.84	24.1	Silty clay
S_5	10.17	6.53	Clayey sand
S_6	25.02	12.7	Clayey sand
S_7	10.09	13.43	Sandy silt
S_8	11.66	25.81	Silty clay
S_9	28.86	36.62	Silty clay
S_{10}	23.42	32.15	Silty clay
S_{11}	26.28	27.28	Silty clay
S_{12}	30.58	24.22	Silty clay

4.4.2 Distribution of REE (Lanthanides, Sc and Y)

The distributions of REE in the estuarine and coastal sediments are presented in Fig 4.3-Fig 4.18. The distribution of REEs in the sediments of Cochin estuary varied as Sc: (7.72 to 20.62)mg/kg; La: (24.46 to 102)mg/kg; Ce: (44.26 to 171.28)mg/kg; Pr: (4.33 to 17.37)mg/kg; Nd:(18.13 to 70.49)mg/kg; Sm: (3.41 to 11.11)mg/kg; Eu: (1.16 to 2.18) mg/kg; Gd: (2.39 to 8.05)mg/kg; Tb: (0.38 to 1.23) mg/kg; Dy: (2.12 to 6.63)mg/kg; Ho: (0.43 to 1.31)mg/kg; Er: (1.3 to 3.85) mg/kg; Tm: (0.18 to 0.60) mg/kg; Yb: (1.10 to 3.16) mg/kg: Lu: (0.17 to 0.47) mg/kg ; Y: (12.62 - 38.90)mg/kg respectively.

REE in the sediments of coastal stations were lower than estuarine stations and varied as Sc: (14.92 to 18.8)mg/kg ; La: (44.02 to 55.73)mg/kg ; Ce: (91 to 102.05)mg/kg; Pr: (8.85 to 10.25)mg/kg; Nd: (37.68 to

43.08)mg/kg; Sm: (7.01 to 7.56)mg/kg; Eu: (1.78 to 1.91)mg/kg; Gd: (5.62 to 6.19)mg/kg; Tb: (0.90 to 1.05)mg/kg; Dy: (4.94 to 5.89)mg/kg; Ho: (0.82 to 1.20)mg/kg; Er: (2.82 to 3.49)mg/kg; Tm: (0.39 to 0.48)mg/kg; Yb: (2.3 to 2.87)mg/kg: Lu: (0.33 to 0.40)mg/kg; Y (26.75 - 33.98) mg/kg respectively.

Ce was markedly high in sediments of estuarine and coastal stations as it was the most abundant REE on earth crust. Lutetium was the least abundant rare earth present in the estuarine and coastal sediments. Rare earth elements (REE) were generally concentrated in the northern stations (S_1, S_2) and showed a gradual decrease towards the central estuary (S_3, S_4, S_7, S_8) and remained at minimum concentrations near the Cochin inlet with sandy sediments (S_5 & S_6). The light REE (LREE) and heavy REE (HREE) showed minimum variations in its spatial distribution. LREEs were slightly lower at S_2 (north estuary). In the coastal region, LREE showed a gradual decrease towards deeper depths, whereas HREE showed higher concentration at intermediate depths [S_{10} (6.8m) & S_{11} (27m)]. Scandium showed pattern similar to that of LREE and Yttrium showed pattern similar to that of HREE in their distribution (Fig 4.3 and Fig 4.4). Correlation tests were carried out to understand the inter-relation between clay minerals and REE in the sediments using statistical software XLSTAT 2014. No significant correlation ($r^2 < 0.5$) was observed between the dominant clay minerals (smectite, kaolinite) and total REE. However REE in Fr 1 showed a linear decrease with increasing kaolinite (Appendix 3; $r^2 > 0.5$)

4.4.3 Distribution of Actinides (Thorium and Uranium)

Thorium is an abundant element in earth crust, as it has three times higher concentration than uranium. Thorium in the estuarine sediments varied from 6.62 to 35.61mg/kg and in coastal sediments varied from 10.95 to 12.66mg/kg (Fig 4.19). Thorium naturally occurs in thorite, uranothorite, thorianite and is a major component of monazite. It is present in significant amount in the minerals zircon, titanite, gadolinite and betafite. Thorium concentrations of about 15.2 to 18.9mg/kg have been reported in fluvial sediments (<4m) of this estuary (Nath et al., 2000), which has only riverine sources. The concentration of Th observed in the estuarine sediments and coastal sediments was comparable with the values reported by Laluraj, 2009, however higher than the values reported by other studies (Shajan et al., 2001; Deepulal et al., 2012). Markedly high concentration in the northern station (S_1) could be due to industrial waste, which has been reported in earlier studies also (Laluraj, 2009; Joseph et al., 1984).

Uranium

Uranium, a radioactive material, is very reactive and naturally present in rocks and soils. U in the estuarine sediments varied from 0.95 to 6.99mg/kg and the coastal sediments showed values in the range 2.2 to 3.31mg/kg (Fig 4.20). The concentration of U observed in the estuarine sediments were lower than the values reported by Laluraj, 2009, but are high compared to other studies in estuary (Shajan et al., 2001; Deepulal et al., 2012). However U concentration in coastal sediments observed during the present study was higher than the earlier reports from coastal region (Shajan et al., 2001; Laluraj, 2009; Deepulal et al., 2012).

4.4.4 Shale Normalisation to identify the elemental enrichment

Shale normalisation values for Rare earth elements, thorium and uranium with respect to global shale along the study region are given in Table 4.4. The normalisation factor (NF) <1 refers to low contamination, 1 < NF < 3 indicates moderate contamination, $3 < NF < 6$ indicates severe contamination and $NF > 6$ indicates extreme contamination. Rare earth elements and uranium showed moderate contamination for estuarine sediments namely S_1, S_2, S_3 & S_4 and for coastal sediments namely S_9, S_{10}, S_{11} & S_{12} respectively. However the central estuarine stations S_5, S_6, S_7 & S_8 showed low of level contamination for all REEs, uranium and thorium. Thorium showed moderate contamination in estuarine stations S_1, S_2, S_3 & S_4, while all other sediments are of low contamination with respect to thorium.

Table 4.4**:** Shale normalized values of Rare earths, U and Th in the estuarine and coastal sediments

Station	**La$_n$**	**Ce$_n$**	**Pr$_n$**	**Nd$_n$**	**Sm$_n$**	**Eu$_n$**	**Gd$_n$**	**Tb$_n$**	**Dy$_n$**	**Ho$_n$**	**Er$_n$**	**Tm$_n$**	**Yb$_n$**	**Lu$_n$**	**U$_n$**	**Th$_n$**
S_1	2.67	1.78	1.95	2.08	2.00	1.98	1.73	1.52	1.32	1.23	1.27	1.32	1.02	1.00	2.26	2.44
S_2	1.38	1.46	1.15	1.32	1.39	1.66	1.34	1.31	1.22	1.17	1.26	1.47	1.07	1.03	1.97	1.13
S_3	1.57	2.15	1.97	1.43	1.55	2.02	1.59	1.59	1.42	1.32	1.35	1.31	1.12	1.09	1.64	1.29
S_4	1.45	1.45	1.16	1.34	1.36	1.67	1.26	1.24	1.15	1.06	1.11	1.06	0.90	0.85	1.48	1.20
S_5	0.72	0.58	0.51	0.55	0.61	1.25	0.51	0.49	0.45	0.43	0.45	0.45	0.39	0.39	0.31	0.45
S_6	0.64	0.56	0.49	0.53	0.62	1.14	0.52	0.53	0.51	0.48	0.49	0.48	0.42	0.40	0.35	0.66
S_7	0.87	0.75	0.68	0.73	0.86	1.48	0.74	0.71	0.66	0.63	0.64	0.63	0.52	0.53	0.53	0.69
S_8	0.79	0.95	0.66	0.81	0.83	1.07	0.87	0.87	0.84	0.83	0.88	0.89	0.80	0.76	1.12	0.86
S_9	1.46	1.33	1.16	1.27	1.32	1.74	1.21	1.16	1.06	0.97	0.99	0.96	0.81	0.77	0.71	0.86
S_{10}	1.27	1.34	1.11	1.27	1.36	1.69	1.30	1.31	1.24	1.15	1.18	1.15	0.96	0.92	1.07	0.87
S_{11}	1.25	1.28	1.09	1.22	1.36	1.77	1.33	1.35	1.26	1.21	1.23	1.19	1.02	0.93	1.04	0.79
S_{12}	1.15	1.14	1.00	1.11	1.26	1.65	1.23	1.23	1.14	1.11	1.13	1.06	0.92	0.88	1.00	0.75

4.4.5. Sources of Rare earth elements

The shale normalized rare earth patterns for estuarine and coastal sediments were depicted in Fig 4.2. Ratios (La_n/Yb_n), (La_n/Gd_n), (La_n/Sm_n), (Sm_n/Yb_n), and (Gd_n/Yb_n) are used to identify relative enrichment or depletion of LREE, MREE, and HREE (Table 4.5). These ratios indicated LREE enrichment over HREE (La_n/Yb_n), LREE enrichment over MREE (La_n/Gd_n

and La_n/Sm_n), and MREE enrichment over HREE (Sm_n/Yb_n, and Gd_n/Yb_n) respectively**.**

Table 4.5: Geochemical ratios of LREE, MREE and HREE to identify their relative enrichment in the sediments of Cochin estuary and adjacent coastal stations.

Station	**$(La/Yb)_n$**	**$(La/Gd)_n$**	**$(La/Sm)_n$**	**$(Gd/Yb)_n$**	**$(Sm/Yb)_n$**
S_1	2.61	1.55	1.33	1.69	1.96
S_2	1.29	1.03	1.00	1.25	1.29
S_3	1.40	1.0	1.01	1.42	1.39
S_4	1.60	1.15	1.06	1.39	1.51
S_5	1.84	1.40	1.17	1.31	1.57
S_6	1.52	1.24	1.04	1.23	1.47
S_7	1.67	1.17	1.01	1.43	1.65
S_8	1.00	0.92	0.96	1.09	1.04
S_9	1.79	1.21	1.10	1.48	1.62
S_{10}	1.32	0.97	0.93	1.36	1.42
S_{11}	1.23	0.94	0.92	1.30	1.33
S_{12}	1.26	0.94	0.91	1.34	1.38

Shale normalized REE pattern of S_8 which are almost consistent, except for Ce and Eu (Fig 4.2). La_n/Yb_n at S_8 is 1; (La_n/Gd_n and La_n/Sm_n) ratios ~ 1; (Sm_n/Yb_n, and Gd_n/Yb_n) ratios ~ 1 and are similar to the values of terrigenous input (Nath et al., 1997). The remaining sediments exhibited an enrichment of light REE relative to HREE (Fig 4.2), with La_n/Yb_n ratios of (1.40-2.51) and (1.23-1.71) of PAAS in estuarine and coastal sediments. All the sediments exhibited enrichment in MREE over HREE, with (La_n/Gd_n) and (La_n/Sm_n) ratios of (1.25-1.69) and (1.29-1.96). Shale normalized REE pattern showed Steep HREE curve and flat LREE curve in the central estuary (S_3, S_4, S_5, S_6, S_7) and in the coastal stations (S_9, S_{10}, S_{11}, S_{12}). Flat shale normalized pattern and LREE enrichment are the characteristics of intermediate and felsic source rock (McLennan, 1989; Nath et al., 1997). These are in agreement with other studies from Cochin estuary and adjacent continental shelf (Laluraj et al., 2009; Deepulal et al., 2012). Shale normalized pattern observed in the sediments of north estuary (S_1 and S_2) showed a deviation from the normal pattern, possibly due to the additional supply of REEs into the northern estuary.

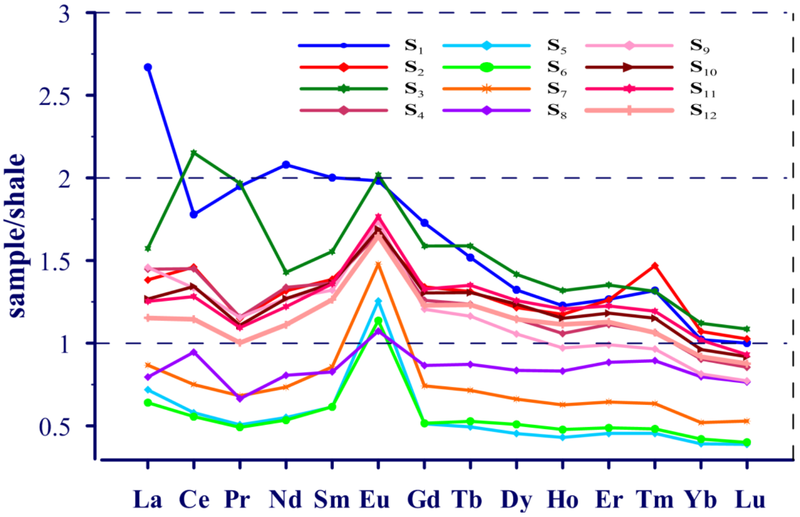

Fig 4.2: Shale normalized pattern of rare earths (REE) from estuarine and coastal sediments during October 2011.

4.4.6. Geochemical proxies to identify the depositional characteristics

4.4.6.1 Ce/Ce* ratio

Due to their multiple oxidation states, Ce and Eu tend to behave differently from their strictly trivalent neighbors under different oxygenation conditions (Piper, 1974, Nath et al., 1997). Based on this, a cerium anomaly relates to the increase or decrease in solubility of Cerium. Under reducing conditions, Ce^{3+} is relatively soluble while under oxidizing conditions CeO_2 precipitates. The Ce anomaly, its enrichment or depletion compared to its neighboring elements, is estimated as Ce/Ce*, where Ce is Ce sample/Ce PAAS and Ce* is the predicted values obtained by the linear interpolation between shale-normalized La and Pr values.

$$Ce^* = \frac{(La_{Sample}/La_{PAAS}) + (Pr_{Sample}/Pr_{PAAS})}{2}$$

Ce/Ce* values >1, <1 and 1 indicates positive, negative and no anomaly, respectively.

Ce/ Ce* ratios calculated in the sediments of Cochin estuary and adjacent coastal station are given in Table 4. 6. Here the Ce/Ce* values were generally positive (0.95 - 1.30), except at S_1. A Ce anomaly ~1 at S_5, S_6, S_7 & S_9 means that the REE are generally derived from terrigenous sources. Still higher values at S_2, S_3, S_4, S_8, S_{10}, S_{11} and S_{12} are indicative of its accumulation in sediments in these regions. Thomas et al., 2003 state that zircons show a positive Ce anomaly due to the incorporation of Ce^{4+} into zircon, since Ce^{4+} has the same charge (0.97 Å) and ionic radius of Zr^{4+} (0.84 Å).

Table 4.6: Geochemical proxies to identify the deposition conditions of REE in sediments of Cochin estuary and adjacent coastal stations.

Stations	Eu/Eu*	Ce/Ce*	U/Th
S_1	1.06	0.77	0.20
S_2	1.22	1.15	0.37
S_3	1.28	1.22	0.27
S_4	1.27	1.11	0.26
S_5	2.23	0.95	0.14
S_6	2.01	0.98	0.11
S_7	1.85	0.97	0.16
S_8	1.27	1.30	0.27
S_9	1.37	1.02	0.17
S_{10}	1.27	1.13	0.26
S_{11}	1.31	1.09	0.28
S_{12}	1.32	1.06	0.28

A negative Ce anomaly (0.77) was noticed at S_1 (northern estuary) indicating its depletion, which has been already reported from this region (Deepulal et al., 2012; Manoj et al., 2016).

4.4.6.2 Eu/Eu* ratio

Europium anomaly is calculated as Eu/Eu*, where Eu is Eu Sample/Eu PAAS and Eu* is a predicted value obtained by the linear interpolation between shale-normalized Sm and Gd values.

$$Eu^* = \frac{La_{Sample}/La_{PAAS}) + (Pr_{Sample}/Pr_{PAAS}}{2}$$

Eu/Eu* values >1, <1 and 1 indicates positive, negative and no anomaly, respectively.

Eu/ Eu* ratios calculated in the sediments of Cochin estuary and adjacent coastal station was given in Table 4.6. The estuarine and coastal sediments showed Eu/Eu* > 1, the values varies as 1.06 to 2.23 showing positive Eu anomaly indicating a dominant terrestrial source. High values were observed at S_5, S_6 and S_7. This was consistent with the results of earlier studies (Nath et al., 2000; Laluraj, 2009; Deepulal et al., 2012). The positive Eu anomaly occurs in areas prominent in plagioclase-rich charnockites and gneissic terrain of southern India (Allen et al., 1985) and also for the rocks of feldspar origin (Taylor and McLennan, 1985). Eu anomaly is controlled by supply from the rivers, biological productivity, and redox condition at the sampling stations. The sediments derived from moderately weathered sediments show a positive Eu anomaly (Manoj et al., 2016). The scavenging of REE by organic coatings and Fe/Mnoxyhydroxides can increase the REE in sediments (Shynu et al., 2013). During the present study high positive Eu anomalies observed at stations (S_5, S_6 and S_7) were due to the depletion of other REE (including Sm and Gd) relative to PAAS. The sandy texture with low clay and organic matter could be responsible for low REE in these regions indicating that sediment texture is a major factor controlling geochemistry of the study area.

4.4.6.3 Uranium as paleo redox proxy:

Due to the enrichment in the suboxic and anoxic waters, U is generally used as an indicator to identify redox environments (Nath et al., 1997 and references there in). Since Th is immobile at low temperature, U/Th ratio is sensitive to changes in U concentration, which varies with redox state of the water. Under oxidized condition, uranium will be in +6 oxidation state ($U^{6+)}$ which is soluble and lead to its release from sediments to lower the U/Th ratios. Under reduced conditions, U^{4+} get deposited in sediments elevating U/Th ratios. The U/Th ratios (Table 4.6) in the sediments of Cochin estuary and adjacent coastal stations were < 1 (0.11 to 0.37) indicating a fairly oxidized environment.

Authegenic Uranium, a parameter based on U and Th concentrations has been suggested as an index of bottom water anoxia and ancient sedimentary sequences (Nath et al., 1997). It is calculated using the formula,

Authigenic U= (Total U- Thorium/3).

Nath et al., 1997 and Wignal and Myers, 1988 place the boundary between oxic and dysoxic environment at 2ppm of authigenic uranium. The sediments of Cochin estuary and adjacent coastal stations showed authigenic uranium less than 1ppm.

Table 4.7: Rare earth elements (Lanthanides, Sc & Y) and Actinides (Thorium and Uranium) in the sediments of Cochin estuary - a comparison with previous studies (values are given in mg/kg).

Elements	**Nath et al, 2000**	**Shajan, 2001**	**Laluraj, 2009**	**Deepulal et al, 2012**	**Present study**
La	47 - 78	-	32.6 - 96.3	28.5 - 52.4	24.26 - 102
Ce	103 - 174	-	75.9 -171.5	50.8 -102.9	44.26 - 171.28
Pr	-	-	7.6 - 16.6	4.9 - 10.0	4.33 - 17.37
Nd	34 - 86	-	21.2 - 70.3	18.6 - 38.8	18.13 - 70.49
Sm	8.05 - 11.8	-	3.5 -11.9	3.6 - 6.9	3.41 - 11.11
Eu	1.84 - 2.49	-	1.0- 2.2	1.25 - 1.59	1.16 - 2.18
Gd	-	-	3.8- 9.4	2.75 - 5.65	2.39 - 8.05
Tb	0.85-1.44	-	0.3-1.4	0.44 - 0.89	0.38 - 1.23
Dy	-	-	1.8- 6.7	2.32 - 4.92	2.12- 6.63
Ho	-	-	0.3- 1.3	0.46 - 1.03	0.43 - 1.31
Er	-	-	0.92- 3.9	1.3 - 2.8	1.3 - 3.85
Tm	-	-	0.11- 0.53	0.18 - 0.38	0.18 - 0.60
Yb	2.12 - 3.21	-	0.61-3.0	1.08 - 2.34	1.10 - 3.16
Lu	0.31 -0.45	-	0.1- 0.47	0.15 - 0.36	0.17 - 0.47
Sc	19.9 - 27.1	3.0 - 26.0	6.1 - 21	-	7.72 - 20.62
Y	-	2.0 - 27.0	16 - 44.6	-	12.62 - 38.90
U	4.11 - 19.3	0.5 - 3.1	1.7- 9.3	1,09 - 2.80	0.95 - 6.99
Th	12.2 - 18.3	3.7 - 12.2	12.5- 31.6	6.34 - 11.31	6.62- 35.61

*The studies of Nath et al., 2000 was carried out in finer sediments (<4µm), while all other studies used bulk sediments: The data obtained from Laluraj, 2009 was the average value for central and north estuary.

The geochemical proxies such as Ce/Ce*, Th/U ratios and authigenic uranium was used to identify the redox conditions prevailing in the study region. The results showed that an oxygenized condition prevailed in the estuarine and coastal region, except at S_1, where high uranium with a negative Ce anomaly was indicative of a reducing environment. Eh of sediment in this region was (-150 to 50) also showing moderately reducing condition.

However, the bottom saturation (DO >4.53mg/l) with mild redox conditions (U/Th 0.20 and authigenic uranium < 1ppm) are supportive of an oxidized environment. Therefore, the Ce anomaly at S_1 needs further explanation.

Table 4.8: Rare earth elements (Lanthanides, Sc & Y) and Actinides (Thorium and Uranium) in the coastal sediments - a comparison with previous studies (values are given in mg/kg)

Elements	Nath et al, 2000	Shajan, 2001	Laluraj, 2009	Deepulal et al, 2012	Present study
La	51 - 61	-	34.9	13.95 - 21.9	44.02 - 55.73
Ce	105 - 151	-	60.9	27.7 -50.9	91- 102.05
Pr	-	-	6	2.8 - 4.8	8.85 -10.25
Nd	42 -78	-	22.4	11.1 - 19.7	37.68 - 43.08
Sm	8.86 - 10.8	-	3.6	1.9 - 3.6	7.01 - 7.56
Eu	1.92 - 2.22	-	0.58	0.54 - 0.79	1.78 - 1.91
Gd	-	-	2.8	1.37 - 3.05	5.62 - 6.19
Tb	0.91 - 1.5	-	0.41	0.19 - 0.49	0.90 - 1.05
Dy	-	-	1.9	1.01 - 2.65	4.94 - 5.89
Ho	-	-	0.36	0.21 - 0.52	0.82 - 1.20
Er	-	-	1.1	0.53 - 1.41	2.82 - 3.49
Tm	-	-	0.13	0.08 - 0.18	0.39 - 0.48
Yb	2.23 - 2.87	-	0.79	0.5 - 1.1	2.3 - 2.87
Lu	0.34- 0.55	-	0.12	0.08 - 0.18	0.33 - 0.40
Sc	21.3 - 24.8	12.0- 59.0	9.61	-	14.92 - 18.8
Y	-	7.0 - 24.0	13.6	-	26.75 - 33.98
U	2.92 - 4.68	0.27 - 2.56	2.1	1.01 - 1.47	2.2 - 3.31
Th	12.1 - 14.9	1.29 - 10.72	16.5	5.53 - 5.74	10.95 - 12.66

*The data obtained from Laluraj, 2009 was the average value for near shore region, south of Kerala

4.4.7 Fractionation of REE (Lanthanides, Sc, Y)

The fractions of REE in the estuarine and coastal sediments (Fig 4.3-4.18) showed that the maximum LREE (La, Ce, Pr, Nd and Sm) concentrations associated with residual fraction. The contribution of LREE in the residual fraction (Fr.4) of the estuarine sediments (%) was La (56 to 84.8), Ce (47.8 to 76), Pr (34.6 to 76.3), Nd (43.7 to 74) and Sm (17.3 to 84.9) respectively. The percentage of LREE in residual fraction (Fr_4) in the coastal sediments varied as La: (61.4 to 75.1)% ; Ce : (55.1 to 55.5)%; Pr : (44.7 to 61.6)%; Nd: (60.4 to 67)%; Sm : (56.4 to 72.2)%.

Organic/sulphidic binding phase (Fr.3) was the second dominant fraction of LREE in the estuarine and coastal sediments. The LREE in organic/sulphidic binding phase (Fr 3) varied from 4.56 to 62.3% in estuarine sediments and 12.96 to 24.2% in coastal sediments. The Fe-Mnoxyhydroxide phase (Fr.2) was lower than organic binding phase for LREE. The LREE in Fe-Mnoxyhydroxide binding phase (Fr 2) varied from 8.1 to 20% in estuarine sediments and 9.2 to 13.3% in coastal sediments. The exchangeable/carbonate bound fractions (Fr 1) of LREE was the lowest fraction in both estuarine and coastal sediments and which account for only 0.69 to 7.67% (estuary) and 0.76 to 1.7% (coast) of LREE. Scandium showed a pattern similar to that of LREE in its fractionation.

The middle rare earth (MREE) and heavy rare earth elements (HREE) in the residual fraction (Fr 4) of both estuarine and coastal sediments were relatively lower than LREE. The MREE and HREE contents in residual fraction (Fr 4) in the estuary varied as Eu: (15.2 to 84.9)% ; Gd : (10.4 to 66.3)%; Tb : (8.7 to 65.4)%; Dy: (3.9 to 63.4)%; Ho : (4.4 to 62.6)%: Er (8.7 to 63.6)% ; Tm : (14.2 to 65.3)%; Yb : (19.4 to 66.9)% and Lu: (18.7 to 68.3)% respectively. The MREE and HREE in residual fraction (Fr.4) in the coastal region was lower than estuarine sediment and varied as Eu: (36.1 to 61)% ; Gd : (33.1 to 50.8)%; Tb : (31.6 to 49.3)%; Dy: (30.7 to 45.4)%; Ho :

(28.3 to 43.3)%: Er (30 to 44.7)% ; Tm : (32.7 to 44.8)%; Yb : (3.9 to 39.1)% and Lu: (35.4 to 47.4)% respectively.

The maximum fraction of heavy rare earths, HREE (Tb, Dy, Ho, Er, Tm, Yb and Lu) was found in organic/sulphidic binding phase (Fr.3) in the estuarine sediments of stations S_1, S_2, S_3, S_4, S_8 and coastal sediment of stations S_9, S_{10}, S_{11}, S_{12}. Sediments in these stations have high organic matter with clayey texture that could favour the strong association of HREE on to it. However in other stations with sandy sediments (S_5, S_6, S_7) the HREE was intensely found in residual binding phase. The percentage of HREE in organic/sulphidic binding phase (Fr.3) varied from 6.8 to 68% in estuarine sediments and 24.5 to 75.7% in coastal sediments. The Fe-Mnoxyhydroxide binding phase (Fr.2) for HREE was lower than organic binding phase. The percentage of HREE in Fe-Mnoxyhydroxide phase (Fr.2) varied from 10.0 to 27.7% in estuarine sediments and 12.1 to 25.8% in coastal sediments. The exchangeable/carbonate bound fractions (Fr.1) of HREE were the lowest fraction found in both estuarine and coastal sediments and which account for only 1.0 to 10.7% of HREE in estuarine sediments and 1.0 to 1.9% of HREE in coastal sediments. Yttrium showed the pattern similar to that of heavy rare earths in its fractionation. Even though REE were mostly concentrated in clayey sediments no significant correlation exists between dominant clay minerals (kaolinite & smectite) and total REE ($R^2 < 0.5$). Perhaps, this could be due to the scavenging of REE by organic matter/organic coatings and Fe-Mn oxyhydroxides in the study region. However REE in Fr 1 showed a linear decrease with increasing kaolinite showing the more available binding sites on Smectite for REE

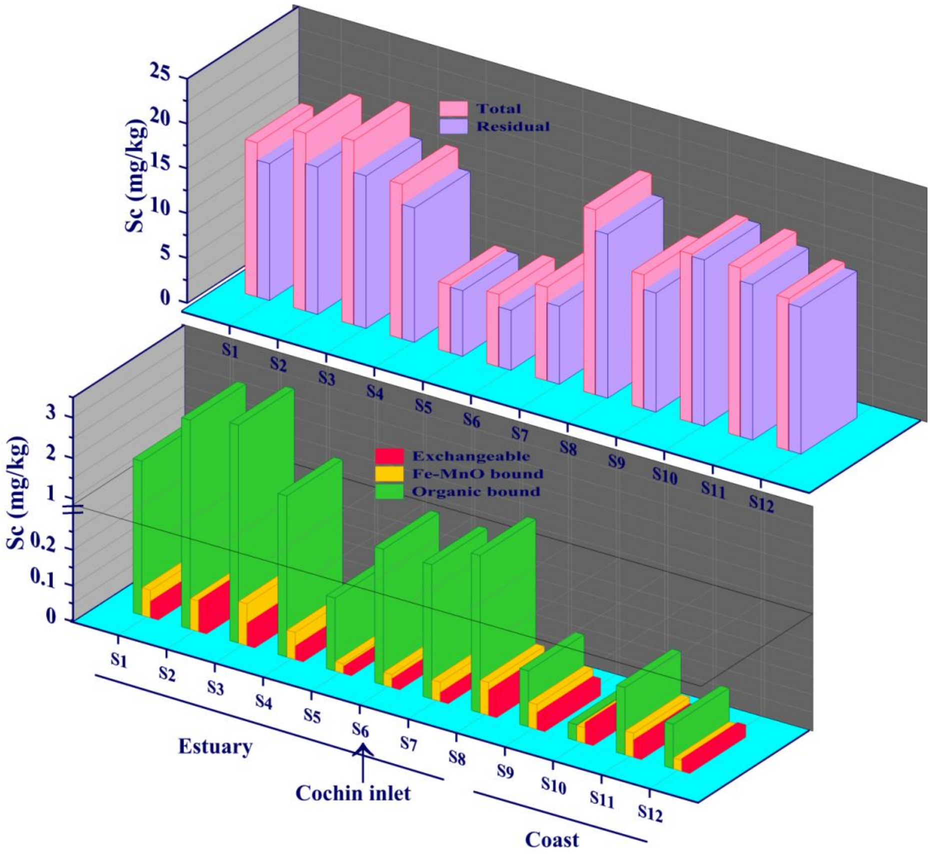

Fig 4.3: Total scandium and its four different fractions in the sediments of Cochin estuary and adjacent coastal region during October 2011.

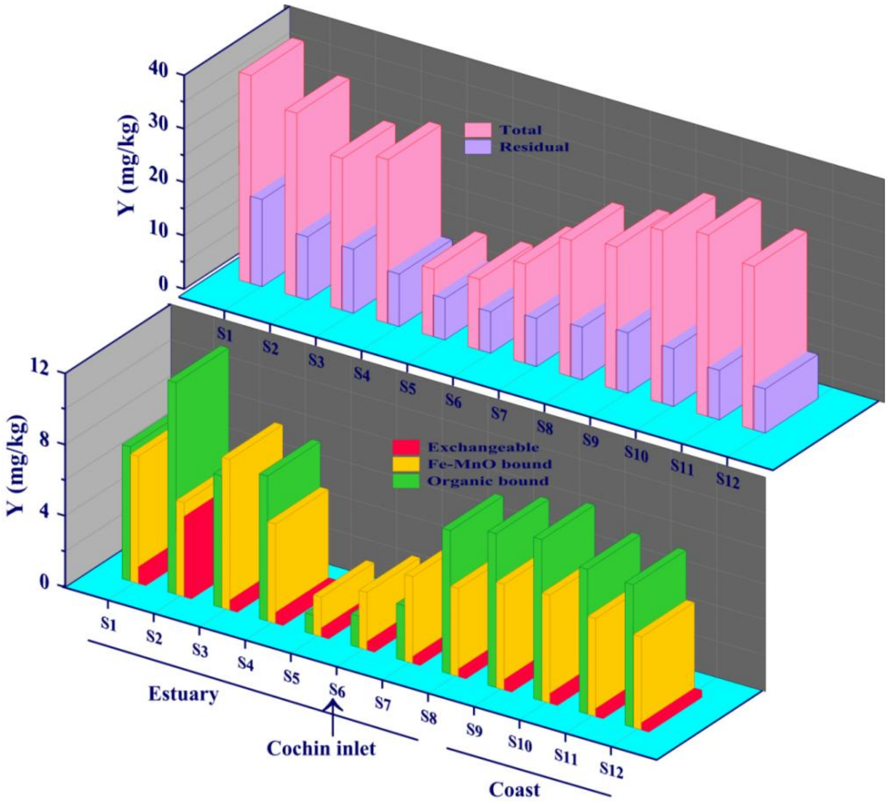

Fig 4.4**:** Total yttrium and its four different fractions in the sediments of Cochin estuary and adjacent coastal region during October 2011.

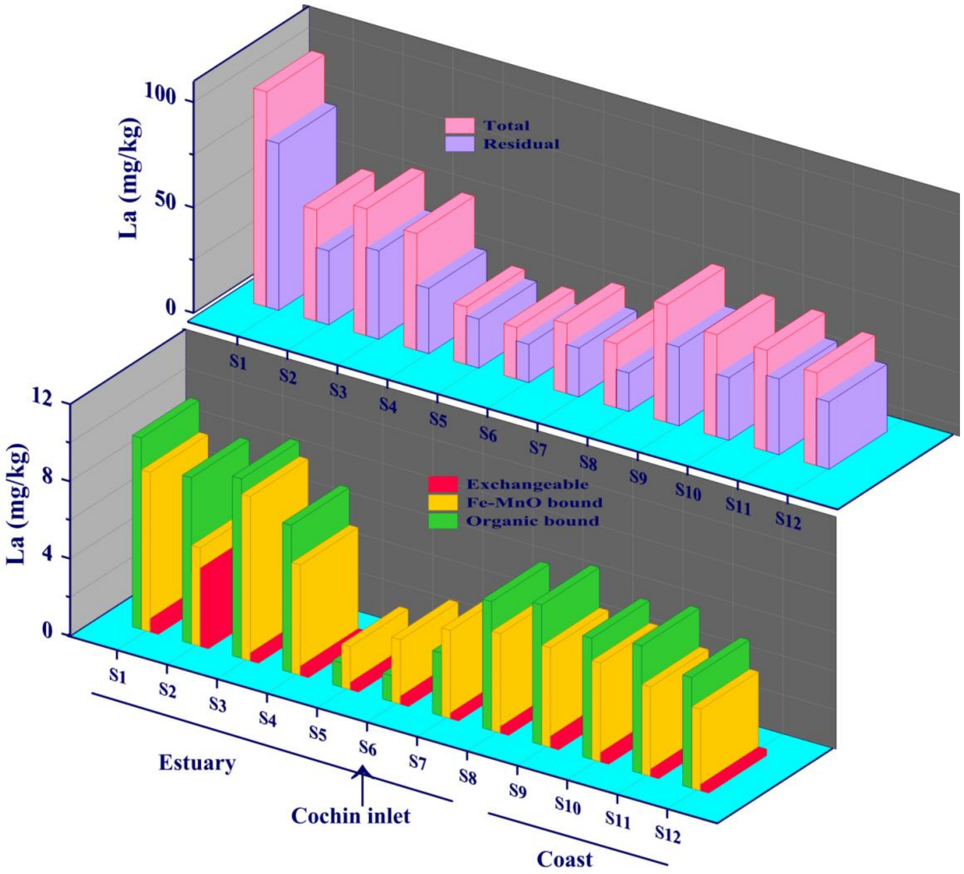

Fig 4.5: Total lanthanum and its four different fractions in the sediments of Cochin estuary and adjacent coastal region during October 2011.

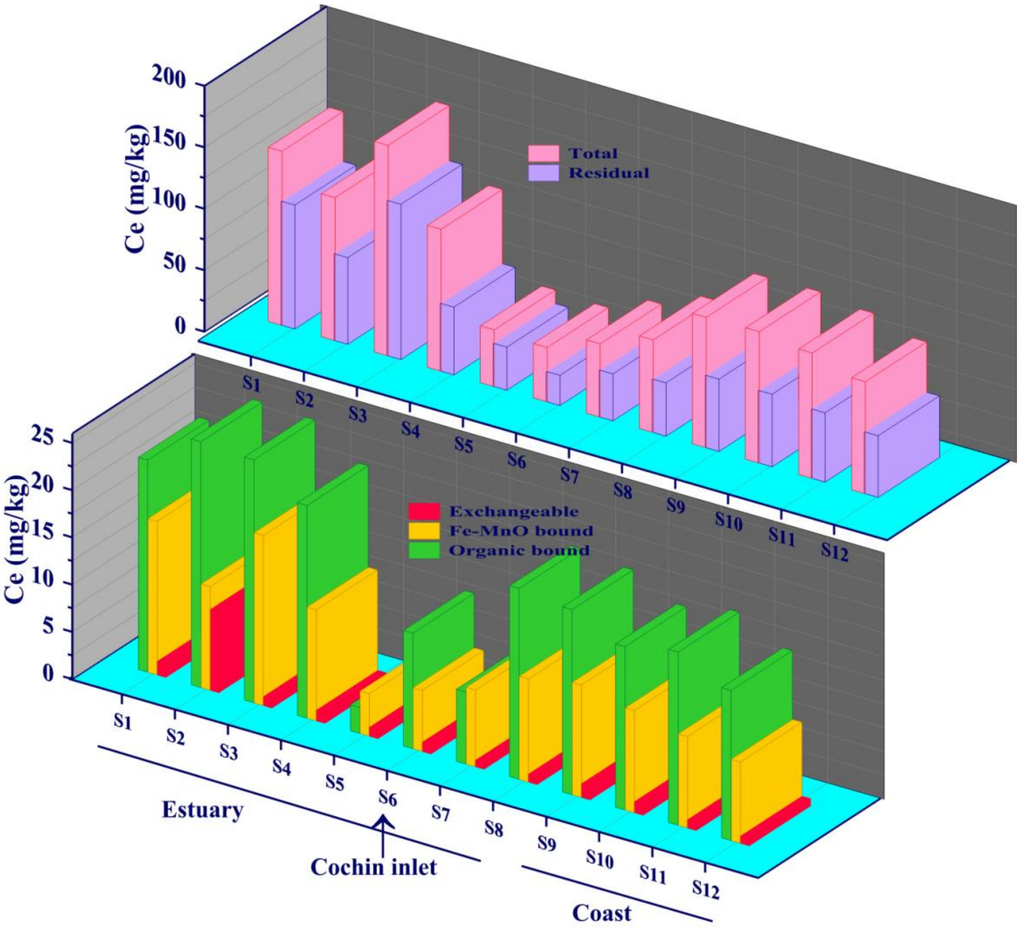

Fig 4.6: Total cerium and its four different fractions in the sediments of Cochin estuary and adjacent coastal region during October 2011.

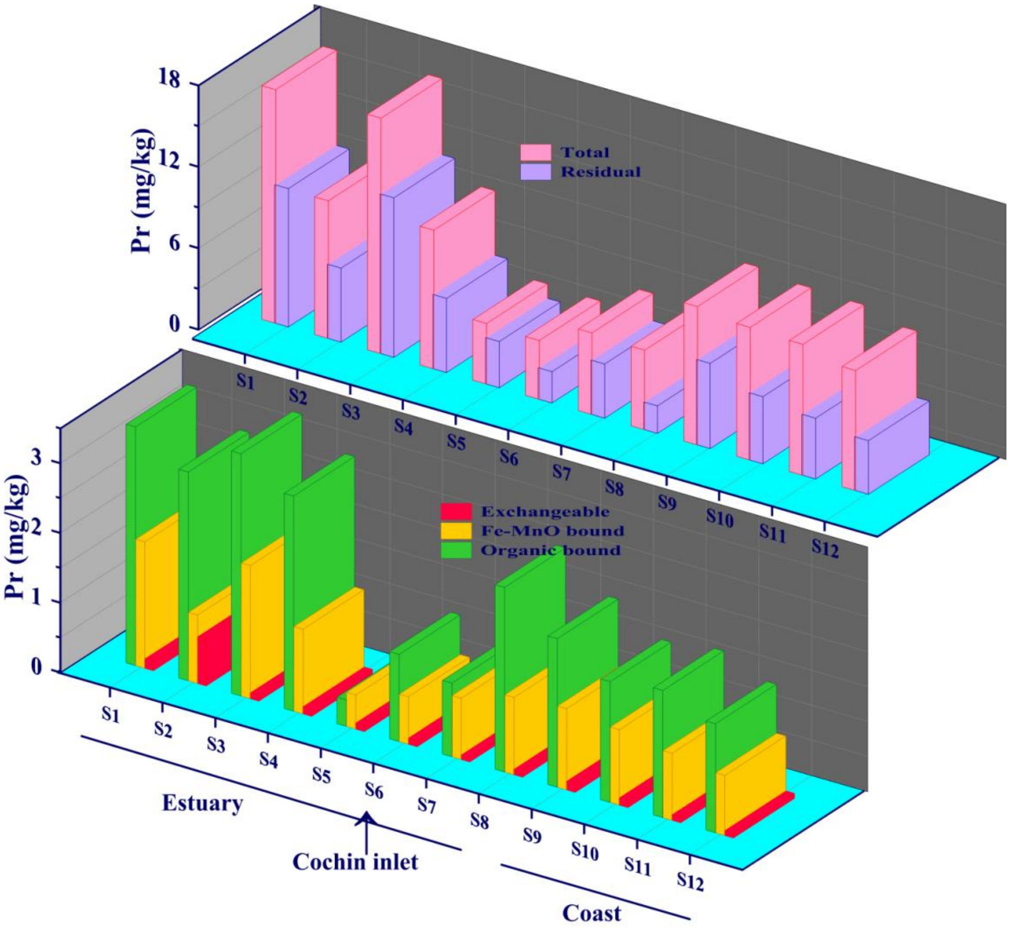

Fig 4.7: Total praseodymium and its four different fractions in the sediments of Cochin estuary and adjacent coastal region during October 2011.

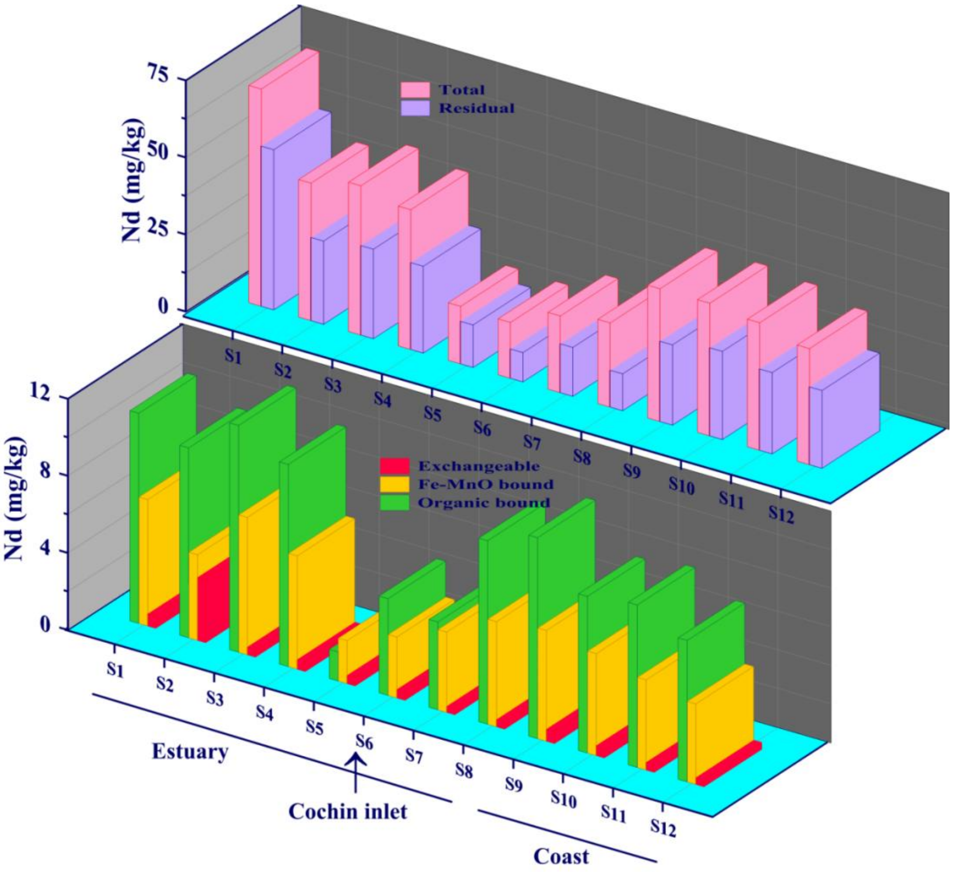

Fig 4.8: Total neodymium and its four different fractions in the sediments of Cochin estuary and adjacent coastal region during October 2011.

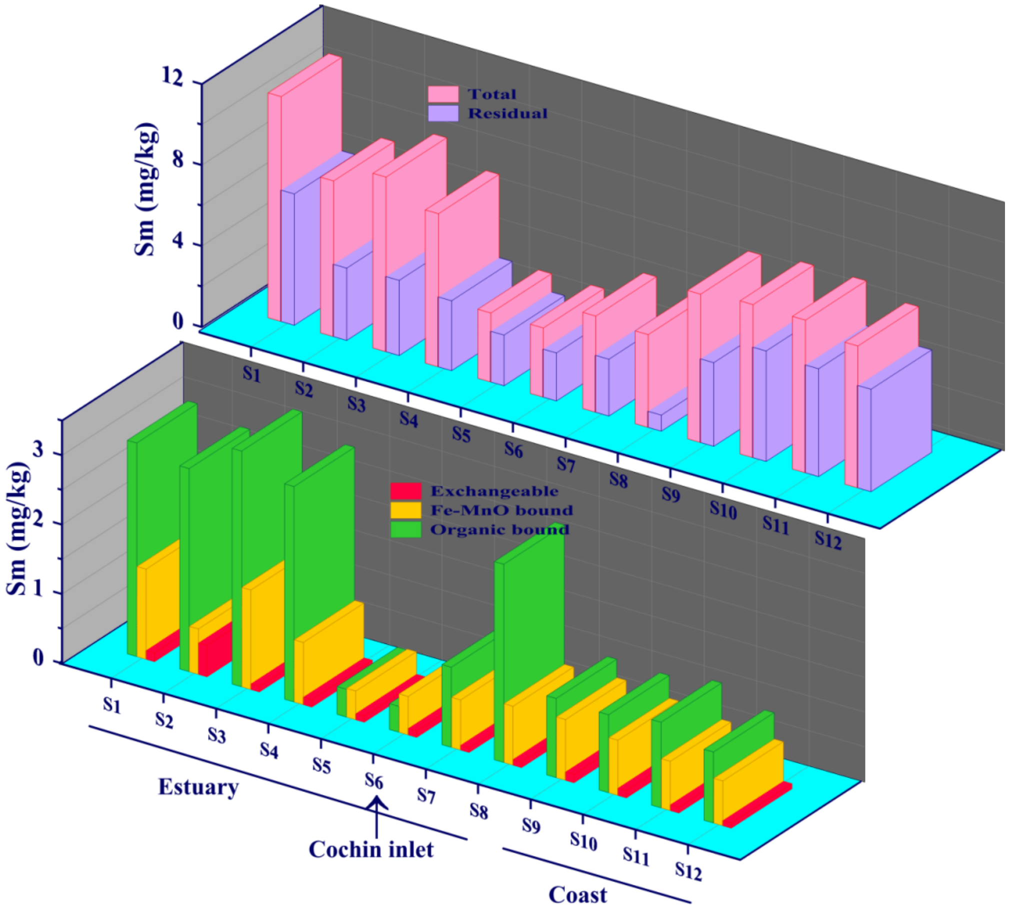

Fig 4.9: Total samarium and its four different fractions in the sediments of Cochin estuary and adjacent coastal region during October 2011.

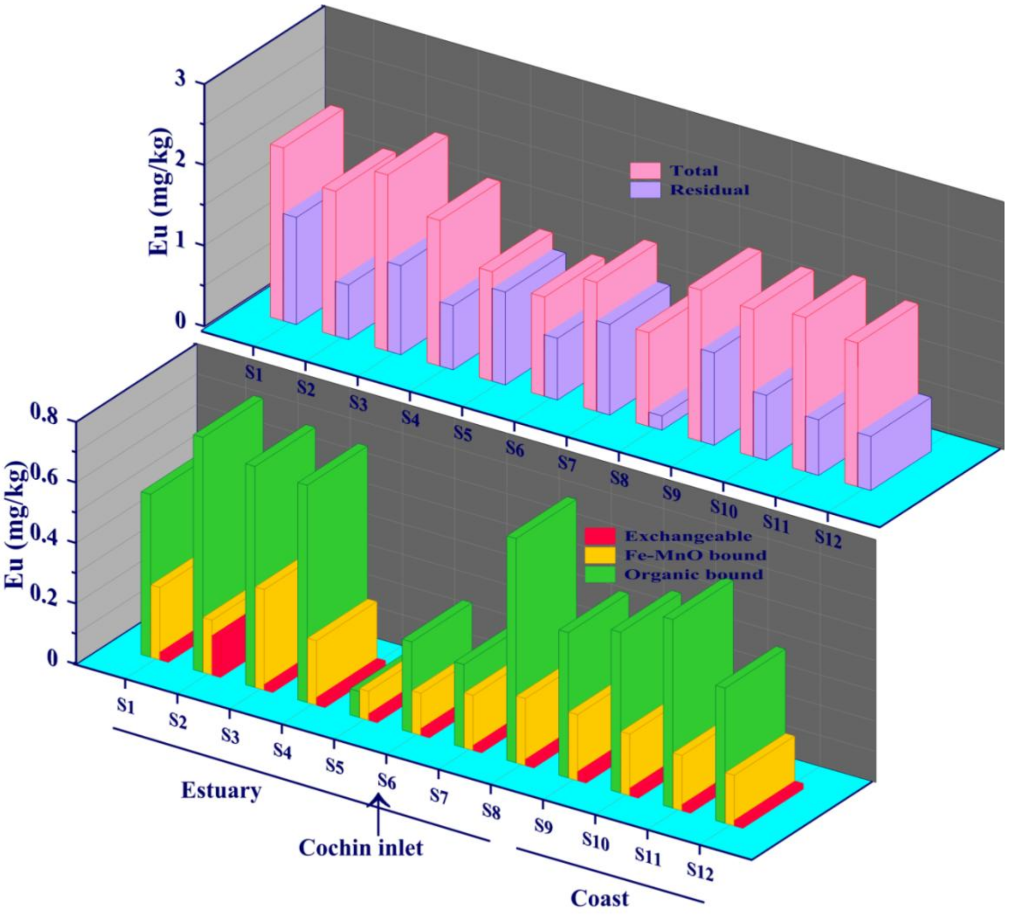

Fig 4.10: Total europium and its four different fractions in the sediments of Cochin estuary and adjacent coastal region during October 2011.

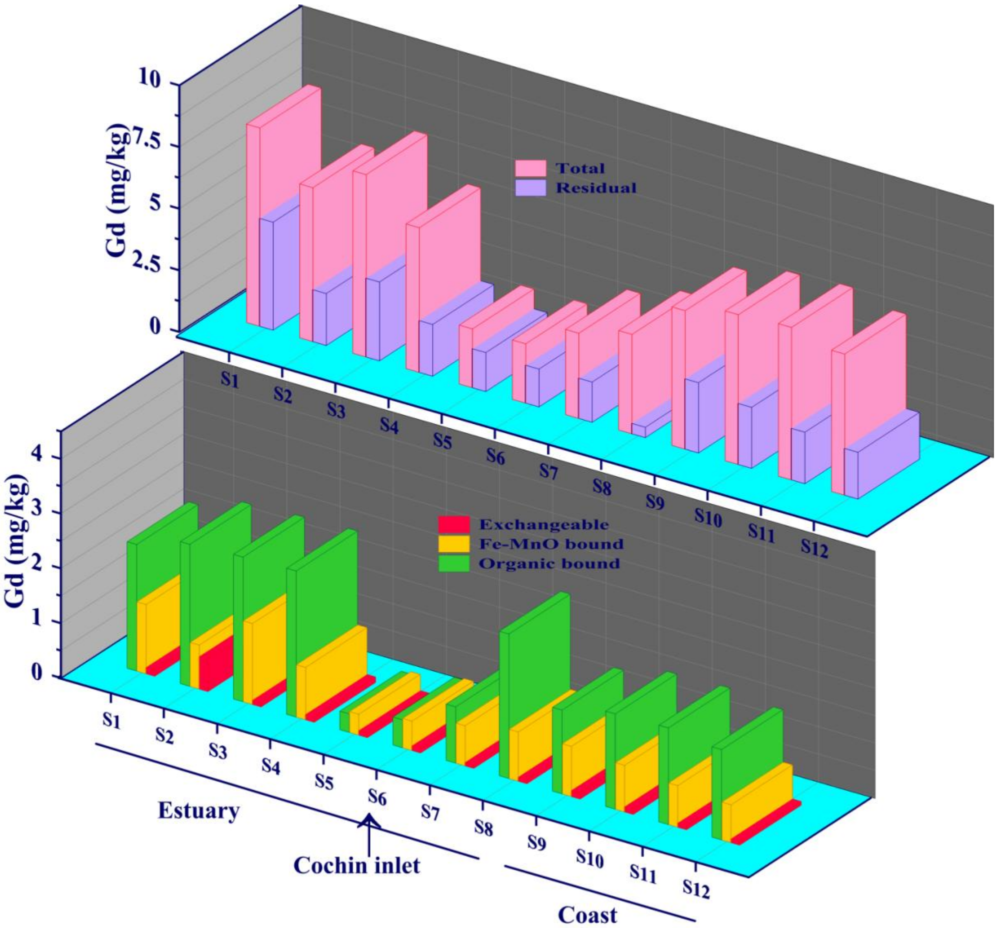

Fig 4.11: Total gadolinium and its four different fractions in the sediments of Cochin estuary and adjacent coastal region during October 2011.

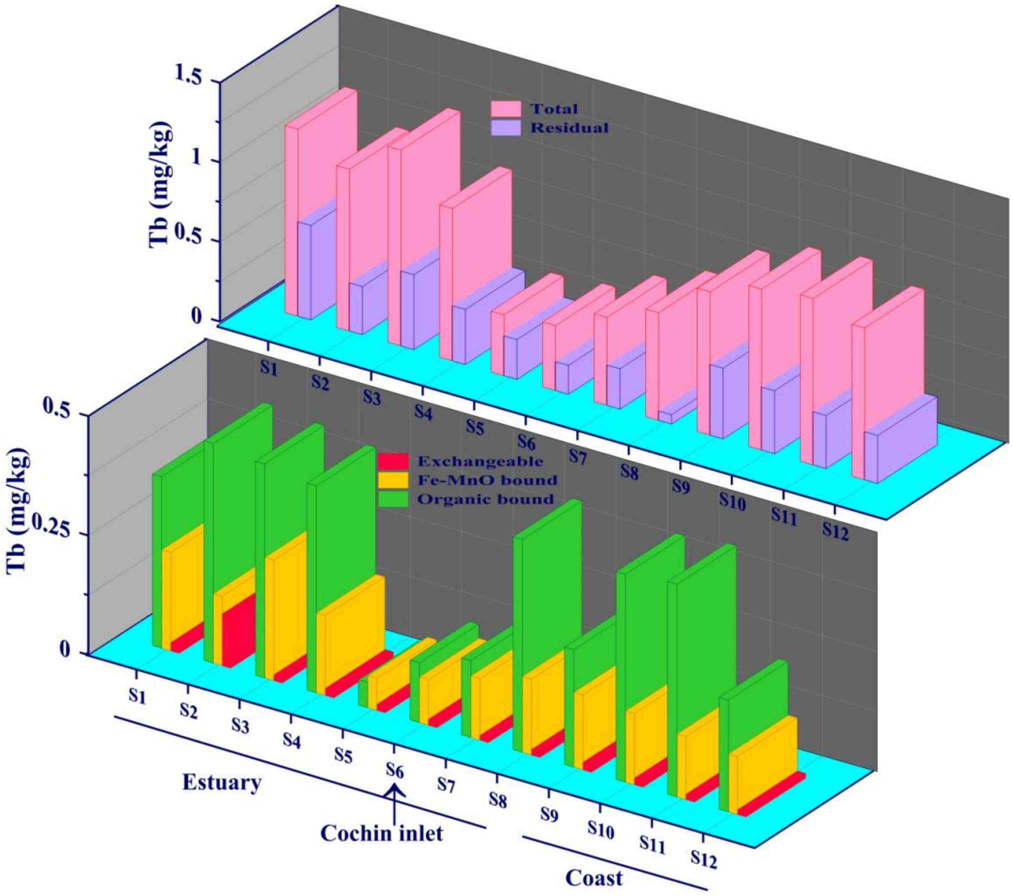

Fig 4.12: Total terbium and its four different fractions in the sediments of Cochin estuary and adjacent coastal region during October 2011.

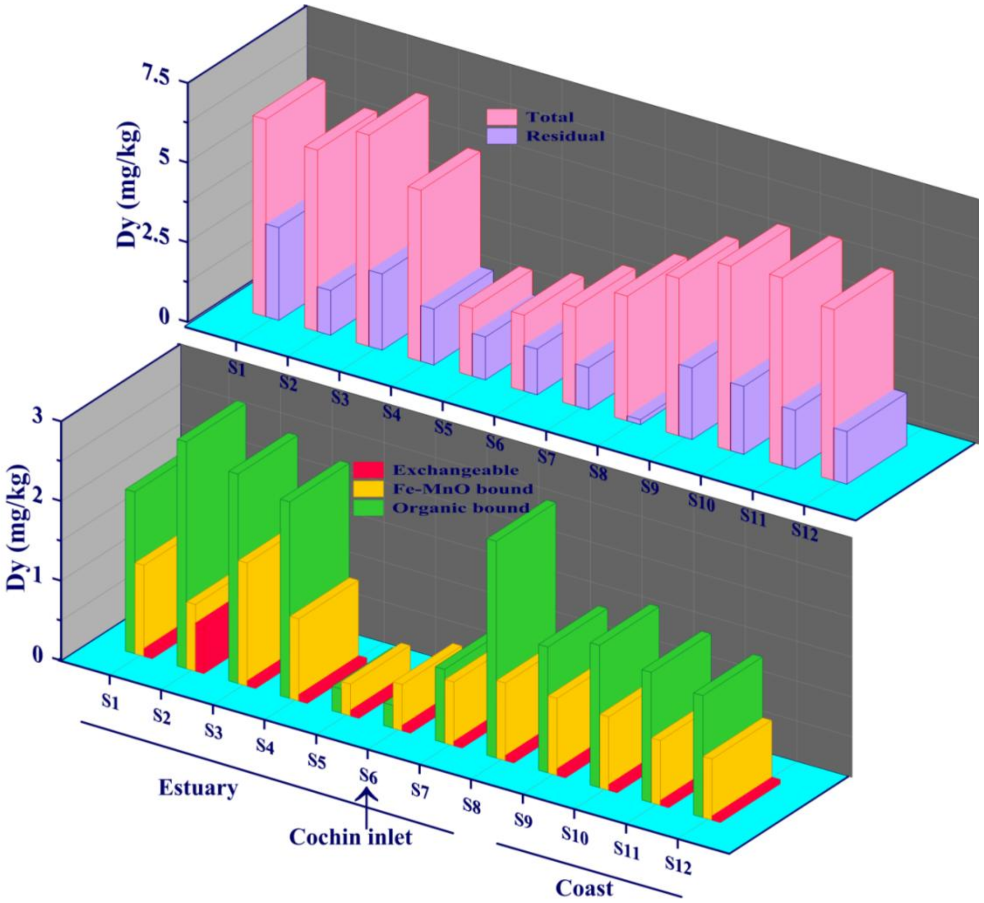

Fig 4.13**:** Total dysprosium and its four different fractions in the sediments of Cochin estuary and adjacent coastal region during October 2011.

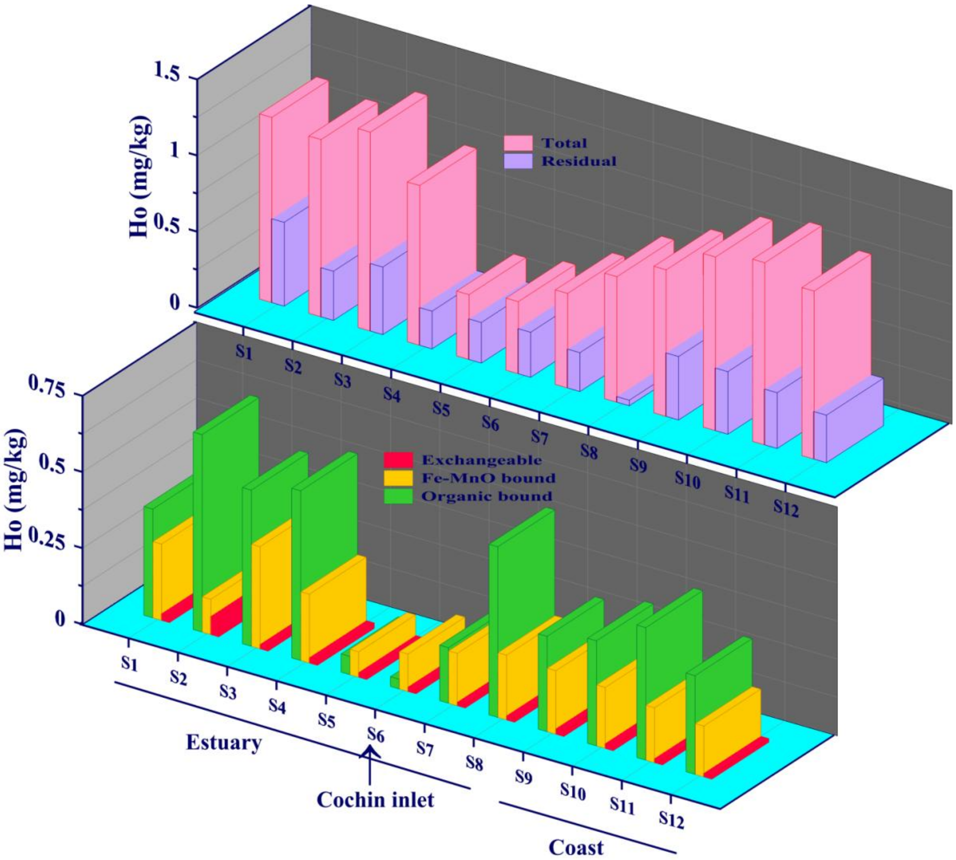

Fig 4.14 : Total holmium and its four different fractions in the sediments of Cochin estuary and adjacent coastal region during October 2011.

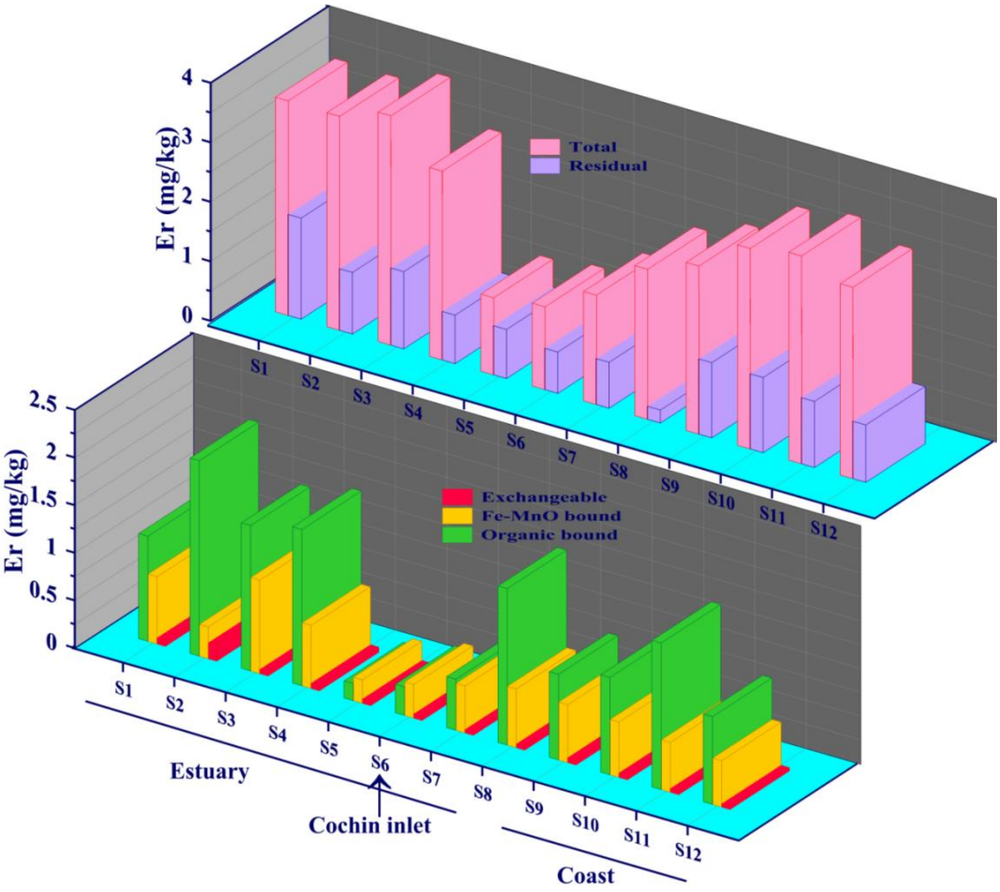

Fig 4.15**:** Total erbium and its four different fractions in the sediments of Cochin estuary and adjacent coastal region during October 2011.

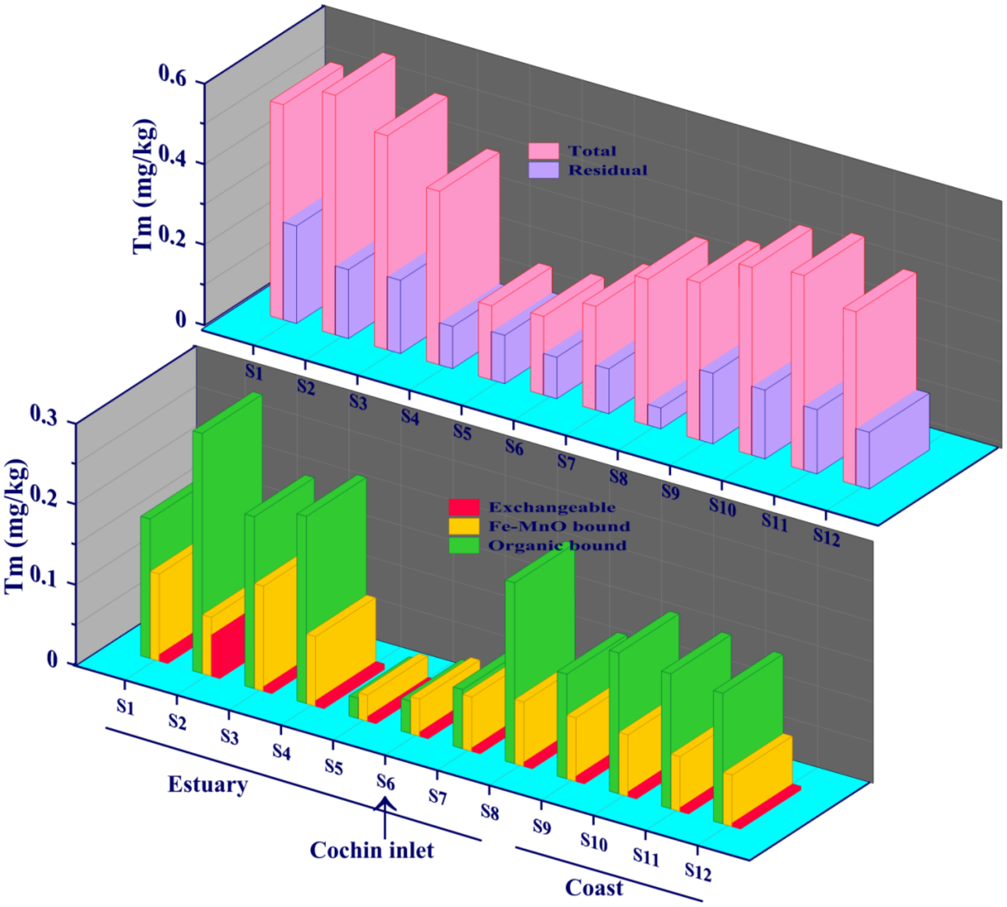

Fig 4.16**:** Total thulium and its four different fractions in the sediments of Cochin estuary and adjacent coastal region during October 2011.

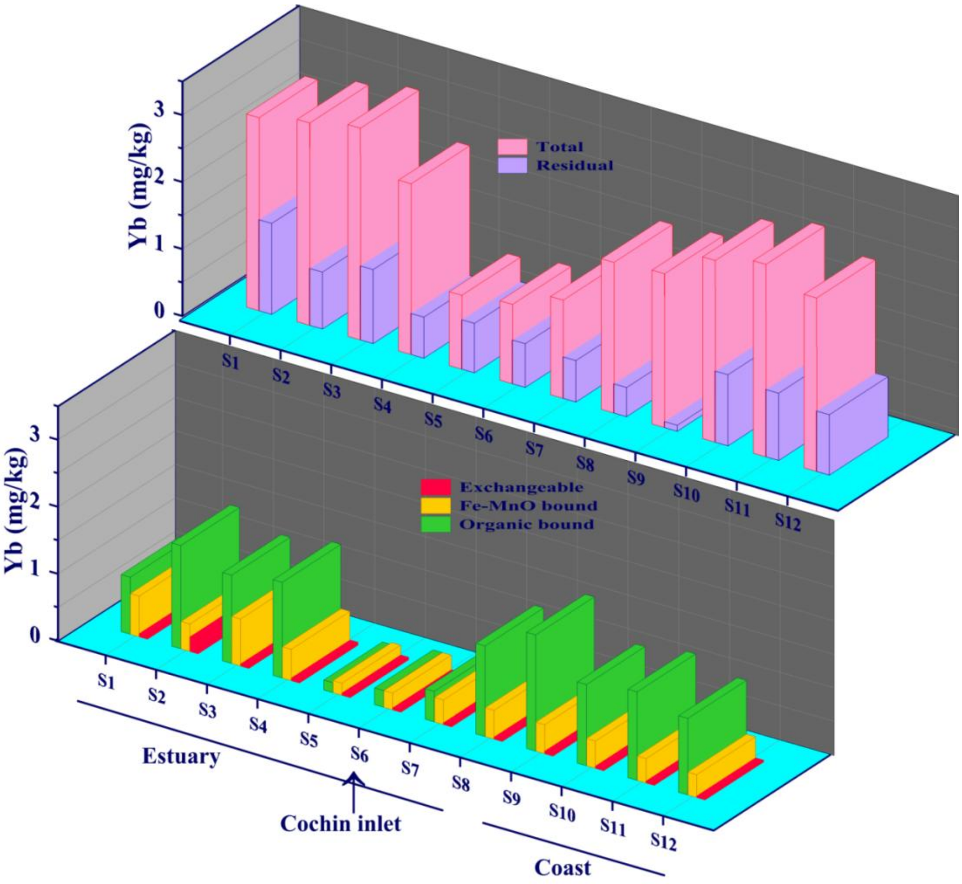

Fig 4.17**:** Total ytterbium and its four different fractions in the sediments of Cochin estuary and adjacent coastal region during October 2011.

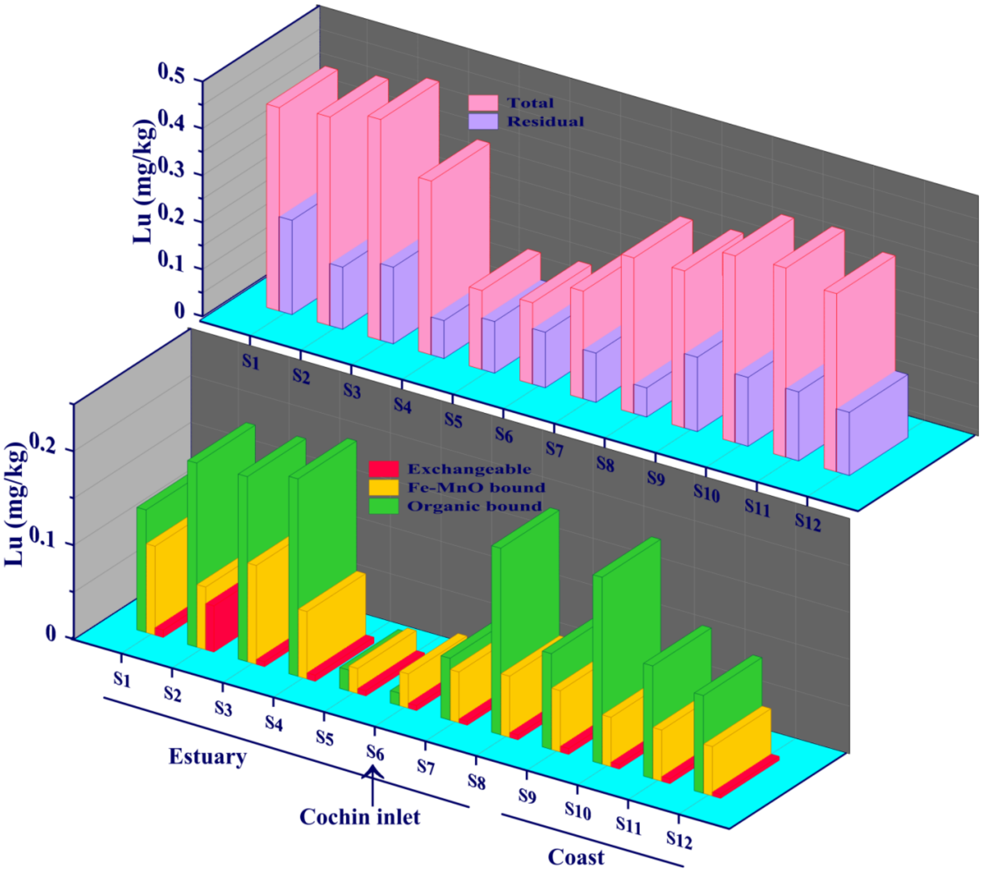

Fig 4.18 : Total lutetium and its four different fractions in the sediments of Cochin estuary and adjacent coastal region during October 2011.

4.4.8 Fractionation of Actinides (Th and U)

The fractions of actinides in the estuarine and coastal sediments (Fig 4.19-4.20) showed (86.5 - 99.5)% of Thorium in the residual phase followed by organic phase (0.1-7.8)%. The thorium in Fe/Mn oxyhydroxide and exchangeable/carbonate phases were the lowest (0.0 to 0.2)% in both estuarine and coastal stations.

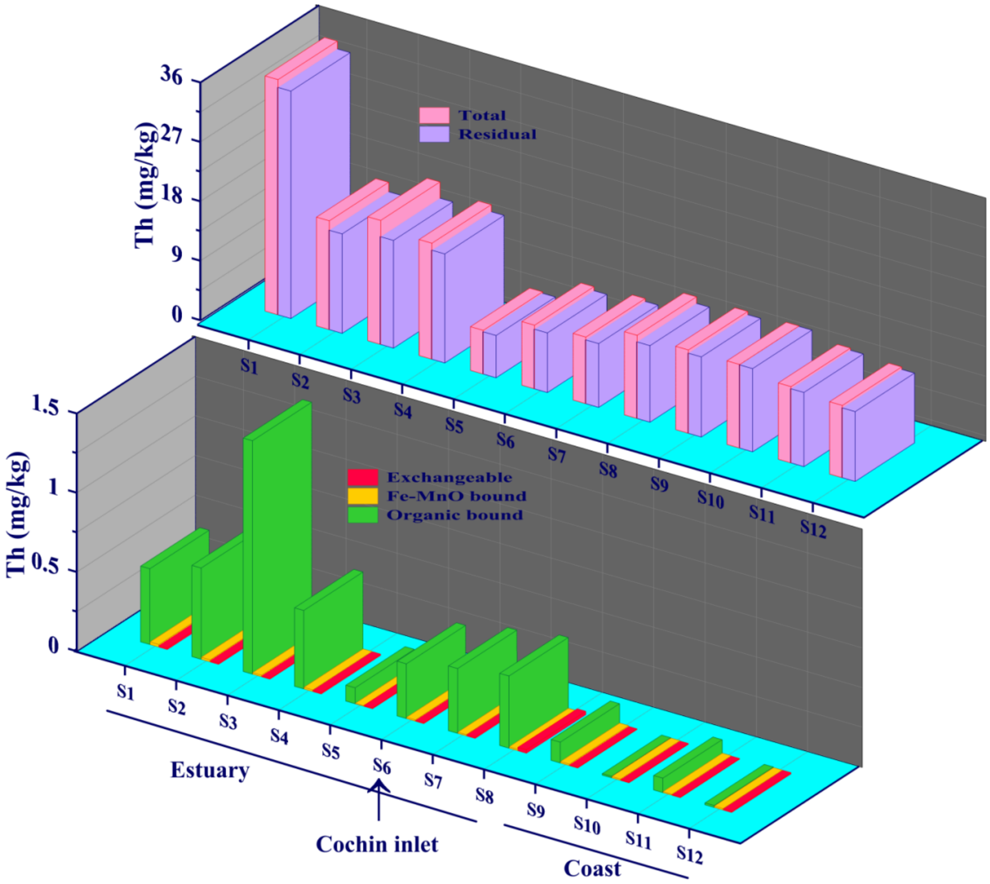

Fig 4.19: Total thorium and its four different fractions in the sediments of Cochin estuary and adjacent coastal region during October 2011

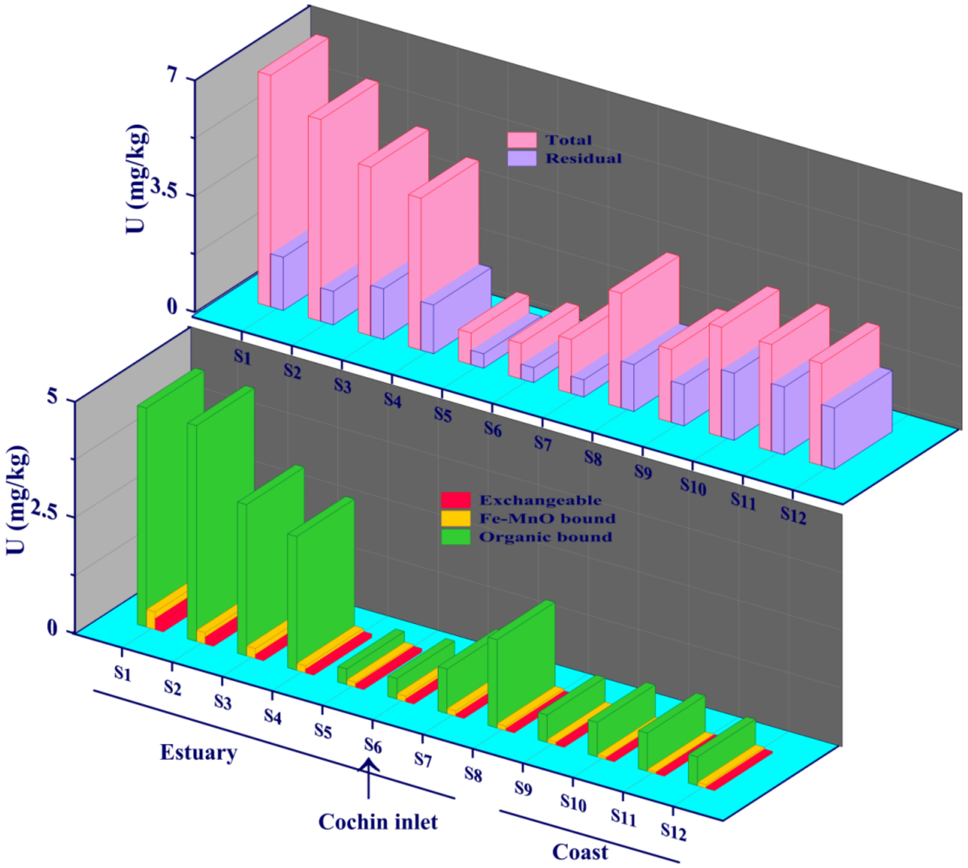

Fig 4.20**:** Total uranium and its four different fractions in the sediments of Cochin estuary and adjacent coastal region during October 2011

Organic/sulphidic phase (Fr.3) was the preferred fraction for Uranium (55.1 to 76.4 %) in the estuary at S_1, S_2, S_3, S_4, S_7 and S_8 due to high organic matter. Stations with low organic matter and sandy sediments (S_5 & S_6) exhibited U (41.7 to 45.5)% predominantly in residual phase (Fr 4). U in exchangeable/carbonate (Fr 1) and Fe/Mn oxyhyrdoxide (Fr 2) phases were poorer than Fr 3 and Fr 4 and varied as (1.4 - 8.0)% and (2.7 - 11.0)% in estuarine sediments. The estuarine sediments showed similar fractionation pattern for uranium and HREE.

Although the coastal sediments were enriched in organic matter, U was preferentially found in the residual phase (56.5 - 63.5)% as compared to the organic phase (20.1 - 26.8%). The uranium in Fe/Mn oxyhydroxide was much lower (1.3 - 2.8)%. The exchangeable/carbonate phase (Fr.1) was the lowest fraction (1.2 - 2.4%) in coastal sediments. The present study shows that organic matter is not a factor controlling the distribution of uranium in coastal sediments. In the estuarine sediments however, the enrichment of uranium was strongly depend upon the organic matter and clay in the sediments.

4.5 DISCUSSION

The sedimentary REE distribution can provide very useful information on the geological and oceanographic processes of a region (Piper, 1974; Murray and Leinen, 1993). There are many studies to reveal the source and depositional pathways of REE in Cochin estuary and its adjacent coastal region (Nath et al., 2000; Siby, 2004; Laluraj, 2009; Deepulal et al., 2012). The present study is a first time attempt to carry out the fractionation of rare earths, thorium and uranium in the sediments of Cochin estuary and adjacent coastal region to understand the fate, transport and depositional characteristics of these elements. Ce was markedly high in sediments of estuarine and coastal stations as it was the most abundant rare earth in earth crust. Lutetium was the least abundant rare earth present in the estuarine and coastal sediments. Enrichment of rare earth elements (REE) in the north estuary (S_1, S_2) and a gradual decrease towards the central estuary (S_3, S_4, S_7, S_8) and to a lowest level near the Cochin inlet (S_5 & S_6) are some of the notable observations.

Further towards the coast, the REE showed a gradual increase and the values similar to the central estuary. This generally indicates the mobility of elements from riverine sources downstream. The deviations in normalized pattern in the north estuary from the global shale could be due to external input. The dynamic nature of the inlet may support swiping of finer particles leading to impoverishment of elements in the sediments. This is consistent with the earlier results showing swift currents at Cochin inlet restricts materials to settle down (Srinivas et al., 2004; Laluraj, 2009). Similar kind of observations with near shore enrichment in the coastal region was reported in previous study (Laluraj, 2009).

The concentration of rare earths, uranium and thorium in estuarine sediments was comparable with the earlier studies (Laluraj, 2009; Deepulal et al., 2012) (Table 4.7 & 4.8). The higher levels of rare earths, uranium and thorium in the coastal sediments during the present study may be due to a corresponding increase in the clay content. Earlier studies (Laluraj, 2009; Deepulal et al., 2012) carried out in coastal region have mostly noticed a sandy texture in this region. Therefore, sediment texture plays an important role in the distribution of rare earths, uranium and thorium in the coastal environment. The fine-grained sediments have greater surface area and can provide more efficient environment for the adsorption of these elements (Wasserman et al., 1998).

Geochemistry of the REE in the Cochin estuary and adjacent coastal region show that there is an enrichment of light rare earth elements (LREE) compared to middle rare earth elements (MREE) and heavy rare earth elements (HREE), which is consistent with previous studies from this region. The LREE enrichment in the sediments of Cochin estuary and adjacent coastal region was preferentially linked to greater felsic granitic compositions (Nath et al., 2000; Laluraj et al., 2009; Deepulal et al., 2012).

Ce anomaly in the study region showed the terrigeneous nature of sediments under oxidized conditions. The slightly negative Ce anomaly in the north estuary may be associated with the biological productivity in the region (Manoj et al., 2016). The feldspars and their secondary products, which are enriched in Eu, might be the cause of a slight positive Eu anomaly in the study region, where the terrain is characterized by plagioclase-rich charnockites (Allen et al., 1985) and feldspar (Taylor and McLennan, 1985). The positive Eu anomalies can occurs in moderately weathered sediments and the Cochin estuarine sediments can be considered as moderately weathered (Manoj et al., 2016).

The fractionation studies were carried out to understand the mechanism behind the deposition of REE, and actinides (Thorium and Uranium) in the Cochin estuary and adjacent coastal region. It was observed that residual phase was the major binding phase for LREE. However for HREE, the preeminent binding phase varied with organic matter in the sediments. It was observed that the preeminent binding phase for HREEs was organic/sulphidic phase in sediments with high organic matter. However, in sediments with low organic matter, HREE was preferentially found in residual phase. Scandium showed fractionation similar to LREEs, while yttrim showed fractionation similar to HREE due to their identical chemical properties. These kinds of fractionation of REE are crucial in their enrichment in the sediments. The high thermodynamic stability of LREE in residual phase could be a reason for its enrichment in sediments. The stability of HREE depends upon the nature of organic compound to which it is associated. The source of organic matter is primarily detritus in nature. The thick tropical vegetation in the catchment areas of rivers and estuaries, mangrove vegetation, high primary productivity, seasonal hypoxia and fine particle size of sediments are responsible for higher concentration of organic matter in the estuary and shelf (Manju et al., 2012; Gireeshkumar et al., 2013). The metal binding to organic matter remains complex with ion exchange and surface adsorption being the major pathways (Brown et al., 2000). It is clear from the study that organic matter content and grain-size are significantly affecting the rare earth concentration in the study area. There are reports that Fe/Mn oxyhydroxides are major carriers of REE in marine sediments and become unstable during fluctuating Eh/pH in the OMZ (Palmer and Elderfield, 1986). The present study shows that the association of REE with Fe/Mn oxyhydroxide was relatively low compared to that in residual and organic phases. The strong neagative correlation between kaolinite and REE in Fr 1 shows that REE in Fr 1 was mostly associated with Smectite.

Thorium in the present study was mainly concentrated in the residual phases. Thorium is generally resistant to weathering and alteration processes (Taylor and McLennan, 1985; Nath et al., 1997). It is significantly present in the minerals, zircon and monazite sands of Kerala. High concentration of thorium in the northern estuary can be due to industrial input.

From the results, it is clear that the fractionation of uranium was similar to that of HREE in estuarine sediments. More specifically, the enrichment of uranium in estuarine sediments was strongly dependent on the organic matter. The estuarine sediments with lower organic matter and low clay content contained low uranium content, while sediments with high organic matter showed high uranium content. Conversely, the coastal sediments containing high organic matter preferentially accumulated uranium in a relatively resistant residual phase. Therefore, organic matter does not support the deposition of U. The presence of high uranium in coastal stations can also be due to bio-mineralization. Uranium was found to precipitate as stable uranyl phosphate mineral along the south west coast of India (Sreedhar et al., 2014). Phosphate solubilizing bacteria present in the monazites of south west coast of India have the ability to release phosphate for uranium mineralization (Desouza et al., 2000; Sreedhar et al., 2014). The present study shows that factors such as organic matter, Fe/Mn oxyhydroxides, sediment texture and mineral surface area are all contributing to the enrichment of REE in the sediments, which in turn, depends on the redox conditions, ion exchange capacity of clay minerals, rate of sedimentation/ flocculation and rate of weathering.

4. 6 SUMMARY AND CONCLUSION

The present study is a first time attempt to carry out the fractionation of rare earths, thorium and uranium in the sediments of Cochin estuary and adjacent coastal region to understand the fate, transport and depositional characteristics of these elements. Rare earth element (REE) geochemistry of sediments from Cochin estuary and adjacent coastal stations showed that the light rare earth elements (LREEs) are the more abundant compared to middle rare earth elements (MREE) and heavy rare earth elements (HREE). Cerium was markedly high in sediments of estuarine and coastal stations as it was the most abundant rare earth in earth crust. Lutetium was the least abundant rare earth present in the estuarine and coastal sediments. Rare earth elements (REE) were concentrated in the northern stations and showed a gradual decrease towards the central estuary and lowest concentration was observed near the Cochin inlet with sandy sediments. The dynamic nature of the inlet may support swiping of finer particles leading to impoverishment of elements in the sediments. The coastal sediments showed high concentration of rare earths and the values were similar to the central estuary. Shale normalized values of rare earths showed felsic source. A deviation in shale normalized pattern observed at northern estuary can be due to additional supply of REE into the estuary in addition to detritus. High thorium content in theses station too supports the external source.

Positive Ce anomaly observed in the study region supports the terrigeneous origin. A slight negative Ce anomaly at northern station could be due to biological productivity. No anomaly or slightly positive Eu anomaly in both estuarine and coastal sediments supports its feldspar origin. Redox constraints like U/Th ratio and authigenic U supports the oxygenated conditions in both estuarine and coastal sediments. Sequential extractions show that LREE was mostly associated with residual phase, while HREE was preeminently found in organic phase in organic rich clayey sediments and in residual phase in organic poor sandy sediments. The high thermodynamic stability of LREE in residual phase could be a reason for its enrichment in sediments. The stability of HREE in sediments depends upon the nature of organic compound to which it is associated. Thorium in the sediment was stabilized in the residual phases.

The organic matter present in estuarine environment makes uranium immobile in sediments, while in the coastal environment, the bio-mineralization seems to be responsible for its accumulation in residual phase. The association of REE with Fe/Mn oxyhydroxides and exchangeable/carbonate phases was relatively low compared to that in residual and organic phases. The study thus highlights the major role of particle size and organic matter in controlling the deposition of REE in the estuarine and coastal environments.

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Chapter 5

INPUT AND EXPORT FLUXES OF TRACE METALS IN THE COCHIN ESTUARY

Contents

5.1. INTRODUCTION

Rivers are by far, the most important media for the transport of solids to the sea. Estuaries act as a transition zone, where a major part of the continental weathering materials are trapped and the remainder is transported to the sea (Aston, 1978; Salomons and Forstner, 1984). Besides, estuaries also act as geochemical filters of toxic materials and pollutants (Kennish, 1991; Spencer et al., 2006) that enhance the deterioration in estuaries. One class of such pollutants comprises the trace metals. The trace metals are naturally found in their background levels on earth’s crust such as Shale’s, Sandstones, and Metamorphic and Igneous rocks (Benjamin and Honeyman, 2000). The release of metals from the crustal rock is influenced by natural events such as rain, wind and chemical weathering, notwithstanding large-scale anthropogenic disturbances such as mining, construction and coal burning.

Thus, the major sources of trace metals to aquatic systems are rivers, atmospheric fallout and anthropogenic activities. Since these elements are persistent in the sediment they are also delayed sources of contamination to the aquatic systems (Kennish et al., 1991; Wood et al., 2012; Machado et al., 2014).

The major types of rock in the study area are crystalline rocks of Archean age, sediments of tertiary age and laterite capping on crystalline rocks and sediments of sub-recent to recent age (Rao et al., 1983; Mallik et al., 1987). Charnockite, Khondalite, Granite gneiss, and Granites are the dominant rocks and at places, they are traversed by basic rocks. Charnockite is widespread in the hill ranges of the Western Ghats from where the rivers of Kerala originate. The heavy mineral suite of the coastal and river sediments of Kerala consists of opaque, hornblende, hypersthene, tremolite/actinolite, pyroxene, epidote, zircon, sillimite, kyanite, staurolite, andalusite, monazite, rutile, sphene, apatite and tourmaline (Reddy and Rao, 1992). The light minerals consist of quartz, feldspar and some mica, while the opaque trace minerals include ilmenite, a little magnetite, rutile, spinel and leucoxene. In the lowlands, the soils vary from sandy to clayey and the erosion status is slight to moderate in the Achankovil, Muvattupuzha and Periyar river basins.

When trace metals enter an estuary, they are exposed to an environment where the chemical and physical properties (pH, redox, surface area and ionic strength) undergo rapid changes (Wen et al., 1999). The important estuarine processes are the precipitation, adsorption and desorption. The chemically reactive parts of suspended particles are normally organic matter (humic/fulvic acid), oxides of Fe, Mg, Al, Si and charged clay. The binding sites on them are capable of scavenging metals from solution. There are several physical (columbic interactions in the surface) and chemical (interior covalent bonds) factors controlling the strength of metal attachment to the particles. The partitioning of trace metals between dissolved and particulate phases is dependent on the in situ processes such as coagulation, flocculation, re-suspension, bioturbation and sedimentation (Santschi et al., 1997). Besides, major meteorological events like storms, high tidal amplitudes and an increased river flow can also alter the partitioning of metals in estuaries.

Desorption of trace metals from particulate material is also an important process in estuaries. Luoma (1983 &1989) had shown that metals present in the particulate form in the aqueous phase are more bio-available than the dissolved metals. Thus, for a real assessment of trace metal pollution, the concentration of metals in suspended matter is an obligatory parameter in addition to their concentrations in dissolved fraction (Church, 1986). More than 90 % of suspended particles brought by rivers are deposited in estuaries and coastal zones, thus only a small percentage reaches the open sea. Therefore, the ultimate sink of most trace metals discharged into the aquatic environment is the estuarine sediment. Estuaries are normally transport zones of both dissolved and particulate matter to the oceans and hence, sources and distribution of trace metals in estuaries and rivers are very essential to evaluate the geochemical budget (Riley and Chester, 1971). Since estuarine systems are dynamic due to strong chemical and physical gradients, studies on trace metal cycling is more difficult in estuaries compared to other aquatic systems (Morel et al., 1991; Millward and Turner, 1995).

The Cochin estuary is one of the largest tropical estuarine systems along the west coast of India. The hydrography of the Cochin estuary is greatly influenced by tides, freshwater water flow and estuarine circulation (Revichandran et al., 2011; Shivaprasad et al., 2013). The flow characteristics and the mixing pattern of Cochin estuary are very peculiar and have great influence in the bio-resources, transportation and waste disposal (Balachandran et al., 2005). The fluvial transport was found to be a perennial and major process behind the evolution and morphology of the Vembanad Lake, also known as the Cochin Estuary (Qasim, 2003). Increased discharge of industrial effluents through the River Periyar has changed the northern estuary into a heavily polluted region, while the sluggish south estuary receives domestic and agricultural effluents from upstream (Kuttanad agricultural fields). Human interventions have led to wide spread reclamation of the estuary, while the construction of hydraulic barriers in the northern and southern parts have created severe flow restrictions and increased sedimentation in the estuary (Balachandran et al., 2005; 2008c).

Discharge of effluents has substantially increased the concentrations of many of the dissolved metals in the estuary (Anju et al., 2011). The concentrations of Zn, Cd and Ni in the estuarine sediments have enriched to such an extent that Cochin Estuary is placed among the most impacted estuaries in the world (Balachandran et al., 2005; Martin et al., 2012; Renjith et al., 2016; George et al., 2016; Salas et al., 2017). There are also reports of minor pollution with respect to Fe, Mg, Cr and Mn in the CE and adjacent coastal waters (Bindu et al., 2015). Hg levels in Cochin estuary (up to 3.0mg/kg in fish) was higher than similar kind of fish caught from other weltands in India (Ramaswamy et al., 2017). Realizing the pressures on Cochin estuary, previous study suggested for adequate conservation plans to minimize the inevitable pollution, consequent to developmental activities

(Ramaswamy et al., 2017). The increase in the Zn concentration in CE has also altered the community of cyanobacteria in the Cochin Estuary (Anas et al., 2015). Therefore, an efficient estuarine management is required based on the activities and pressures operating on this ecosystem (Elliotta and McLusky, 2002; Millennium Ecosystem Assessment, 2005; European Commission, 2012). In view of this, the present study proposes to identify the source, fate and transport of trace metals in the Cochin estuary.

5.2. STUDY REGION AND METHODOLOGY

5.2.1. Regional Setting

Metal fluxes through the Cochin estuary can be quantified by measuring their respective fluxes across the river end stations and at Cochin inlet, where exchange of materials between the estuary and sea occurs. A total of 14 locations were selected for the present study to identify the source, fate and transport of trace metals in the Cochin estuary (Fig 5.1). The geographic locations of sampling sites (Table 5.1) are labeled from S_1 to S_{14}. They are S_1 (Neeleswaram), an upstream site of River Periyar near to Central Water Commission (CWC) Gauge station. S_2 is at Purappallikkavu where a temporary sand barrier constructed prevents salt water intrusion during pre-monsoon period (During the present sampling period, the bund construction at S_2 was in progress). S_3 is at Moolampilly where River Periyar enters the Cochin Estuary (CE) after receiving effluents from the industrial area (Eloor). S_5 is at Vettikkattumuku in the upper reaches of the River Muvattupuzha. Since this river bifurcates before its entry to the CE, samples were collected from these two branches of Muvattupuzha i.e S_6 (Murinjupuzha) and S_7 (Ithipuzha). S_8 (Kariyar) is another branch of Muvattupuzha river entering the north Kuttanad region. The major activities in this region are clam shell processing, paddy cultivation and fish farming. There were lot of weeds in the Ithipuzha and Kariyar during the sampling period. Thanneermukkam barrier remains closed from December to April every year, during which, the southern part of the estuary remains almost stagnant. S_9 is Kidangoor, an upstream end of River Meenachil (CWC Gauge station). S_{10} is at Kumarakom, the southernmost part of the Vembanad Lake where River Meenachil enters the CE. S_{11} is at Pallathuruthy in south Alappuzha through which, River Pamba enters the Kuttanad agricultural fields. S_{12} is at Keezhvaypur (CWC Gauge station) in the River Manimala (tributary of River Pamba). S_{13} is at Aranmula (upstream end of River Pamba) and S_{14} is at Mudiyyoorkonnam (in the River Achankoil). This region was turbid during the sampling period.

Table 5.1**:** Details of sampling sites selected for the study

Sl No	**Station name**	**Station code**	**GPS coordinates**	
1	Periyar	S_1	10° 10' 22.3"N	76° 27' 38.1"E
2	Purappillikkavu	S_2	10° 8' 39.2"N	76° 16' 59.9"E
3	Moolampilly	S_3	10° 2' 17.6"N	76° 16' 8.2"E
4	Cochin inlet	S_4	9° 58' 15.3"N	76°14 ' 42.1"E
5	Muvattupuzha	S_5	9° 48'21.1"N	76° 27' 14"E
6	Murinjupuzha	S_6	9° 49'17.3"N	76° 23' 31.8"E
7	Ithipuzha	S_7	9° 46'50.6"N	76° 22' 29.6"E
8	Kariyar	S_8	9° 42' 5.8"N	76° 24' 10.9"E
9	Meenachil	S_9	9° 40' 34.6"N	76° 36' 33.9"E
10	Kumarakom	S_{10}	9° 35' 47.8"N	76° 25' 46.3"E
11	Pallathuruthy	S_{11}	9° 27' 47.2"N	76° 21' 46.5"E
12	Manimala	S_{12}	9° 25' 55.9"N	76° 40' 3.4"E
13	Pamba	S_{13}	9° 19' 43.6"N	76° 41' 6.2"E
14	Achankoil	S_{14}	9° 14' 2.7"N	76° 38' 20.6"E

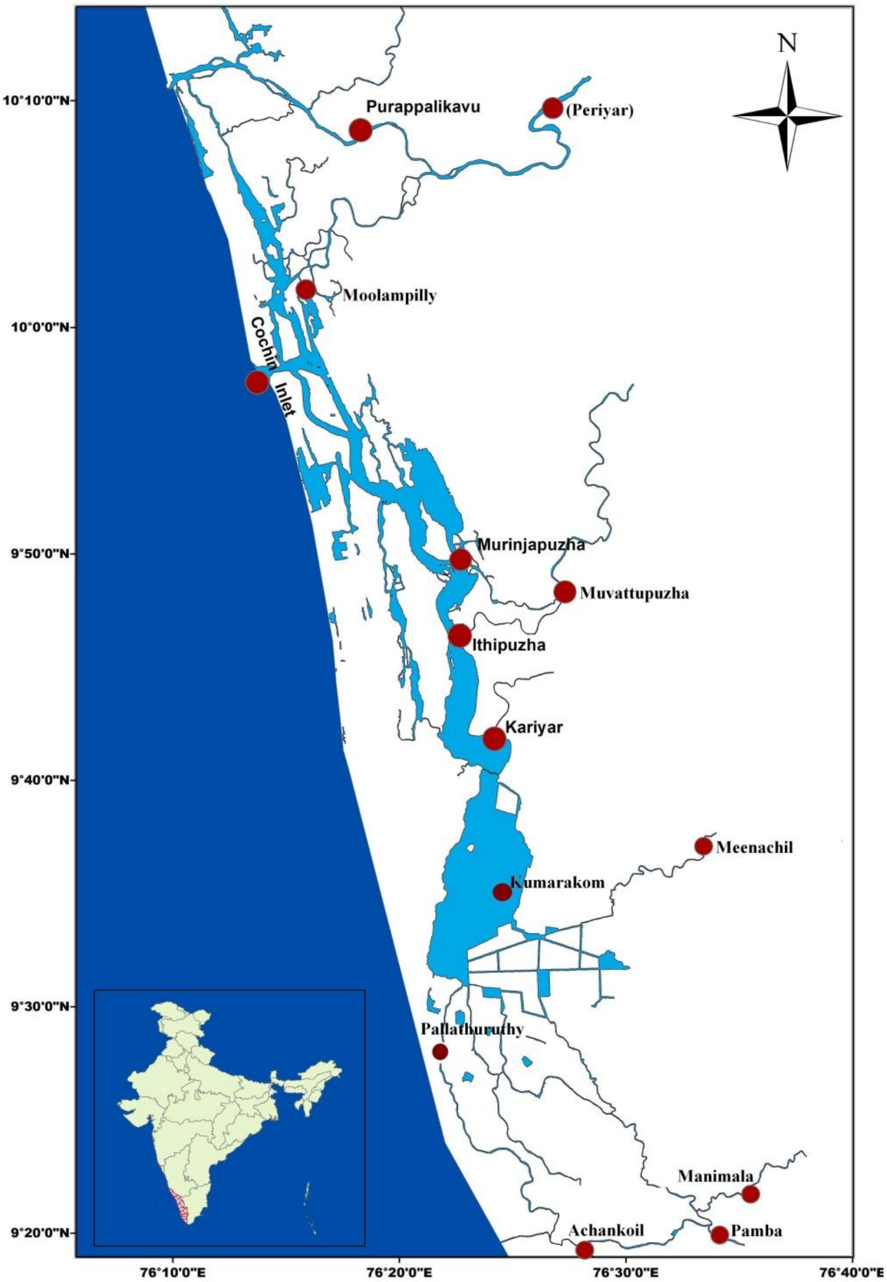

Fig 5.1: Cochin estuary and rivers discharging into the system; the red dots symbolize the station locations for the present study.

Cochin inlet, (S_4) is a region where considerable exchange of materials occurs between the sea and the estuary as it is the major opening to the sea. S_4 showed dynamic nature due to the opposing effect of tidal forcing and river discharge. The depth of the channel at S_4 is 10-15 m (Shivaprasad et al., 2013). There is strong stratification at the inlet during heavy discharge periods, while it gets eroded during post and pre monsoon periods, when well mixed condition prevails (Bincy et al., 2013; Shivaprasad et al., 2013).

5.2.2. Sampling and analysis

River sampling was carried out during the period 28-30th October 2015. For the flux measurements, the instantaneous cross sectional flow through each of the six rivers (locations S_1, S_5, S_9, S_{12}, S_{13} and S_{14}) were measured (one time measurement) using an Acoustic Doppler Current Profiler (ADCP-Teledyne River Ray-600 KHz) with bottom-track capability. The dissolved and particulate metal contents of water samples collected from the surface and near bottom were analysed and used in the computation of metal input fluxes through each rivers. Although the metal fluxes through other 4 locations (locations S_3, S_6, S_7 and S_8) were also measured during the same period, these values were not included while computing the net fluxes (input-export) through the estuary as they were located in the upper estuary.

Since the flushing time of Cochin estuary is ~2.5 days during this period (Vinita et al., 2015a), the measurements to quantify the export fluxes through the Cochin inlet were conducted after 3 days of the river sampling (during 3-4th November 2015). A tide gauge was moored at Cochin inlet to obtain the water level variations during the flux measurements. The metal fluxes across the Cochin inlet was computed based on the time series observation for 27 hrs using ADCP and water sample collection at 3hr intervals from the surface, 7.5m and 15m depths. The water flux obtained from ADCP was extracted as surface, mid and bottom fluxes using MATLAB. The measured metal concentration and water flux at each depth was used to compute the instantaneous cross sectional transport, which on integration over the tidal cycle, gives the net fluxes across the inlet.

Temperature and salinity at each location (14 locations) were measured using a conductivity-temperature depth profiler (CTD 19 plus, Sea-Bird Electronics). The atmospheric conditions and sampling time were noted at all locations. Water samples were collected from the surface, mid and bottom using Niskin sampler (Hydrobios-Kiel) for pH, dissolved oxygen, heavy metals and suspended particulate matter. The samples for dissolved oxygen were fixed immediately after collection and later, analyzed according to Winkler's method (Grasshoff et al., 1999). pH was measured using pH meter (Eutech pH 2700, accuracy ±0.001). The water samples for trace metals were kept in ice, brought to the lab and filtered through a pre-weighed 0.45micron millipore filter paper (dried at 60° C, kept in desiccators and weighed) to separate suspended particulate matter and the filtrate were preserved at $pH < 2$ using con.HNO_3 until extraction. The extraction was done with APDC (2%), DDDC (2%) and chloroform at pH 4.5 (adjusted with ammonium acetate). The filter paper containing the suspended solids was washed with 5 ml of Milli-Q water (Owens et al., 1997) to remove sea salts and dried at 60°C in an air oven to constant weight. The filter paper together with the suspended solids was weighed and the difference in weight was taken as the weight of suspended particles (mg/l). Each filter paper was separately stored in polyethylene petry dishes at -20° C until the extraction for trace metals. The extraction was done by digestion with a mixture of HNO_3+$HClO_4$ (5:2) in Teflon vessels on a hot plate (110°C) to dryness (Balaram and Rao, 2002). The residue was re-dissolved in 2% ultrapure HNO_3 (with 1ppm of Rhodium as internal standard) and analyzed by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). Certified reference material was used to validate the method.

5.3. RESULTS AND DISCUSSION

5.3.1 General Hydrography

Trace metals are transported to the ocean by rivers in dissolved and particulate forms. In estuaries, where river water and coastal or oceanic waters of widely different compositions are mixed, strong gradients in chemical properties occur (Burton, 1976). These variations may affect the distribution of dissolved and particulate components of trace metals. Therefore, hydrographical parameters are vital tools while attempting to characterize the distribution pattern of trace metals during their transport and also in the partitioning of metals in different phases. The freshwater input, currents and tidal range are useful to explain the physical behavior and transport properties in an estuary. The fresh water discharges through 6 rivers into the Cochin estuary are depicted in Fig 5.2. The water level variations at Cochin inlet on 3rd-4th November 2015 are given in Fig 5.9. As the observation was made between a spring and neap tide, the maximum tidal range observed was 0.56m (Fig. 5.9). The salinity at the upstream locations varied from 0.022 to 0.024. The salinity at upper estuary (S_3, S_6, S_7 and S_8) varied from 0.032 to 0.450 (Fig 5.3). As the water column at the Cochin inlet was stratified, there exist strong vertical gradient in salinity. The salinity at the surface, mid and bottom waters varied between 3.23 to 31.68; 13.23 to 33.48 and 31.98 to 33.78 respectively (Fig 5.9).

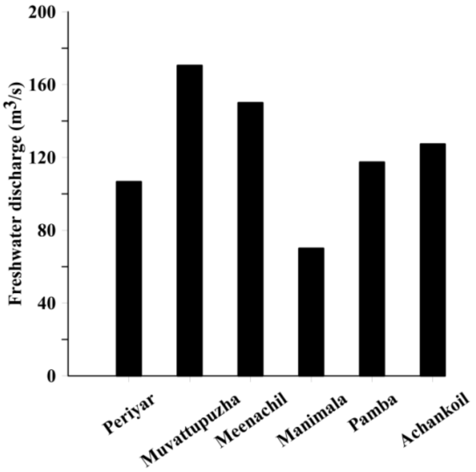

Fig 5.2**:** Fresh water discharges (m3/d) into the Cochin estuary from 6 major rivers on 28th-30th Nov 2015

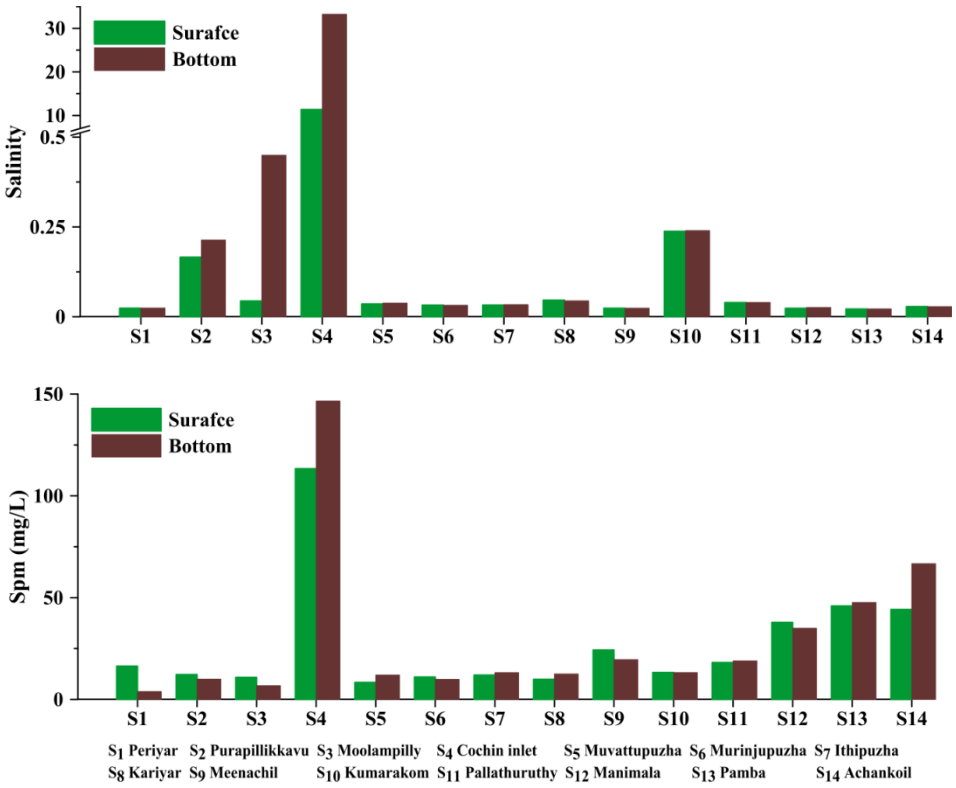

Fig 5.3: Distribution of Salinity and SPM (mg/L) observed at the rivers on 28th-30th Oct-15 and at the Cochin inlet (time series average) on 3rd-4th Nov-15.

5.3.2 Suspended particulate matter

Suspended particulate matter (SPM) plays a major role in the geochemical cycling of elements. The composition and variability of suspended particulate matter in the river-ocean boundary are affected by many complex geochemical processes (precipitation and flocculation, desorption-adsorption etc.) and by physical processes (river flow, tidal energy, currents) and are, therefore, often difficult to interpret (Morris et al., 1978; Turner et al., 1991, 1994).

5.3.2.1 Suspended particulate matter in the upper and lower reaches of rivers

Suspended particulate matter (SPM) in the upstream varied from 3.88 to 66.7mg/L (Fig 5.3). SPM was very low in River Periyar and very high in rivers Achankoil and Pamba. SPM levels in the rivers generally followed an order Achankoil > Pamba > Manimala > Meenachil > Muvattupuzha > Periyar. SPM in the lower reaches of rivers varied from 6.8 to 18.9mg/L and followed the order Pallathuruthy > Kariyar > Kumarakam/Ithipuzha > Moolampilly > Murinjupuzha. An increasing trend in SPM was noticed towards the south of the estuary with maximum SPM at Pallathuruthy. Sedimentation, re-suspension and erosion processes may change SPM concentrations in the water column (Michaelis, 1990), influencing the trace metal distribution in the estuary (Luoma and Phillips, 1988; Vollmer et al., 1990).

5.3.2.2 Suspended particulate matter at the Cochin inlet

Suspended particulate matter at the inlet varied widely during a tidal cycle between 5.83 to 718.5mg/L (Fig 5.13). The maximum SPM in the surface was during the lowest ebb period (21-24hr) and the minimum SPM was during the withdrawal of flood at 33hr (next day 9am). The SPM was generally low at mid-depth (12.45 to 102.9mg/L), though it was high (102.87mg/L) during flood tide at 30-33hr. SPM was always high in the bottom (9.13 to 701.14mg/L), especially during ebb tide (highest low tide) at 12hr and 39 hr (next day 3pm). The increase in SPM can be due to the estuarine mixing (Balachandran, 2001) indicating the effect of fluvial discharge and dredging.

5.3.4 Distribution of trace metals

5.3.4.1 Concentration of trace metals in the six rivers

There was a large variability in the distribution of metals among the dissolved and particulate phases of rivers. The concentration of metals in dissolved phase followed the trend Fe > Mg > Zn > Cr > Ni and that in the particulate phase followed an order Fe > Mg > Cr > Mn > Zn > Ni. Dissolved Fe in the rivers varied from 30 to 60µg/L (Fig 5.5) with maximum in the River Achankoil and minimum in the River Manimala. Dissolved Mg in rivers varied from 6 to 30µg/L with slightly higher concentration in Muvattupuzha and a lower concentration in Pamba and Periyar (Fig 5.5). The dissolved Zn in the rivers varied from 1.5 to 4.3µg/L with maximum in Meenachil surface (4.3µg/L) and minimum in the Manimala (1.5µg/L) (Fig 5.4). Dissolved Zn was not present in measurable levels in the River Pamba during the study period. Traces of dissolved Cr (2.21µg/L) and Ni (0.086µg/L) was observed only in the River Periyar (Fig 5.6) and the concentration of dissolved Co, Cu, Cd, Mn and Pb were below measurable levels in all the 6 rivers. The dissolved metals in all the 6 rivers studied were comparable with the values reported by Central Water Commission (CWC), India and were well within the permissible and acceptable limit of drinking water recommended by Bureau of

Indian Standard (BIS 10500-2012) and World Health Organization (WHO). As the toxicity of metals in rivers were not solely depends on the dissolved fractions, particulate trace metals in river water were analyzed.

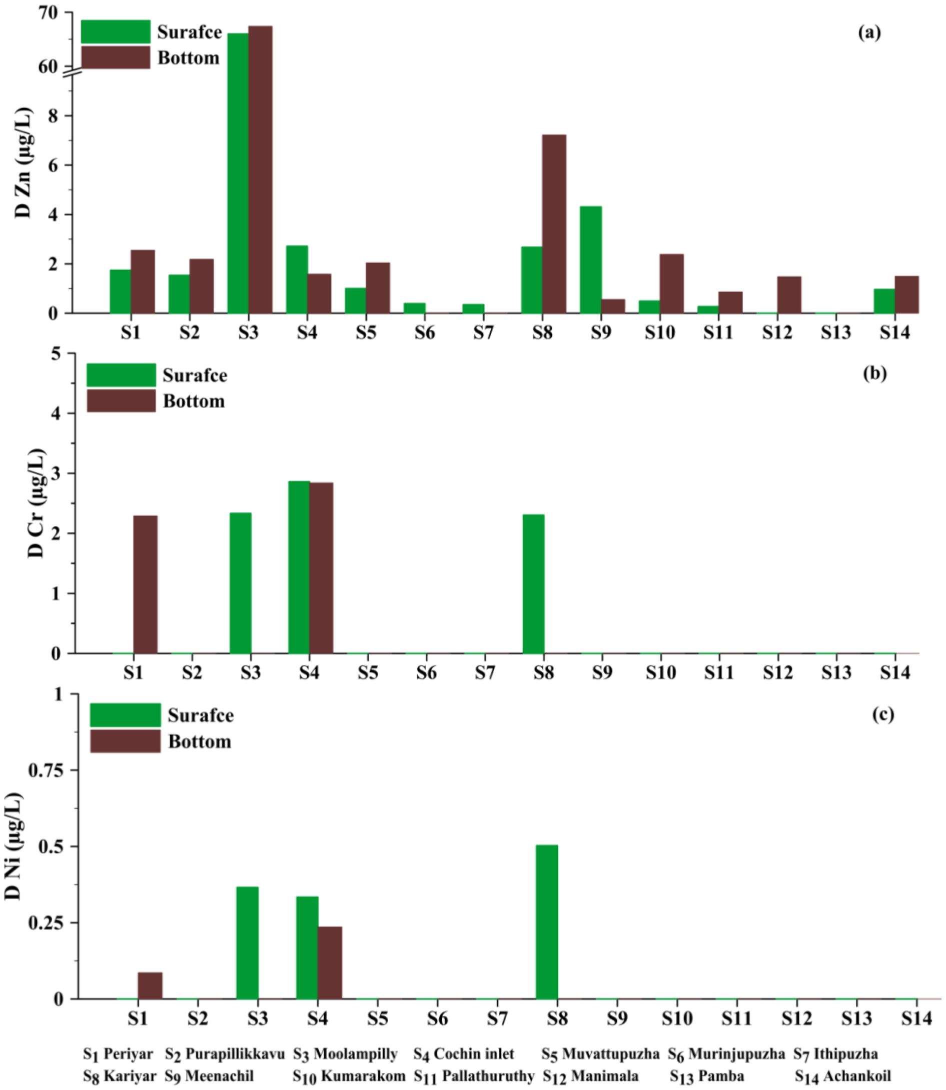

Fig 5.4: Distribution of dissolved Zn, Cr and Ni (µg/L) observed at the rivers on 28th-30th Oct-15 and at the Cochin inlet (time series average) on 3rd-4th Nov-15. (a) DZn; (b) DCr; (c) DNi.

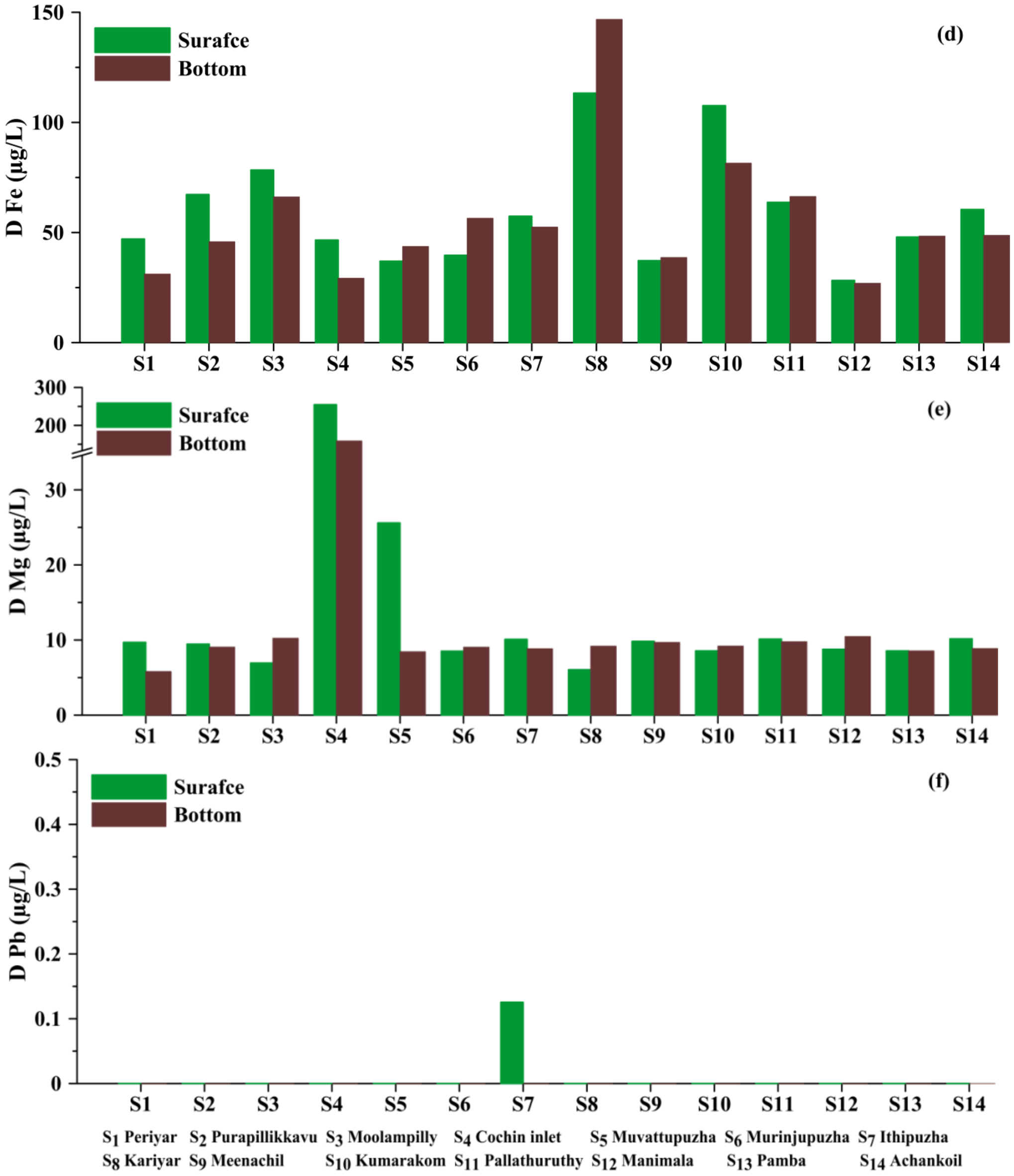

Fig 5.5: Distribution of dissolved Fe, Mg and Pb (µg/L) observed at the rivers on 28th-30th Oct-15 and at the Cochin inlet (time series average) on 3rd-4th Nov-15. (d). DFe; (e). DMg; (f). DPb.

The concentrations of all the metals analyzed in suspended particles were several times higher than in dissolved form. Fe in particulate phase varied from 3.8% to 11.2% with maximum concentration at the bottom of Periyar and minimum at the surface of Periyar showing weathering of hinterland rocks and re-suspension are the sources of particulate Fe into the rivers. Iron oxide is a major component of laterite, the major soil occurring in low and midlands of Kerala (Dept of Mining and Geology, DMG, Kerala, 2016). Thus, the high particulate Fe in rivers could be eroded from this polymetallic ore. Particulate Mn was present in appreciable levels in the rivers, Periyar (390 & 1970µg/g), Muvattupuzha (20 & 39.5µg/g), Pamba (512.4 & 89.4µg/g) and Achankoil (436.2 & 694.9µg/g) with maximum concentration in Periyar (Fig 5.8). Under highly oxygenated condition Fe and Mn exist as oxides and hydroxides which are insoluble in water leads to lower soluble Fe and absence of soluble Mn in all the six rivers. The presence of carbonates and sulphates in these rivers also support Fe precipitation (CWC, 2014). Zn in particulate phase varied from non-detectable level to 179.8µg/g at the upstream with maximum concentration in Manimala. Particulate Zn was in non-measurable levels in Muvattupuzha and Periyar rivers (Fig 5.6).

Cr in particulate phase showed moderate values in the Rivers, Periyar (130.2 & 2613µg/g), Muvattupuzha (45.1 & 537.8µg/g) and Pamba (58.8µg/g). Particulate Ni (188µg/g) was present only in the River Meenachil. However the concentrations of particulate Co, Cu, Cd and Pb were below measurable levels in all the rivers. Mg in particulate phase varied from 0.24 to 1.2% with maximum concentration in Periyar and minimum concentration in Manimala. Mg^{2+} in the river waters are supplied by weathering of ferromagnese minerals including pyroxenes and amphiboles as well as dark colored micas (biotite), which are abundant in the host lithology (Thomas et al., 2015).

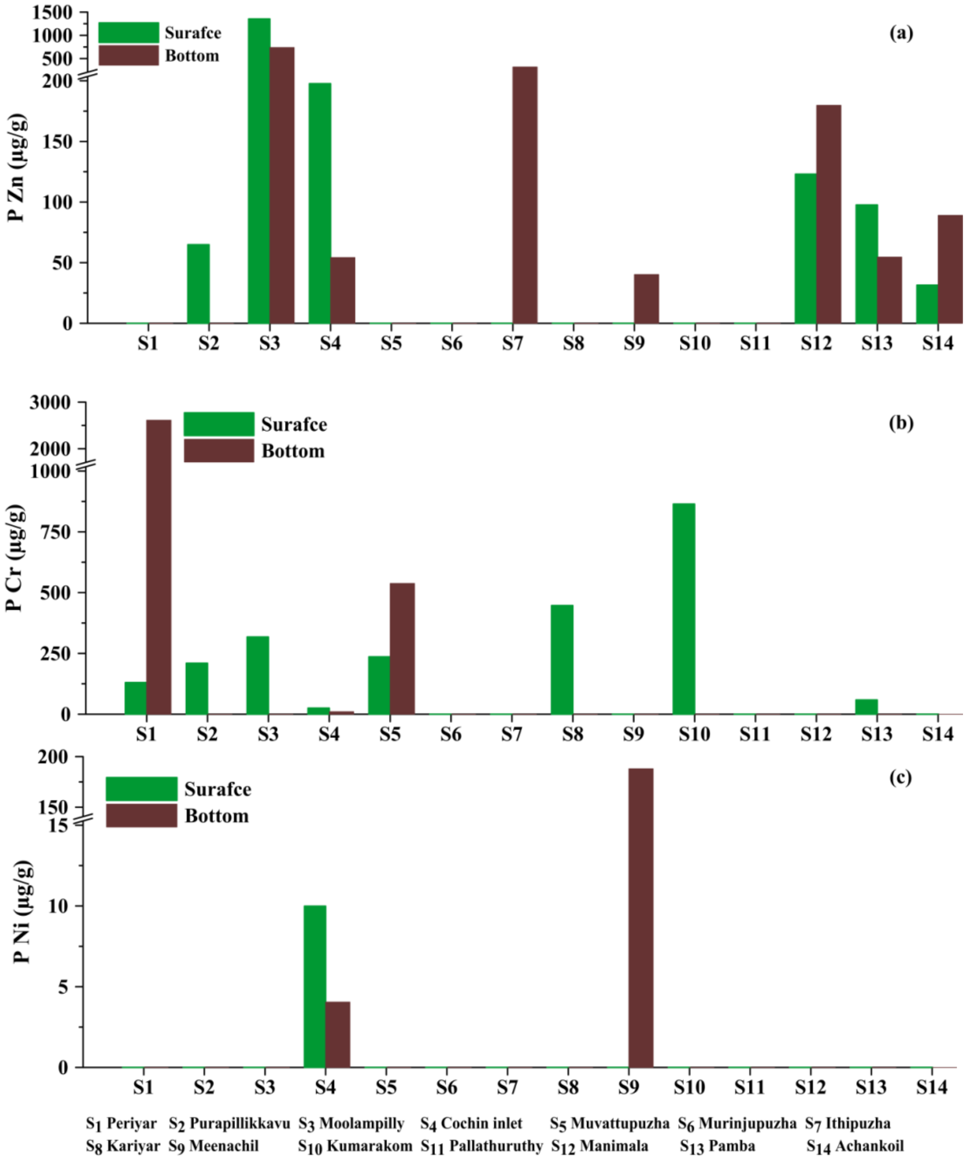

Fig 5.6: Distribution of particulate Zn, Cr and Ni (µg/g) observed at the rivers on 28th-30th Oct-15 and at the Cochin inlet (time series average) on 3rd-4th Nov-15. (a) PZn; (b) PCr; (c) PNi.

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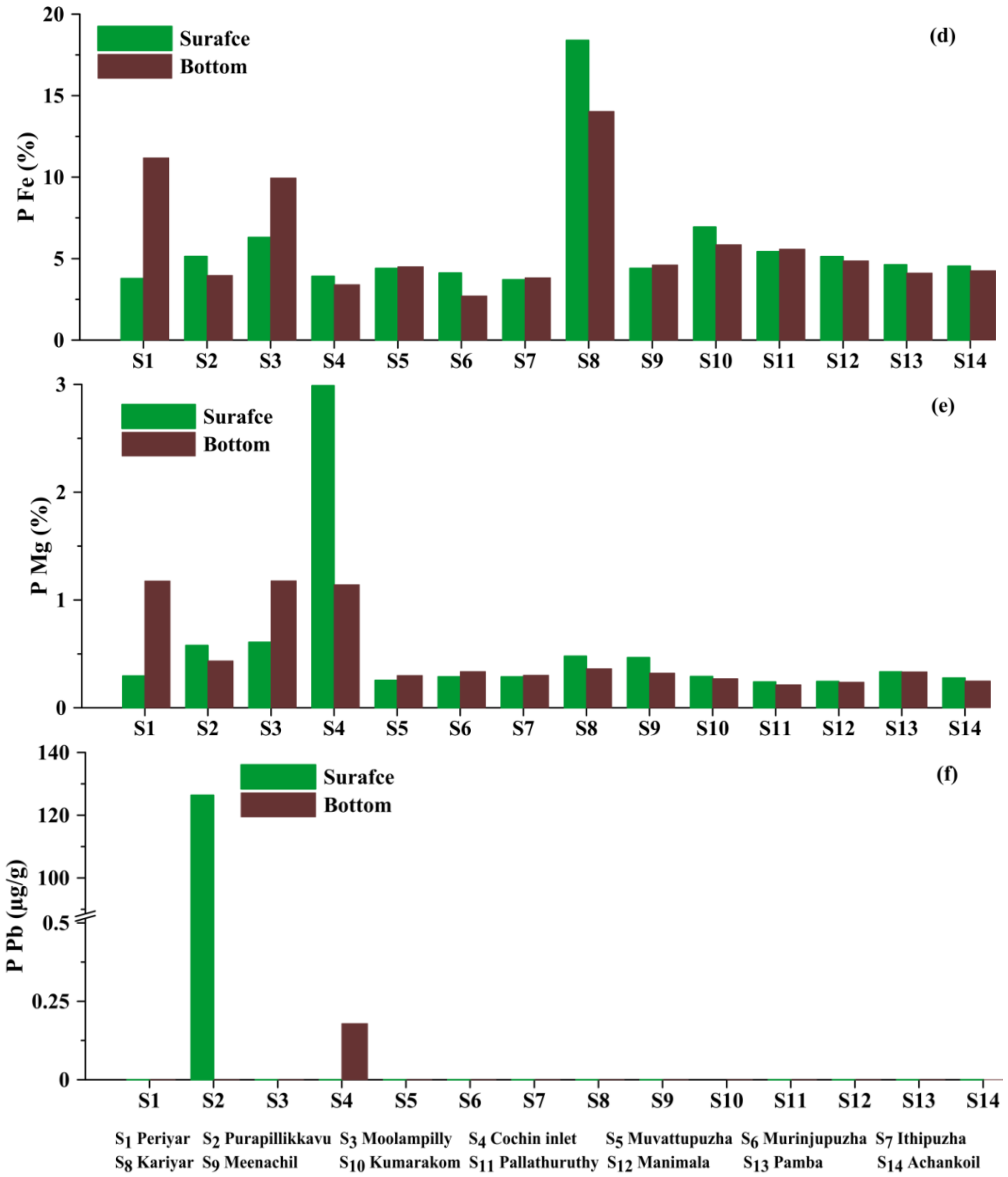

Fig 5.7: Distribution of particulate Fe, Mg (%) and Pb (µg/g) observed at the rivers on 28th-30th Oct-15 and at the Cochin inlet (time series average) on 3rd-4th Nov-15. (d). PFe; (e) PMg; (f) PPb.

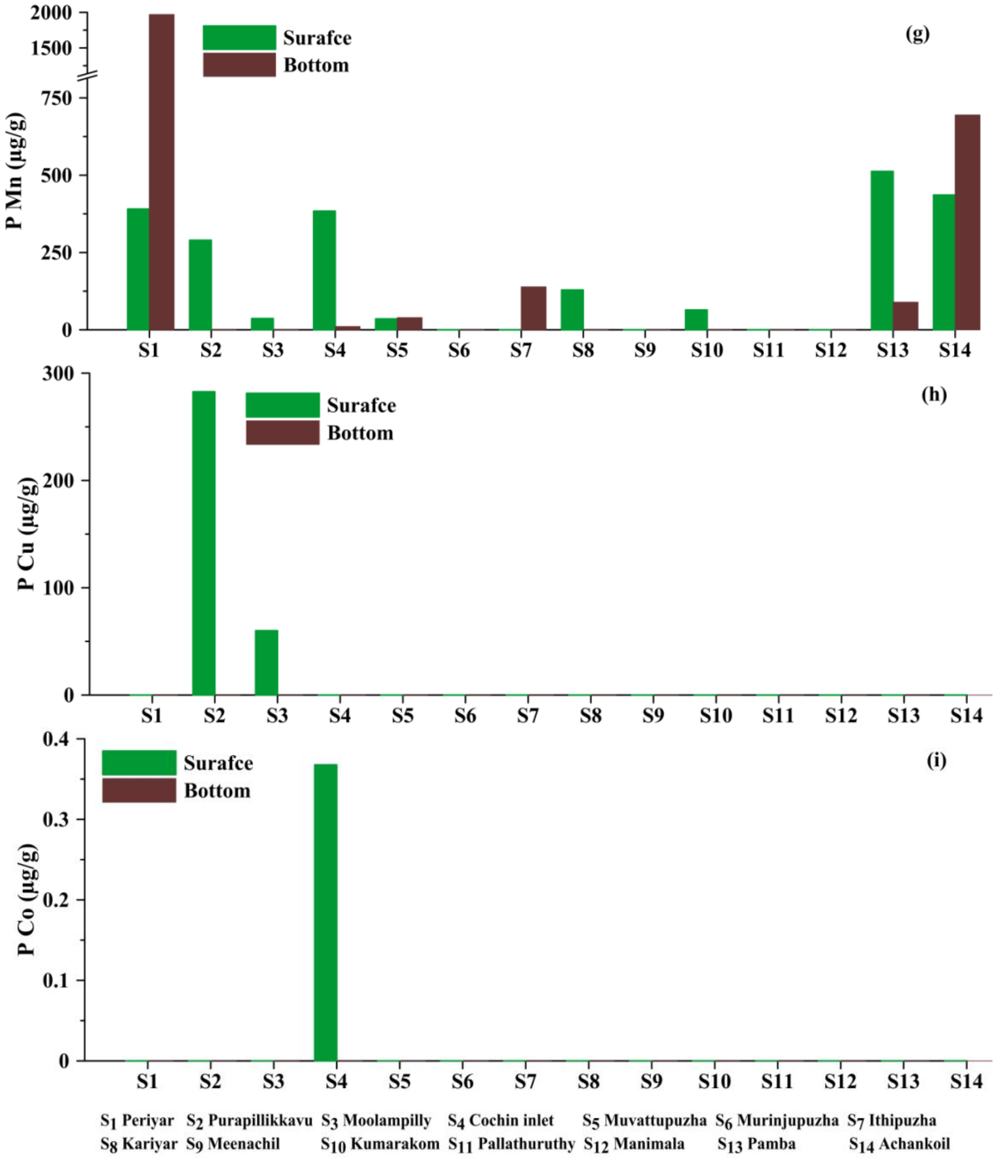

Fig 5.8 : Distribution of particulate Mn, Cu and Co (µg/g) observed at the rivers on 28th-30th Oct-15 and at the Cochin inlet (time series average) on 3rd-4th Nov-15. (g). PMn; (h) PCu; (i) PCo.

The concentration of particulate Zn and Mg observed during the present study were comparable with the concentration reported in World Rivers Average SPM values (WRSPM) and that in Post Archean Australian

Shale (PAAS) indicating the natural origin of these metals in all the 6 rivers. The concentration of particulate Fe, Cr, Ni and Mn was higher than that in the PAAS and WRSPM. Higher concentration of iron, manganese, nickel and chromium in particulate matter of these rivers could have derived from Laterite, a polymetallic ore in the low lands and midlands of Kerala enriched with these metals. The high Chromium in rivers might also be derived from various anthropogenic activities in river basins (e.g., fertilizer residues from farmlands and plantations, domestic sewage from settlement clusters). All the six rivers showed wide variation in their particulate trace metal distribution depending on the nature of alluvium that is deposited and the characteristics of the catchment area through which the river flows.

5.3.4.2 Distribution of trace metals in the lower reaches of rivers (upper estuary):

The distribution of metals in dissolved phase follows the sequence Fe > Mg > Zn > Ni > Cr (Fig 5.4 to Fig 5.5). Concentration of dissolved Zn (nd-67µg/L), Mg (0.006-0.01%) and Fe (0.04-0.15%) in the lower reaches of rivers were higher in Moolampilly (northern side) and Kumarakam (southern side) regions. Dissolved Ni and Cr were present only at the surface of Moollampilly (0.4 & 2µg/L) and Kariyar (1.0 & 2.3µg/L) suggesting their source from Periyar and Muvattupuzha rivers. Pb was not observed in any of the upstream regions while its presence in Ithipuzha (0.1µg/L) confirms its addition through non-point source. The possible sources of lead to this region may be derived from the pigments used in paints and from petroleum products and sewage discharge. Dissolved Cd, Cu, Mn and Co was not in measurable levels in the lower reaches of the rivers.

The distribution of metals in particulate phase at the lower reaches followed the trend Fe > Mg > Zn > Cr > Cu > Mn. Particulate Fe (µg/g) showed an increasing trend from upstream towards the lower reaches for all the rivers except Muvattupuzha. In Muvattupuzha, the Fe concentration (4.5%) at upstream reduced to 3.4% and 3.7% towards the lower reaches (Murinjupuzha and Ithipuzha). However higher particulate Fe (16.2%), higher than in WRSPM and PAAS observed at Kariyar, north of Kumarakom can be possibly due to the sewage disposal and land use pattern. High particulate Fe in Pallathuruthy (5.5%), Kumarakom (6.3%) and Moolampilly (8.1%) regions indicate its additional input from human activities. Particulate Mn was lower at the lower reaches all the rivers.

Particulate Cr in Purapillikkavu (209.7µg/g), Moolampilly (317.8µg/g), Kariyar (447µg/g) and Kumarakom were higher than that in WRSPM (130µg/g) and PAAS (110µg/g). Particulate Cr was high in the Muvattupuzha river while it was absent towards the lower reaches, Murinjupuzha and Ithipuzha region showing its deposition while traversing towards the lower reaches (Fig. 5.6). A similar trend was noticed in the distribution of Cr in the Periyar too. A substantial reduction in the suspended solids towards the lower reaches due to meandering of Periyar River has been reported (Paul, 1980). Meandering reduce the flow velocity and support sedimentation. The distribution of particulate trace metals in these rivers can be generally attributed to the progressive sorting of minerals to which it is associated. During deposition, the denser minerals settle quickly, while the lighter minerals are transported further downstream. It is reported that due to the high competency of river water, settling of low gravity minerals do not take place in the upstream, while they increasingly get deposited towards downstream (Seralathan, 1979; Lewis, 1984; Kundras, 1987; Padmalal, 1997). The strong association of Fe and Cr towards the denser particles during the present observation might have resulted in their rapid settling and lower particulate Fe and Cr at the lower reaches. Bio-accumulation can also be a factor for the absence of Cr in both dissolved and particulate phases of Ithipuzha and Murinjupuzha. The lower reaches of Muvattupuzha are rich in black clam and these filter feeders are capable of removing heavy metals from the aquatic systems (Cherian, 1990; Renjitha et al., 2011). Absence of Cr in Murinjupuzha, Ithipuzha, and Pallathuruthy shows that the transport of Cr into the estuary through this region was negligible. However, high concentration of particulate Cr in Kumarakom shows the anthropogenic addition from farm lands nearby.

The trace metals Zn, Cu and Pb at the lower reaches of rivers were several times higher than in the upstream regions. Particulate Zn was high at the lower reaches of Periyar and Muvattupuzha even though it was completely absent in the upstream. The concentration of particulate Zn in Moolampilly (1353µg/g), Sand bridge (64.8µg/g), and Ithipuzha (319.3µg/g) were higher than that in PAAS (85µg/g) and WRSPM (208µg/g) pointing out the anthropogenic addition of Zn from industrial areas nearby. The particulate Cu in Purappillikkavu was greater than that in PAAS (50µg/g) and WRSPM (75.9µg/g). High concentration of particulate Cu at Purapillikkavu (282.7µg/g) and Moolampilly (60µg/g) confirm their anthropogenic sources in the estuary. The particulate Pb at Purapillikkavu (126.4µg/g) and Kumarakom (84.9µg/g) was also higher than that in PAAS (20µg/g) and WRSPM (61.1µg/g). Murinjupuzha and Pallathuruthy were the least affected regions, where all the trace metals (Ni, Cu, Cr, Cd, Cu, Pb, Co and Mn) measured were completely absent except dissolved Zn in trace levels.

5.3.4.3 Distribution and variation of trace metals at the Cochin inlet

The water level variations and salinity at Cochin inlet are given in Fig 5.9. The intra-tidal variation in both dissolved and particulate Mg, Fe, Cr, Zn, Cd, Ni and Mn at the Cochin inlet for a period of 27hrs at 3 hr intervals on 3rd-4th November 2015 are depicted in Fig 5.10-5.13.

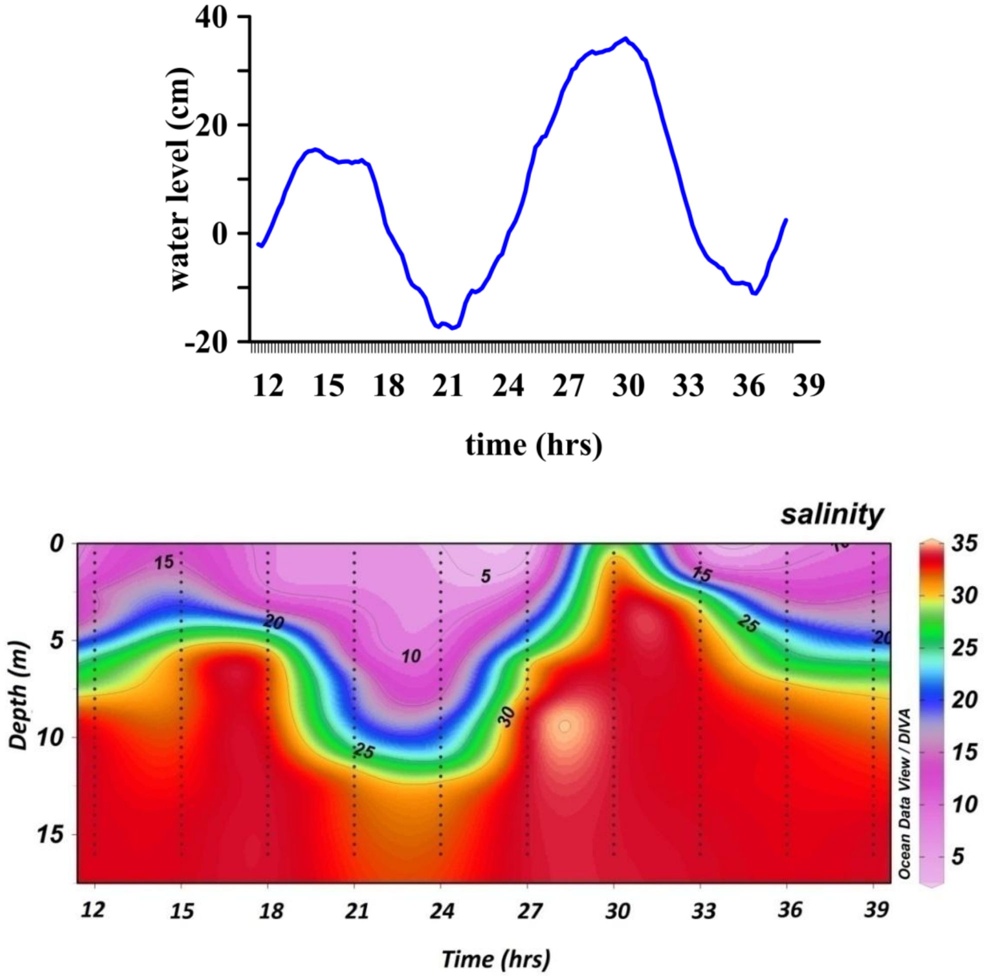

Fig 5.9: Variations in the water level (cm) and salinity profile at the Cochin inlet on 3rd Nov 12.00hrs to 4th Nov 15.00hrs, 2015.

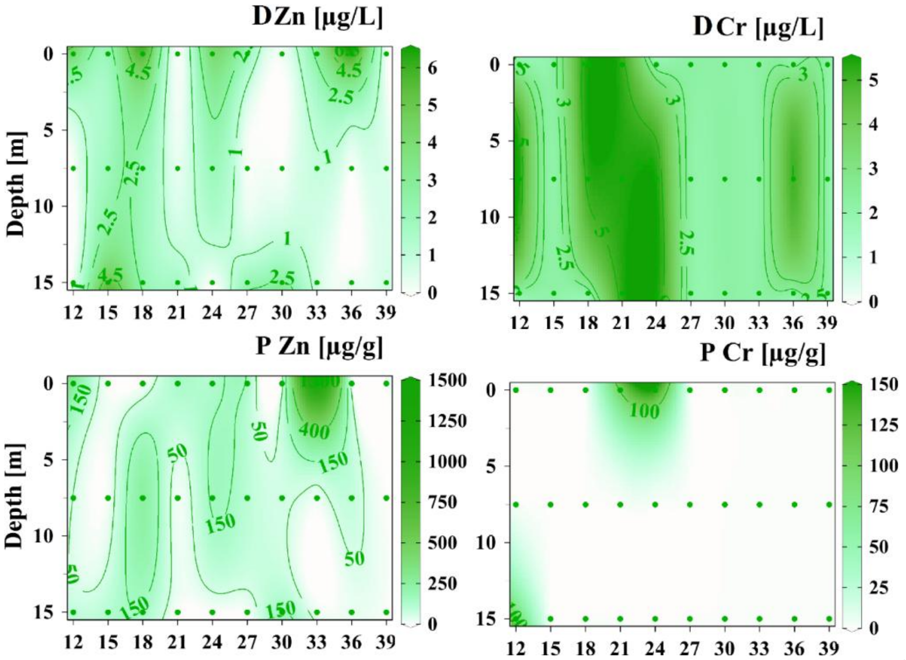

Fig 5.10: Intra-tidal variation in the dissolved (µg/L) and particulate (µg/g) Zn and Cr at the Cochin inlet on 3rd Nov 12.00hrs to 4th Nov 15.00hrs, 2015.

Dissolved Co, Cu and Pb were not present in measurable levels at the Cochin inlet, while other dissolved metals like Mg (28.8-947µg/L), Fe (9.7-125.3µg/L), Cr (2.14-5.55µg/L), Zn (0-6.15µg/L) and Ni (0-0.64µg/L) showed appreciable concentrations. The concentration of dissolved Mn and Cd were 10µg/L and 3.3µg/L respectively during one of the sampling time while it was non-detectable during all other time periods (Fig 5.10-5.13).

The particulate metals followed a sequence Fe > Mg > Zn > Mn > Cr > Ni at the Cochin inlet. The concentration of particulate metals increased with SPM (412 & 718mg/L), but Ni and Cr showed a depletion at the bottom due to their dissolution at higher salinity. Ni was mostly bound to particles when suspended particles increased at surface. Towards the bottom, at higher salinity Ni was mostly found in dissolved form owing it's desorption from particles at higher salinity. Cr attached to particles increased with SPM in surface shows that Cr is concentrated in riverine suspended particulate matter. Similar to Ni, desorption of Cr at higher salinity leads to more dissolved fraction of Cr at the mid and bottom of the water column. Particulate Mn showed dissolution at mid depth at 36hrs. High concentrations of particulate Fe, Mn, Cr, Ni and Pb in the bottom water at 12hrs were associated with high SPM during the ebb period following the re-suspension. Cu was completely absent in particulate matter at the inlet while, particulate Pb (1.8µg/g) was present in the bottom during flood at 12hrs. Particulate Co was present only at the surface during the ebb tide at 24hrs, indicating its riverine source.

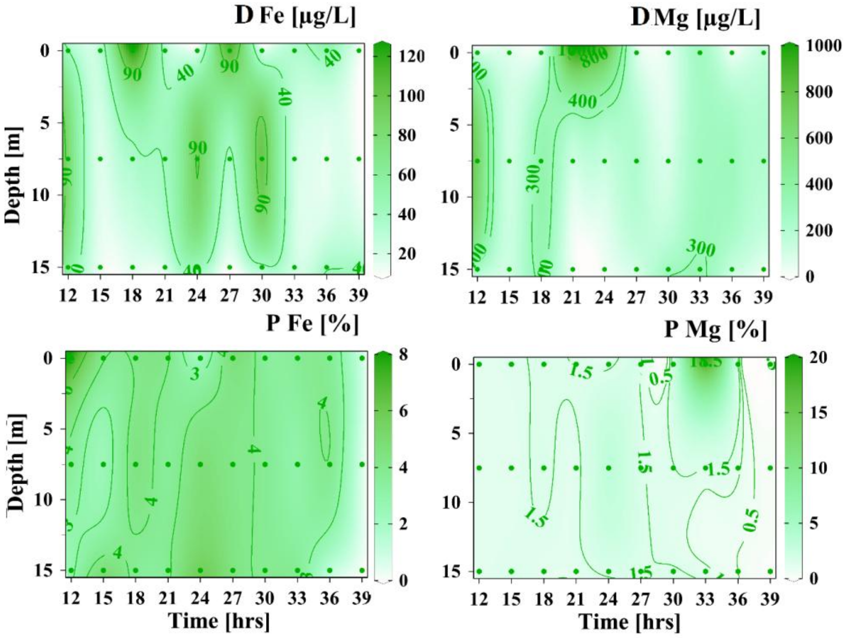

Fig 5.11: Intra-tidal variation in the dissolved (µg/L) and particulate (%) Fe and Mg at the Cochin inlet on 3rd Nov 12.00hrs to 4th Nov 15.00hrs, 2015.

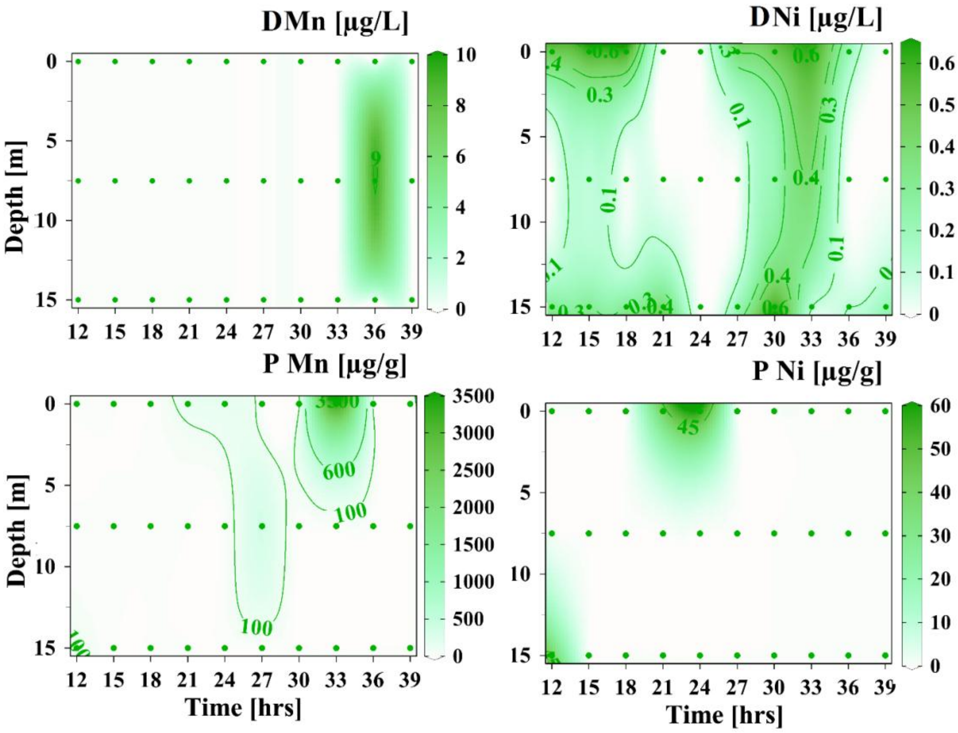

Fig 5.12: Intra-tidal variation in the dissolved (µg/L) and particulate (µg/g) Mn and Ni at the Cochin inlet on 3rd Nov 12.00hrs to 4th Nov 15.00hrs, 2015.

Fe in both dissolved and particulate phase displayed similar trend in its distribution. Dissolved Fe varied inversely with salinity suggesting its riverine origin. Particulate Cr, Ni and Co showed significant mutual correlations besides having good linear correlation with SPM (Table 5.2). Correlation of these trace metals with SPM suggests that these metals are concentrated through the rivers and re-suspension. Particulate metals (Fe, Zn and Mg) also showed strong inter relationship and have no significant correlation with other parameters represent similar sorbent for their association on to particles.

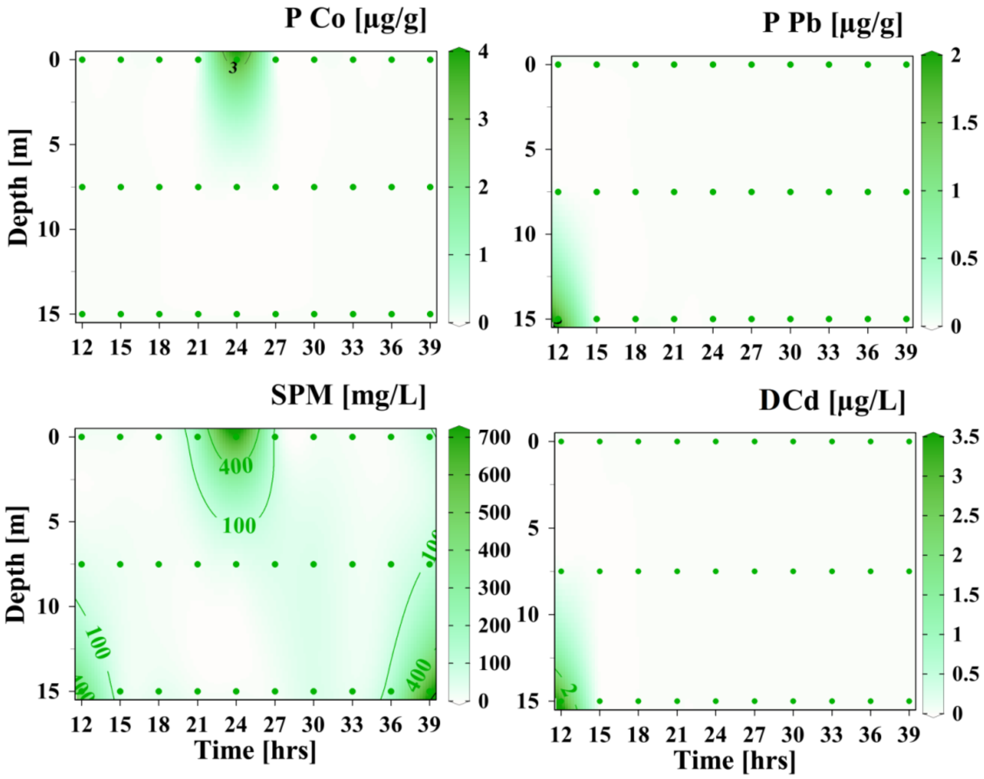

Fig 5.13: Intra-tidal variation in the particulate Co and Pb (µg/g), dissolved Cd (µg/L) and SPM (mg/L) at the Cochin inlet on 3rd Nov 12.00hrs to 4th Nov 15.00hrs, 2015.

5.3.4.4 Discussion

Higher suspended particles in the rivers (Meenachil, Manimala, Achankoil and Pamba) discharging south of the estuary may leads to higher SPM at the Kumarakom and Pallathuruthy. The high SPM at the Cochin inlet can be explained as due to the combined effect of river flux and re-suspension (Shibu et al., 1992). Mg showed an increase in the concentration towards downstream along with SPM concentrations due to higher adsorption with increase in salinity. Under oxidizing conditions, Mn exists as oxide and hydroxide which are highly insoluble in water account for the absence of Mn in dissolved phases and high particulate fraction in rivers. A reduction in particulate Mn towards the lower reaches was due to their removal into the sediment. Cr was mainly bound with suspended particles in the upstream region however the increase in dissolved Cr towards the inlet region implies it's desorption from particulates at higher salinity.

With increased salinity at the inlet, elements like Na, K and Ca ions compete with trace metals for adsorption sites displacing both weakly and moderately sorbed metals such a Cr, Cu, Ni and Pb and release them to water column. The dissolution of Cr and Ni was noticed at higher salinity. However, metals such as Fe, Mn and Zn are relatively stable even at higher salinity may be due to their strong bond to particles. Therefore, the distribution of metals between the particulate and the dissolved phase at the Cochin inlet predominantly depends on the availability of sorbents and results from the operation of surface forces.

High particulate metals associated with maximum turbidity were reported in other ecosystems (Gonzalez et al., 2007). Moreover, the association of plankton with metals can alter partitioning of metal between water and SPM (Fisher et al., 1984). The minimum concentration of dissolved metals at the inlet can also be attributed to high chlorophyll *a* (bloom) during the present observation.

The enrichment of Fe in the upstream and lower reaches, both in suspended and dissolved form and its least abundance at the inlet region suggest the flocculation of Fe bound particles towards downstream, as observed early (Sankaranarayanan and Reddy, 1973; Nair et al., 2013). The flocculation processes greatly modify the metal concentrations and their partition between dissolved and particulate phases in estuaries (Bernhard et al., 1986).

Under low fluvial discharge, the salinity increases in the estuary which increases the dissolution and desorption of metals from particulate matter (Wang et al., 2009). Increasing river discharge however, implies high suspended material input or re-suspension and low salinity as evident from the present study at the inlet. This can increase the adsorption and precipitation processes resulting in a maximum particulate metal and minimum dissolved metal concentration.

A comparison of dissolved and particulate trace metals partitioned in the study area with previous reports showed (Table 5.3, 5.4) that particulate Cu and Fe have increased over the years (Paul and Pillai, 1983; Ouseph et al., 1992; Rajamani, 1994; Nair et al., 2013). However, particulate Mn was relatively lower than reported by Paul and Pillai, 1983, though it was higher than other reports (Ouseph et al., 1992; Rajamani, 1994; Nair et al., 2013). Dissolved fractions of all the metals were comparable with the earlier studies (Ouseph et al., 1992; Rajamani, 1994; Unnikrishnan, 2000; Balachandran, 2001; Nair et al., 2013; Anas et al., 2015).

Table 5.2 Correlation matrix (Pearson (n)):

Variables	salinity	P Zn	PCu	P Ni	P Co	P Mn	P Cr	P Pb	P Fe	P Mg	D Zn	D Ni	D Fe	D Mn	D Cr	D Mg	SPM	pH
salinity	**1.00**																	
P Zn	-0.21	**1.00**																
PCu	-0.20	0.15	**1.00**															
P Ni	-0.03	0.01	-0.05	**1.00**														
P Co	-0.10	0.01	-0.03	**0.71**	**1.00**													
P Mn	-0.25	0.01	0.24	0.16	0.12	**1.00**												
P Cr	-0.25	0.19	0.21	0.13	0.10	0.11	**1.00**											
P Pb	-0.24	-0.06	**0.81**	-0.05	-0.03	0.22	**0.59**	**1.00**										
P Fe	**-0.46**	0.28	0.06	-0.16	-0.13	-0.02	0.10	0.12	**1.00**									
P Mg	**0.46**	0.06	-0.11	0.13	0.07	-0.15	-0.18	-0.17	-0.05	**1.00**								
D Zn	-0.25	**0.90**	0.11	-0.05	0.00	-0.07	0.13	-0.05	**0.38**	0.00	**1.00**							
D Ni	**0.32**	0.12	-0.07	-0.09	-0.11	-0.23	-0.09	-0.15	-0.09	**0.37**	0.09	**1.00**						
D Fe	**-0.43**	0.14	0.12	-0.12	-0.15	0.01	0.12	0.23	**0.50**	0.03	0.20	0.01	**1.00**					
D Mn	-0.02	-0.06	-0.04	-0.06	-0.03	-0.08	0.21	-0.05	0.25	-0.09	-0.06	-0.16	-0.14	**1.00**				
D Cr	**0.55**	-0.01	-0.17	0.13	0.00	-0.24	-0.17	-0.24	-0.29	**0.69**	-0.11	0.24	-0.07	0.04	**1.00**			
D Mg	0.29	-0.03	-0.12	**0.67**	**0.47**	0.03	-0.02	-0.14	-0.27	**0.35**	-0.15	-0.09	-0.23	0.01	**0.48**	**1.00**		
SPM	0.15	-0.06	-0.07	**0.69**	**0.64**	0.11	0.05	-0.08	**-0.39**	-0.09	-0.09	-0.07	-0.15	-0.07	0.04	**0.40**	**1.00**	
pH	**0.86**	-0.10	-0.18	0.11	0.03	-0.28	-0.24	-0.25	**-0.47**	**0.64**	-0.15	**0.48**	**-0.33**	-0.07	**0.71**	**0.43**	0.21	**1.00**

Values in bold are different from 0 with a significance level alpha >0.05

Table 5.3 Comparison of dissolved trace metals (µg/L) observed in rivers on 28th-30th Oct-15 with previous reports

Rivers	Fe (µg/L)	Cr (µg/L)	Cu (µg/L)	Ni (µg/L)	Pb (µg/L)	Z n (µg/L)	Cd(µg/L)	Mg (µg/L)	Reference
Periyar	1		1.0-10	1	-	1.0-81	0.1	-	Paul & Pillai., 1983
Periyar	1.1	-	10	0.2	8	40	0.2	-	Ouseph., 1992
Periyar	0.00-220	0.00-2.02	0.00-49.07	0.00-18.77	0.00-4.06	0-37	0.00-0.09		CWC, 2014
Periyar*	24-56	0.39-1.64	0.12 - 26.08	0.0-10.46	0.14-4.26	3.0-55	0.00-0.34		CWC, 2014
Meenachil*	28-540	0.35-1.30	0.68-13.63	0.00-7.78	0.08-4.17	1.0-67	0.00-0.32		CWC, 2014
Muvattupuzha	0.00-180	0.00-1.97	0.00-8.24	0.00-12.54	0.00-4.46	0.0-21	0.00-0.55		CWC, 2014
Muvattupuzha*	20-480	0.61-3.24	0.67-46.49	0.00-14.04	0.21-3.91	2.0-60	0.00-0.38		CWC, 2014
Pamba	20-490	0.14-2.06	0.28-33.47	0.00-8.58	0.03-7.15	2.0-44	0.00-0.09		CWC, 2014
Pamba	24-530	0.33-2.54	0.42-37.53	0.00-9.08	0.03-4.21	1.0-77	0.01-0.07		CWC, 2014
Pamba*	10-510	0.23-5.11	3.02-23.32	0.00-7.29	0.01-3.97	4.0-74	0.05-0.33		CWC, 2014
Periyar	31-47	2.29	0	0.086	0	17-26	0	5.8-9.6	present study
Muvattupuzha	37-44	0	0	0	0	1.0-2.0	0	8.4-25.6	present study
Meenachil	37-39	0	0	0	0	0.6-4.0	0	9.6-9.8	present study
Manimala	27-28	0	0	0	0	0.00-1.5	0	8.7-10.4	present study
Pamba	48	0	0	0	0	0	0	8.5	present study
Achankoil	49-60	0	0	0	0	1.0-1.5	0	8.8-10.1	present study
**BIS	300	50	50	20	10	500	3		BIS-10500-2012

*The geographic location similar to our study area; ** Drinking Water Standards for Trace & Toxic metals (BIS-10500-2012)

Table 5.4 Comparison of dissolved trace metals (µg/L) observed at the lower reaches of rivers and CE on 28th-30th Oct-15 with previous reports

Location	Fe	Zn	Mn	Cr	Cu	Cd	Pb	Ni	Mg	Reference
KC	0.1-306	0.26-346	nd	-	<1.0	0.5-7.0	0.5-19	-	-	Rajamani, 1995
Off Cochin	24-381	19-31	-	-	5.2-11.9	-	-	-	-	Balachandran, 2000
Inlet	799	4.36	0.63	4.7	0.68	-	-	4.56	-	Anas et al., 2015
Inlet	9.6-125	nd-6.2	nd-9.5	2.0-5.5	nd	3.3	nd	nd-0.65	29-948	Present study
Kuttanad	9.0-390	2.0-390	0.05-120	0.08-07.2	0.3-8.5	0.4-6.0	0.6-41	0.3-18.2	1.0-520	Unnikrishnan, 2000
CE(north)	<1.0	20-30	12.0-70	-	1.0-3.0	<0.1-4.0	-	<1.0	-	Paul and Pillai, 1983
CE	0.2-0.8	145-216	-	-	10.4- 18.8	2.2-3.4	8.0-14.0	0.4-0.6	-	Ouseph et al., 1992
CE	0.1-64	0.5-89	nd		0.1-6.0	0.1-0.59	6.0-24	-	-	Rajamani, 1994
CE	100-460	4.0-47	-	-	1.0-3.0	-	-	-	-	Balachandran, 2001
CE	50-400	20-140	10.0-90	-	1.0-3.0	0.15-10	20-80	5.0-10	-	Nair et al., 2013
CE(north)	7.0-68.3	6.36-105.9	nd-0.13	0.07-0.009	nd-0.44	-	-	nd-5.51	-	Anas et al., 2015
***LR & CE**	39-147	nd-67.4	nd-9.7	nd-2.3	nd	nd	nd-0.13	nd-0.5	6.0-10.2	Present study

*LR-Lower reaches of rivers discharging into Cochin estuary: CE- Cochin Estuary: KC-Kerala Coast

Table 5.5 Comparison of particulate trace metals (µg/g) observed at the lower reaches of rivers and CE on 28th-30th Oct-15 with previous reports (Concentration of Fe and Mg was represented in percentage)

Location	Fe (%)	Zn	Mn	Cr	Cu	Cd	Pb	Ni	Mg(%)	Co	Reference
KC	0.29-2.5	11.18-954	74.2-1103.8		23.6-168.1	nd-190	100-449				Rajamani, 1994
Inlet	0.06-7.8	nd-1307.9	nd-3483.4	nd-148.1	nd	nd	nd-1.79	nd-59.2	0.02-18.1	nd-3.7	Present study
kuttanad	0.25-43.3	54-4602.5	$210\text{-}2.7{*}10^5$	6.59-925	7.62-1559	0.56-191.5	8.8-2556.8	8.9-860.4			Unnikrishnan, 2000
CE (north)	2.96	1131	500		107	95		274			Paul and Pillai., 1983
CE	7.4-8.1	150-2200	-	-	65-230	50-150	60-180	10.0-80			Ouseph et al., 1992
CE	1.15-6.4	654-1748	35.78-89.47		31.9-33.8	5.0-48	250-990				Rajamani, 1994
CE	<2.0	<200	<40		12.0-40.0	5.0-25.0	<100	10.0-30.0			Nair et al., 2012
***LR & CE**	2.7-18.4	nd-1353.62	nd-289.88	nd-864.4	nd-282.7	nd	nd-126.4	nd	0.21-1.2	nd	Present study

5.3.5 Input-export fluxes of trace metals

5.3.5.1 Input Fluxes

Input of Zn:

The inputs of trace metals incident through the 6 major rivers to the Cochin estuary are depicted in Fig 5.14. The input fluxes of Zn through Periyar, Muvatttupuzha, Meenachil, Pamba, Manimala and Achankoil on 28th-30th November 2017 was 19.8kgd^{-1}, 22.4kgd^{-1}, 37.2 kgd^{-1}, 36.1kgd^{-1}, 37.7kgd^{-1} and 50.2kgd^{-1} in which the transport through Periyar, Muvattupuzha and Meenachil was entirely in dissolved form whereas the transport through Pamba, Manimala and Achankoil was mostly bound to suspended particles. The Zn concentration was high in river Manimala, though its fluxes were lower than through Achankoil. The total input of Zn through all the six rivers was 20.3.57kg^{-1}d, which account for the natural addition of Zn through geochemical processes such as weathering, dissolution and scavenging.

The effect of effluent discharges into the Periyar through the industrial zone of Eloor was well reflected in the transport of Zn into the estuary through Moolampilly (upper estuary). The Zn flux through Moolampilly region towards downstream during the study period was 182.6kgd^{-1}, which was ~10 times higher than the riverine flux. As, Moolampilly is a region prone to salinity fluctuations at the bottom in accordance with the tidal incursion and as the flux measurement at Moolampilly was a one-time cross sectional measurement using ADCP at the ebb period, the value observed during the present observation can vary a little with respect to ebb-flood variations. The transport of Zn through Moolampilly was mainly in dissolved form (87.8%).

The discharge of Zn through upper reaches of Muvattupuzha was 22.4kg/d, which was entirely in the dissolved form. When the river bifurcates into two branches, Murinjupuzha and Ithipuzha, the partitioning of Zn modified in the branches before entering the Cochin estuary. While, the flux of Zn through Ithipuzha was mostly particulate bound, the flux through Murinjupuzha (1.45kg/d) was entirely in dissolved form. Nearly 4.8kg of Zn associated with particles and 0.4kg of Zn in dissolved form was inflowing the Cochin estuary per day through Ithipuzha. The higher association of Zn to particles in Ithipuzha branch was due to the higher suspended particles. A small branch of Muvattupuzha is inflowing the estuary through the Kariyar and the Zn fluxes through this region were 0.02kg/d (mostly in dissolved form)

Input of Cr:

The present study identifies the source of Cr into the estuary. The input fluxes of Cr through Periyar, Muvatttupuzha and Pamba, on 28th-30th November 2017 was 139.5kgd^{-1}, 95.06kgd^{-1} and 13.9kgd^{-1} and was mostly bound to suspended particles (Fig 5.14). Cr was completely absent in the rivers Meenachil, Manimala and Achankoil. Accordingly, the total Cr influx into the estuary was 247.5kgd^{-1} during the study period.

The transport of Cr through Moolappilly, the upper estuary (lower reaches of Periyar) was merely 7kgd^{-1} (54.5 % particulate), because of its removal on to the coarser sediments. The high concentration of Cr in the residual and Fe-Mn oxide fractions in the sediments of Moolampilly with clayey sand texture also support this finding (Chapter 3). Even though greater transport of particulate Cr (95.06kg/d) was noticed at the upstream of Muvattupuzha, a very less amount (0.01kg/d) was found to flow through Kariyar. Rapid settling of Cr bound to coarser suspended particles might have resulted in the absence of Cr at Murinjupuzha and Ithipuzha region. High filtration capabilities of some molluscs also significantly increase the removal of these elements through sedimentation (Hawkins et al, 1996). Thus presence of filter feeders reported at lower reaches of Muvattupuzha can also contribute to the lower Cr levels in this region.

Input of Fe:

Even though concentration of Fe (7.4%) was higher in Periyar compared to Muvattupuzha (4.5%), the rate of transport of Fe through Muvattupuzha ($8.55td^{-1}$) was higher compared to the River Periyar ($7.33td^{-1}$) (Fig.5.14) due to higher freshwater flow. The transport of Fe ($11.15td^{-1}$) through river Manimala was slightly higher than Muvattupuzha in which 98.5% transported Fe was bound to particles. The river Meenachil discharged about 13.31tons of Fe per day and the river Pamba discharged about 21.22 tons of Fe per day towards the lower reaches. The greater discharge of Fe was through river Achankoil and the transport was mainly through particulate phase. About 27.44 tons of Fe was discharging into the estuary per day through river Achankoil. The variations in the transport rate can be attributed to the suspended loads and water flux. The concentrations of Fe in rivers Manimala, Muvattupuzha and Meenachil were higher, though the Fe influx was higher through Achankoil and Pamba. The lower water flux of river Manimala and lower suspended particles in Meenachil and Muvattuppuzha account for this discrepancy. It is obvious that the major source of Fe into the estuary was riverine and the major contributor was river Achankoil due to higher suspended particles and higher water flux. The contribution of rivers towards the Fe influx follows the order Achankoil > Pamba > Meenachil > Manimala > Muvattupuzha > Periyar.

As the Moolampilly region (upper estuary) accumulated more SPM, the particulate iron concentration was much lowered. Moreover, weak flow in this region also reduced the downstream transport of Fe (2.15td^{-1}). The transport of Fe through Murinjupuzha branch was 3.0td^{-1} (mostly particulate, 88.1%) while the flux through Ithipuzha was 1.12td^{-1} (mostly particulate, 89.6%). The reduced transport towards lower reaches was due to its low concentration as well as lean flow. Particulate Fe was high at Kariyar, but its fluxes were also low 0.0064td^{-1} (particulate, 93.3%) due to lowered water flow.

Input of Mg:

The input of Mg through river periyar was 757.8kgd^{-1} in which, 90.6% was as particulate (Fig 5.14). Despite its higher concentration in Periyar, the Mg flux through Muvattupuzha was slightly high (781kgd^{-1}) where 67.8% was in particulate form. Similarly, the inputs of Mg through Meenachil, Manimala, Pamba and Achankoil rivers were also mainly contributed by particulate fraction and the fluxes were 1245.5, 588.2, 1666 and 1705.1kgd^{-1} respectively.

Input of Mn:

The transport of Mn to lower reaches was completely in particulate phase (Fig 5.14). The flux of Mn through river Periyar was 110.09kgd^{-1}. The flux of Mn through river Muvattupuzha was relatively low (6.98kgd^{-1}). The River Pamba contributed 142.73 kg of Mn per day towards the lower reaches. However, Mn was entirely absent in Rivers Meenachil and Manimala. The flux of Mn through Achankoil River was relatively high (344.97 kgd^{-1}) compared to other 5 rivers. This could be due to the high turbidity (spm:44.2-66.7mg/L) in this river. It’s clear that the major source of Mn to the estuary was rivers and especially, the River Achankoil. The contribution of rivers towards the Mn influx follows the order Achankoil > Pamba > Periyar > Muvattupuzha.

A decrease in flux was observed towards the upper estuary. The rate of transport at Moolampilly was only 0.4kgd^{-1}. The rapid deposition of Mn bound to particles while traversing towards the estuary could be the reason for such a decrease. Similarity in the reduction of Fe, Mn and Cr towards the lower reaches shows that Cr mostly bound to Fe-Mn oxyhydroxides in the suspended particles (Chapter 3), gets settled towards downstream. Mn was entirely absent in Murinjupuzha, at the same time a considerable influx was observed at the Ithipuzha towards the lower estuary. Higher suspended particles and low flow in Ithipuzha may favor the adsorption of Mn to particles than Murinjupuzha. About 2.1kg of Mn was entering the lower estuary per day through Ithipuzha and about 0.0024kg of Mn was entering through the Kariyar.

Input of Ni:

Major portion of Ni entering the estuary was through river Periyar (0.396kgd^{-1}) in dissolved form (Fig 5.14). From Moolampilly region, the flux of dissolved Ni (0.5kgd^{-1}) increased towards downstream due to the presence of industrial activities. There was also a very low input of dissolved Ni through Kariyar (0.0008kgd^{-1}), probably from the nearby small scale industries. In general, the Nickel input to the Cochin estuary was in dissolved form and mainly through anthopogenic sources.

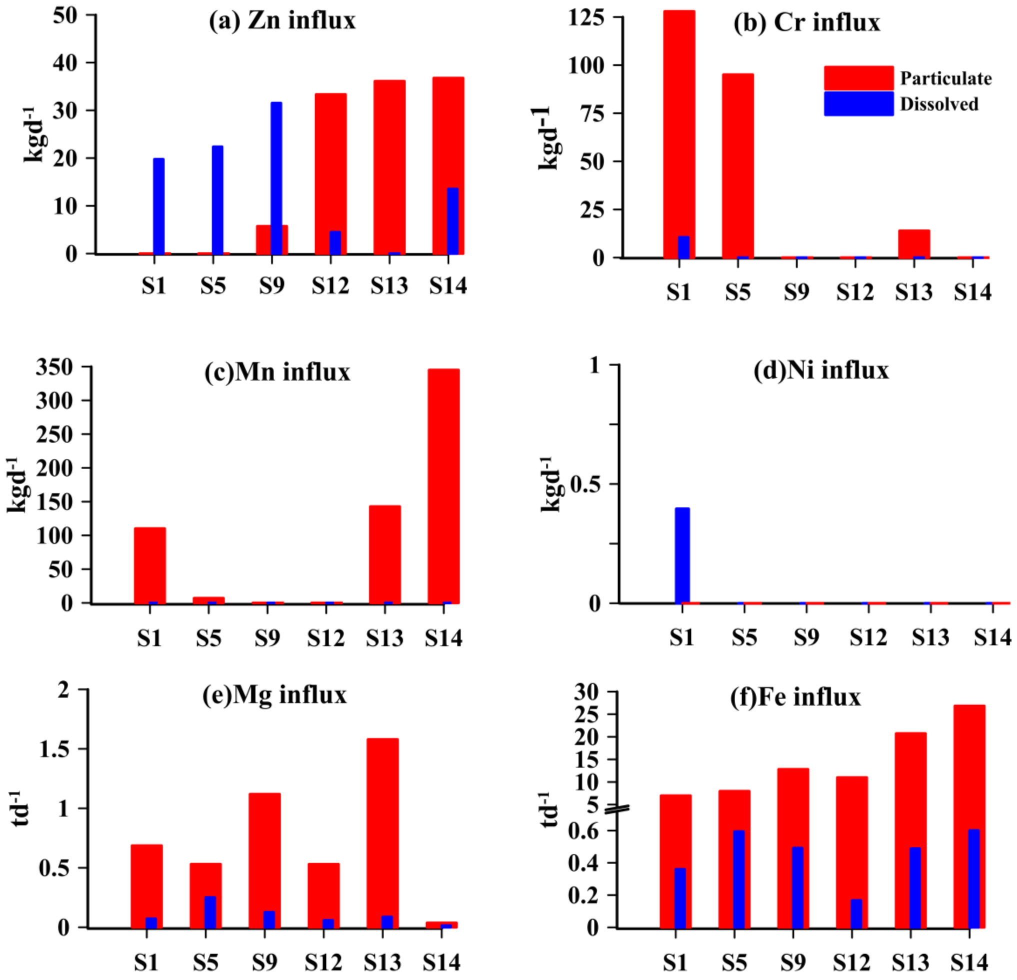

Fig 5.14: Input flux of dissolved and particulate trace metals (kgd^{-1}) through rivers into CE on 28th -30th Oct, 2015. (a) Zn; (b) Cr; (c) Mn; (d) Ni; (e) Mg; (f) Fe. [Fe & Mg fluxes are represented in td^{-1}].

Input of Pb:

Lead was not present in any of the six rivers during the present study. About 0.1kg of Pb (dissolved) was entering the estuary per day through

Ithipuzha due to anthropogenic input (pigments in paints, petroleum products, land drainage and sewage discharge).

Input of Cu:

Cu was non-detectable in the upstream of any of the rivers. However, the Cu flux of nearly 0.7 kgd^{-1} through Moolampilly towards downstream accounts for the anthropogenic input into the region.

Discussions

The combined freshwater discharge from six major rivers into the estuary on 28th-30th October 2015 was $58.559 Mm^3d^{-1}$. The major discharge was through Muvattupuzha and Achankoil and least discharge was through River Manimala (Fig 5.2). Fe, Mn, Mg and Cr inputs to the Cochin estuary were primarily from lithogenic sources whereas the inputs of other trace metals such as Zn, Cu, Ni and Pb has anthropogenic sources too, which may lead to trace metal pollution in the estuary and adjacent coastal region. The results point out that suspended particulates are the major carriers of trace metals in the estuary, which is in agreement with previous observations (Shibu et al., 1992). However, input of some of the trace metals like Zn and Ni through the rivers Periyar and Muvattupuzha was mainly in dissolved form. The poor adsorption sites for Zn and Ni or their greater stability in dissolved state might be the reason for such behavior. In the present study, it was observed that the partitioning of most of the trace metals between the dissolved and particulate phases was controlled by river flow, turbidity, salinity and the available sites on suspended particles. Recent studies have shown that fluxes of materials through riverine suspended particles are 20 times greater than the combined flux of dissolved materials and atmospheric dust (Gaillardet et al., 2003; Jickells et al., 2005; Walling, 2006).

From the results it is clear that trace metals such as Ni, Cu, Co, Mg and Pb are increasingly concentrated in suspended solids as they traverse from the upstream towards high saline zones. However, there are some other metals (Fe, Mn, Cr) that showed a reversing trend, when there was a rapid deposition (scavenging by Fe and Mn hydroxides and SPM) to estuarine sediments. Thus suspended particles play a vital role by acting simultaneously as a source and sink of trace metals. The results illustrate that the difference in the river geochemistry is principally controlled by its tributaries (Meyer et al., 1988), land use pattern (Townsend et al., 1983; Bucker et al., 2010) and soil type (Harmon et al., 2009; Leite et al., 2010), whereas their downstream transport was regulated by the suspended particles and estuarine processes

5.3.5.2 Residual fluxes at the Cochin inlet

The net riverine water flux per day (input) on 28th-30th October 2015, the export/ residual flux at inlet on 3rd and 4th November 2015 and the computed net water flux per tidal cycle through Cochin estuary on 3rd and 4th November 2015 are presented in Table 5.6.

Table 5.6 River input (28th-30th Oct-15), export at Cochin inlet (3rd-4th Nov-15) and net water flux (Mm^3) through Cochin estuary during Oct-Nov 2015.

Water Flux			
Input (Mm^3d^{-1})	**Export (Mm^3 /tidal cycle)**	**Net flux through CE (Mm^3/tidal cycle)**	**Net flux relative to input flux**
58.559	67.095	6.096	9.993%

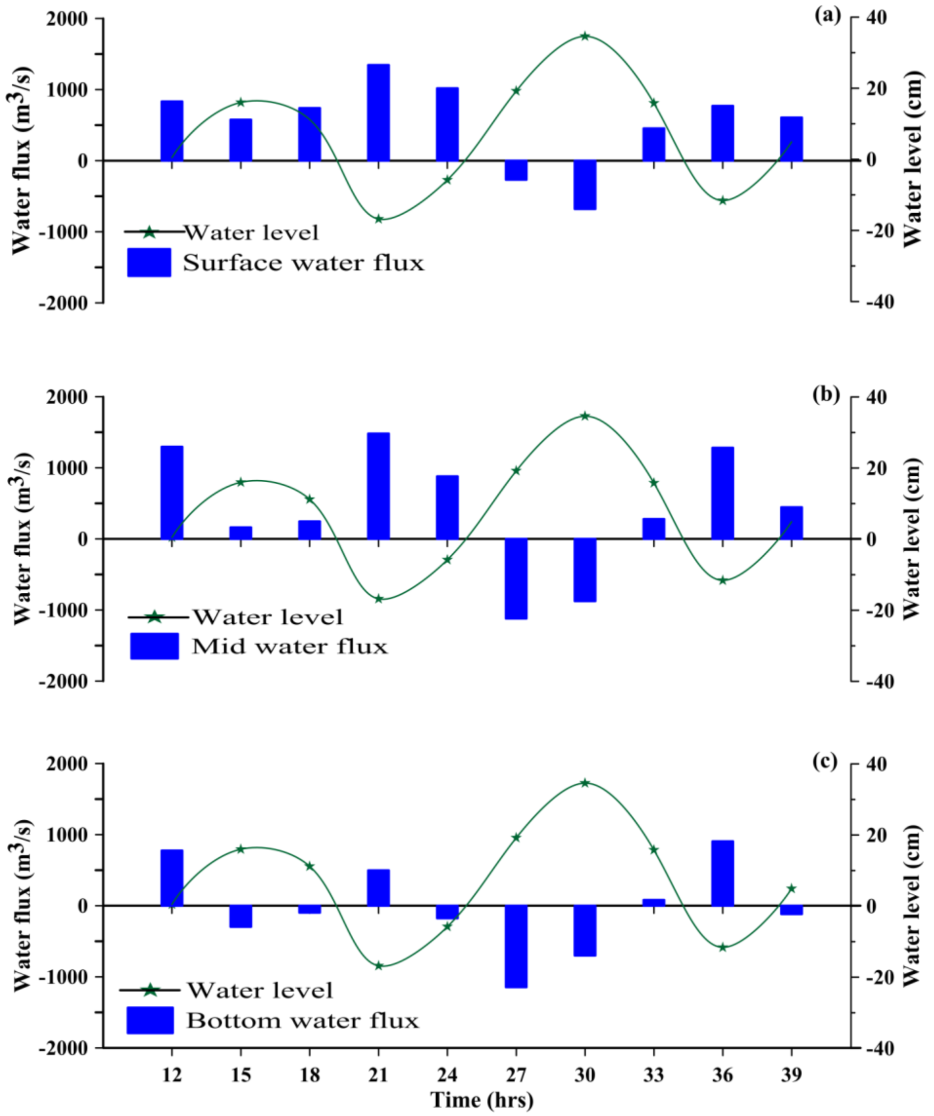

Fig 5.15: Water flux (m^3s^{-1}) for each 3 hour intervals through surface (a), mid (b) and bottom (c) water at Cochin inlet on 3rd-4th November 2015

The freshwater discharge from six major rivers into the estuary was measured on 28th-30th October 2015 (58.559Mm^3d^{-1}). As the flushing time of ~ (2.5) days was reported in Cochin estuary (Vinita et al., 2015a) for wet season, the time series measurements were conducted at Cochin inlet on 3rd and 4th November 2015 between a spring and neap tide to compute the export fluxes. The flux measurements recorded using ADCP were then partitioned into three layers using MATLAB. Variations of water flux (surface, mid and bottom) with respect to tide are depicted in Fig 5.15.

The net water flux at the Cochin inlet through surface, mid and near-bottom during 3 - 4th November 2015 was 45.76, 29.44 and -8.18Mm^3/tidal cycle respectively, showing the vertical changes in the bidirectional flow (Fig 5.16). Surface and mid depth water flux was directed seaward (+ve) and the bottom flux was directed landward (-ve). The residual flow during this period (sum of surface, mid and bottom flux) was 67.095Mm^3/tidal cycle indicating a net export (Table 5.6).

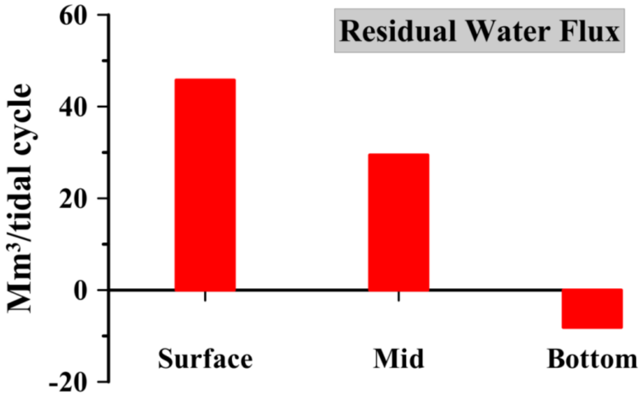

Fig 5.16**:** Residual water flux (Mm^{3}tidal cycle^{-1}) through surface, mid and bottom water at Cochin inlet on 3rd-4th November 2015

During the observation, the advection of seawater through the bottom and its influence on the surface salinity was noticed only during the highest high water (HHW) at 27hr. For all other time period irrespective of ebb/flood tide, the surface and mid depth water flow was directed seaward, resulting in a net seaward flow. Intertidal and seasonal changes will also influence the water exchange at the inlet, as the major controlling factors are the tides and freshwater discharge. It is to be noted that being a monsoonal estuary, the inlet exhibited a net export during most of the time. The Cochin estuary has a very good flushing (42 times/yr.) capability (Revichandran et al., 2011). The fluxes of trace metals (Zn, Cr, Fe, Mg, Ni, Mn, Pb, Cu, Co and Cd) through the Cochin inlet on 3rd-4th November 2015 are depicted in Fig 5.17-5.23. It can be seen that during this period, the major part of the trace metal fluxes across Cochin inlet was through particulate form and directed seaward.

The flux of dissolved and particulate Zn through surface, mid and bottom water at the Cochin inlet were (0.166 & 1.31)t, (0.036 & 0.007)t and (-0.052 & 0.085)t/tidal cycle respectively, indicating a net export of (0.150 &1.397)t/tidal cycle. There was import of dissolved Zn (-0.052t/tidal cycle) through the bottom, which could be due to the high dissolved Zn concentration during flooding (15-18 hr and 27-30hr). The dissolution of Zn ion is found to increase at high salinity (Chester, 2009). The flux of dissolved and particulate Cr through surface, mid and bottom water at the Cochin inlet were (0.172 & 1.46)t, (0.172& 0.0)t and (0.172 & 0.176)t/tidal cycle respectively, also indicating a net export of (0.515 & 1.636)t/tidal cycle. The adsorption of Cr increased with increasing turbidity, i.e with an increase in the concentration of suspended matter leads to increased particulate export.

The fluxes of Fe (dissolved and particulate) through surface, mid and bottom through the Cochin inlet were (2.05 & 297.77)t, (1.093 & 2.659)t and (0.127 & 31.694)t/tidal cycle respectively. A net export of (3.271 & 332.12) t/tidal cycle at the inlet is thus, attributed to the increased concentration of Fe and increased fresh water flow. Similarly, Ni fluxes (dissolved and particulate) at Cochin inlet through surface, mid and bottom were (0.01&0.582)t, (-0.001 & 0.004)t and (-0.004 & 0.0)t/tidal cycle respectively. The Ni flux was also mainly associated with particulate material. Dissolved Ni was high in the bottom, probably due to it’s desorption from particles at higher salinity. Higher Ni at bottom during flood period leads to higher dissolved flux directed landward. The net export of Ni at the inlet was (0.005 & 0.586) t/tidal cycle. Pb was observed only in particulate phase at the bottom during ebb (12hr) and indicated a net export (0.003t/ tidal cycle). Particulate Co also showed a net export of (0.029t/tidal cycle). Dissolved Cd showed a net export (0.0025t/tidal cycle), probably through remobilization from sediments during ebb tide (12 hr).

The Mn fluxes (dissolved and particulate) through surface, mid and bottom water at the Cochin inlet were (0.0 & 1.796)t, (0.102 & -0.233)t and (0.0& 0.184)t/tidal cycle respectively. Dissolved Mn was not present during the observation, except at 33hr (ebb tide) in the mid depth (9.5µg/L), which caused an export flux of 0.102t/tidal cycle. In aquatic systems, manganese solubility increases at low pH as well as under low oxidation-reduction potential (Heal, 2001). As the pH was high (7.83) at inlet at 33hr and the entire water column was well oxygenated (5.01-6.34mg/L), the presence of Mn at mid depth (9.5µg/L) could be due to some other reason. Manganese is an essential element in phytoplankton and therefore, can be a source during its decomposition (Nadaska et al., 2012). High saline waters containing high concentrations of nitrate, chlorides and sulphate can also increase the solubility of Mn and its uptake by plankton (Reimer, 1999).

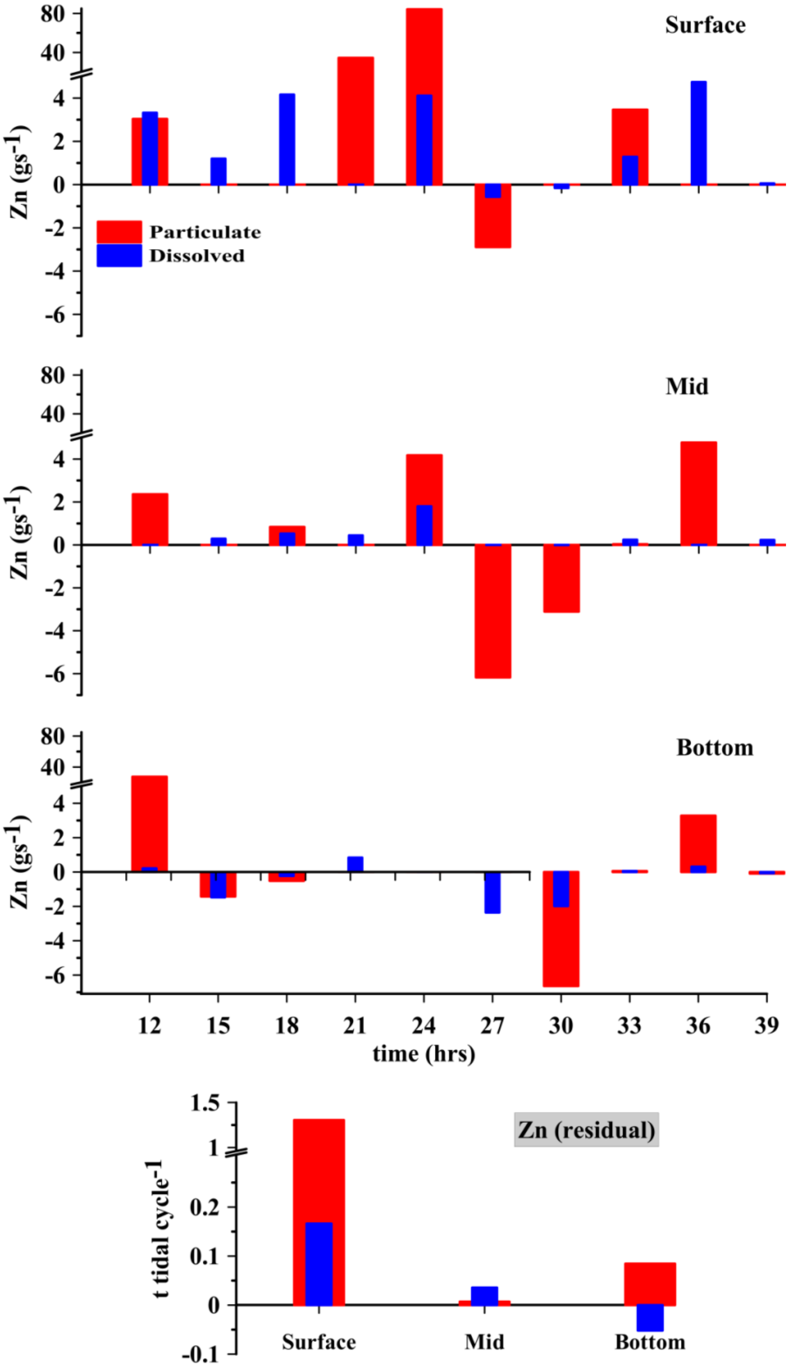

Fig 5.17**:** Zn flux (gs^{-1}) for each 3 hour intervals and the residual flux (t/tidal cycle) through surface, mid and bottom water at Cochin inlet on 3rd-4th November 2015.

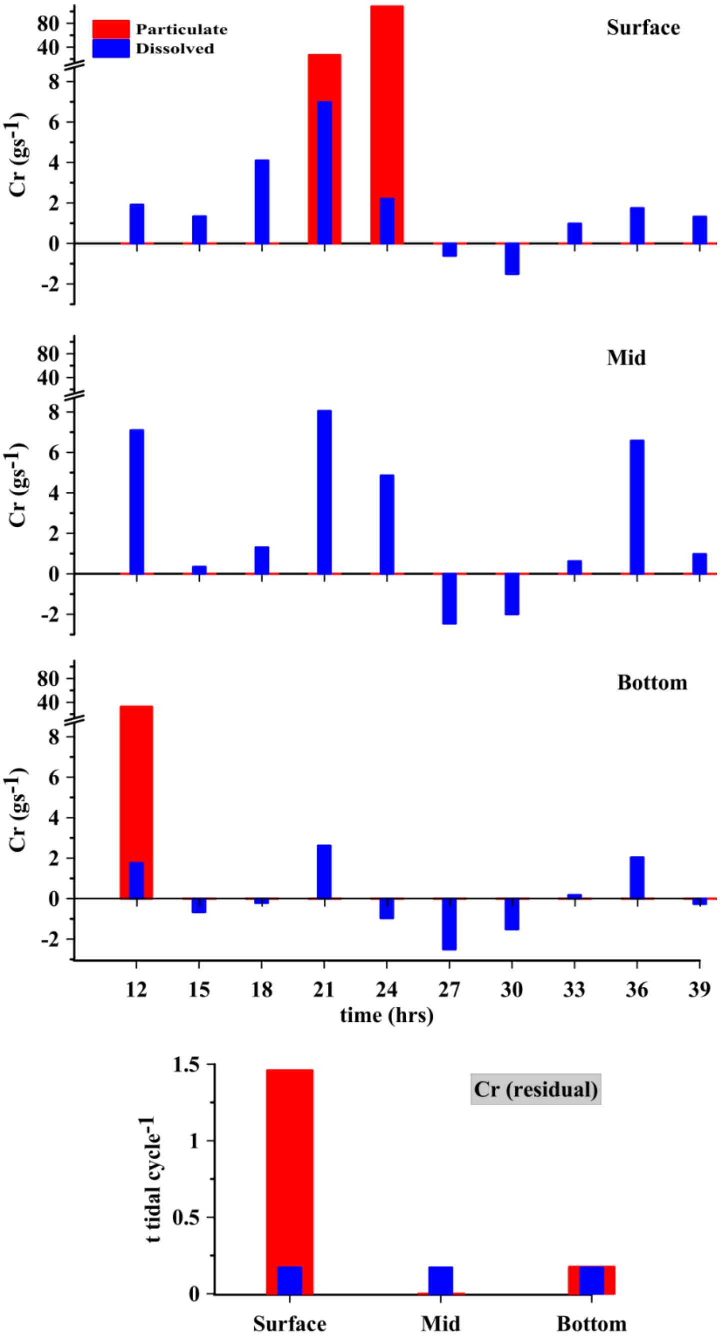

Fig 5.18**:** Cr flux (gs^{-1}) for each 3 hour intervals and the residual flux (t/tidal cycle) through surface, mid and bottom water at Cochin inlet on 3rd-4th November 2015

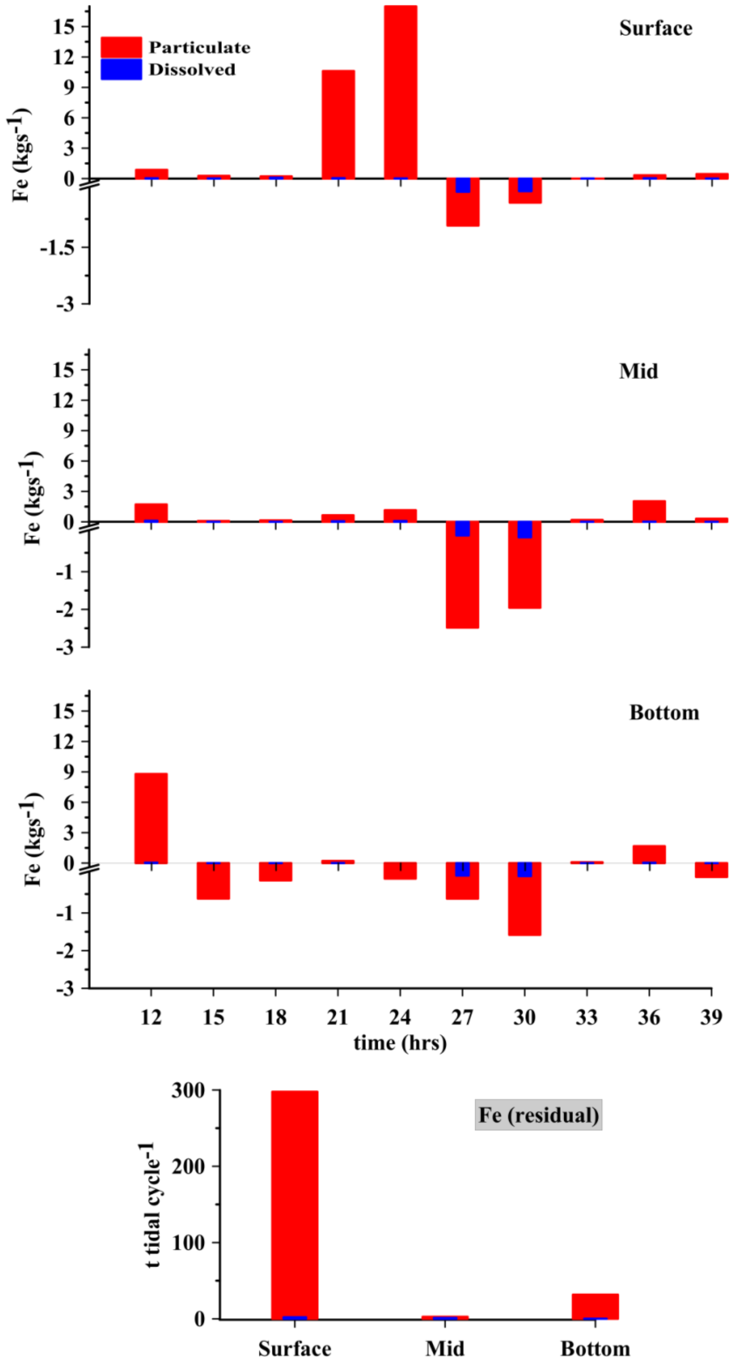

Fig 5.19: Fe flux (kgs^{-1}) for each 3 hour intervals and the residual flux (t/tidal cycle) through surface, mid and bottom water at Cochin inlet on 3rd-4th November 2015

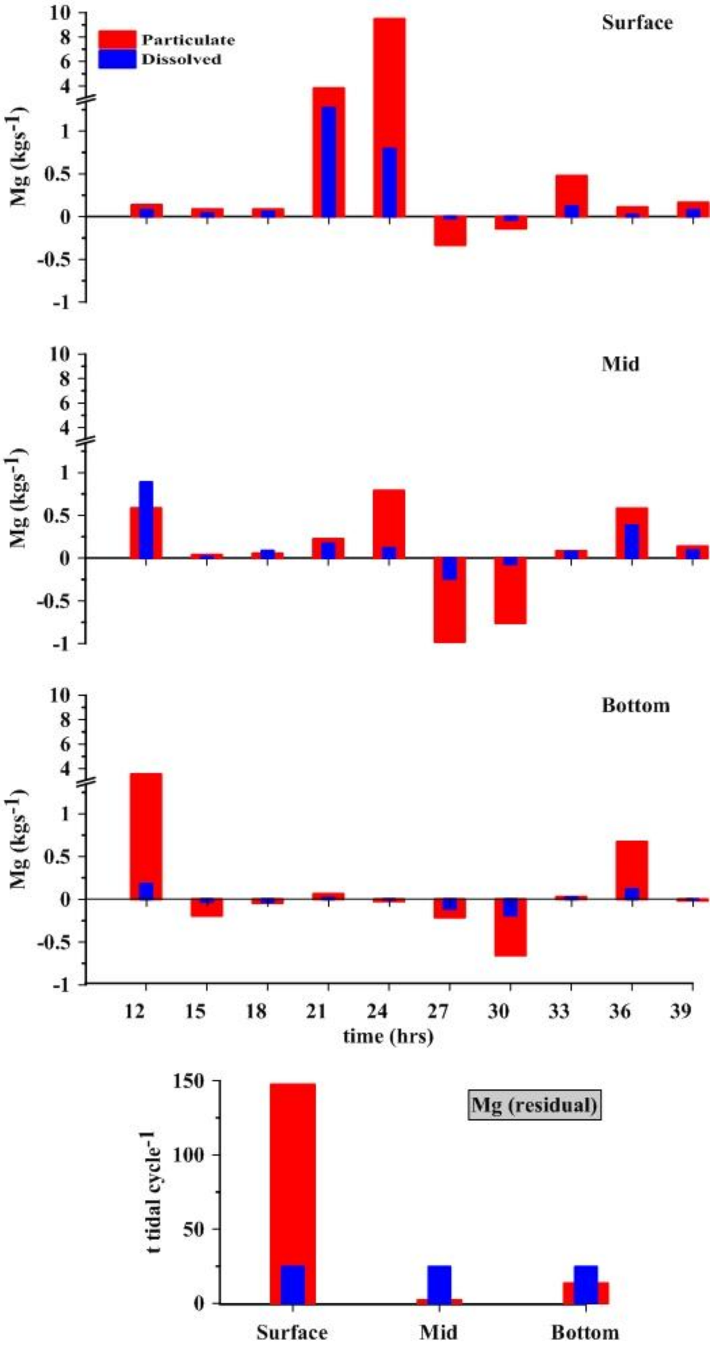

Fig 5.20: Mg flux (kgs^{-1}) for each 3 hour intervals and the residual flux (t/tidal cycle) through surface, mid and bottom water at Cochin inlet on 3rd-4th November 2015.

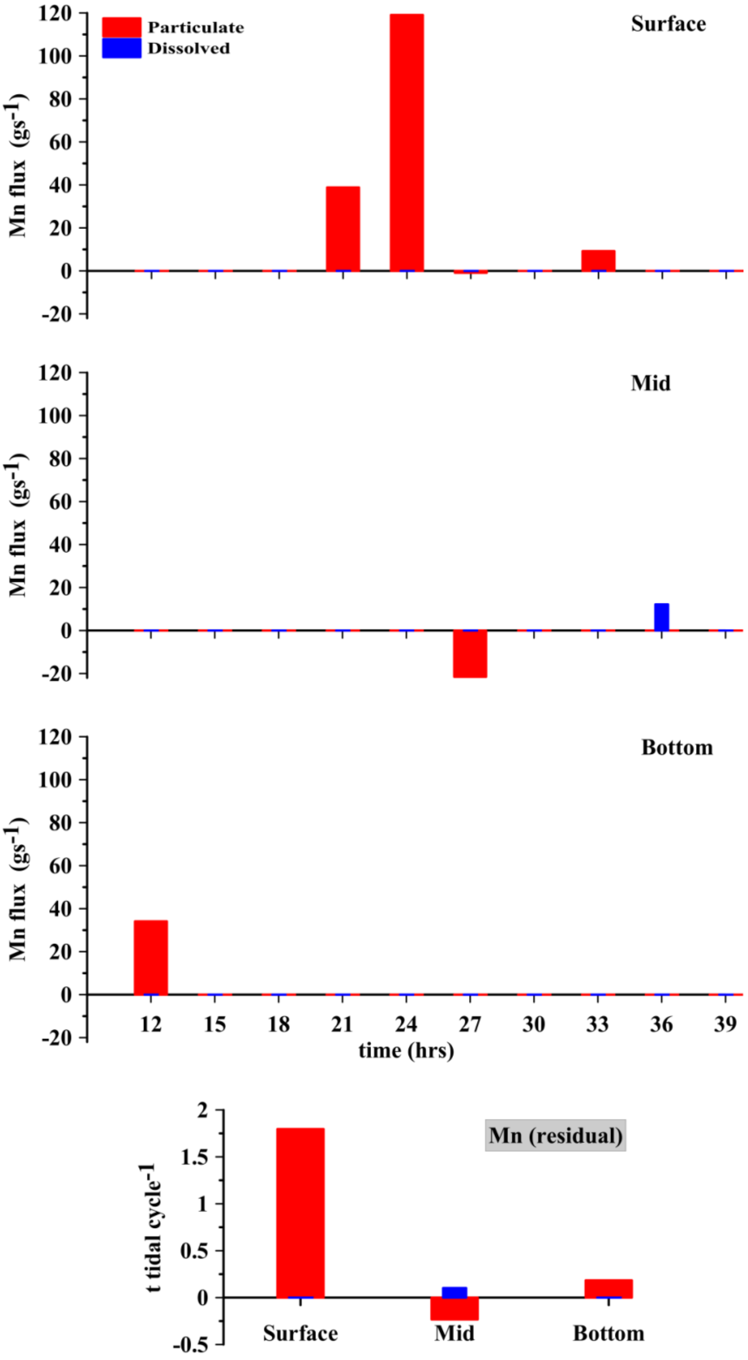

Fig 5.21**:** Mn flux (gs^{-1}) for each 3 hour intervals and the residual flux (t/tidal cycle) through surface, mid and bottom water at Cochin inlet on 3rd-4th November 2015.

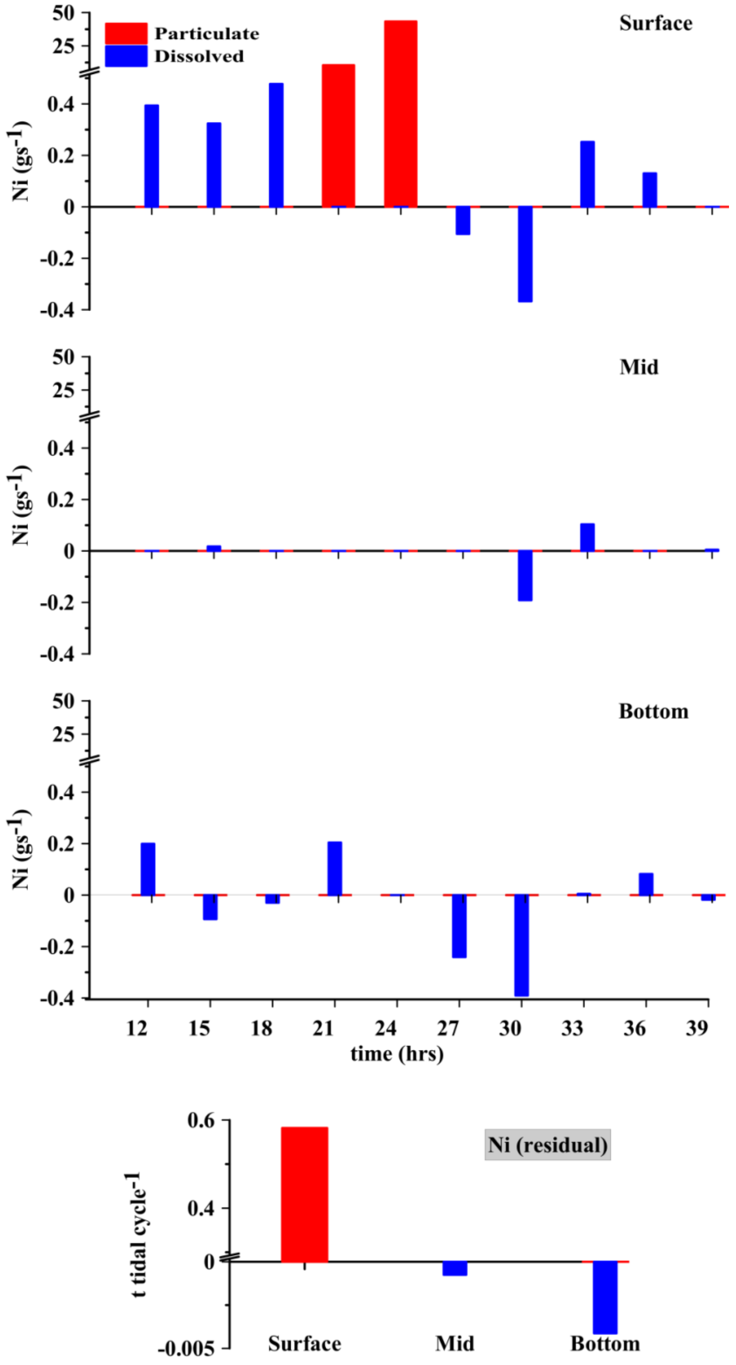

Fig 5.22: Ni flux (gs^{-1}) for each 3 hour intervals and the residual flux (t/tidal cycle) through surface, mid and bottom water at Cochin inlet on 3rd-4th November 2015.

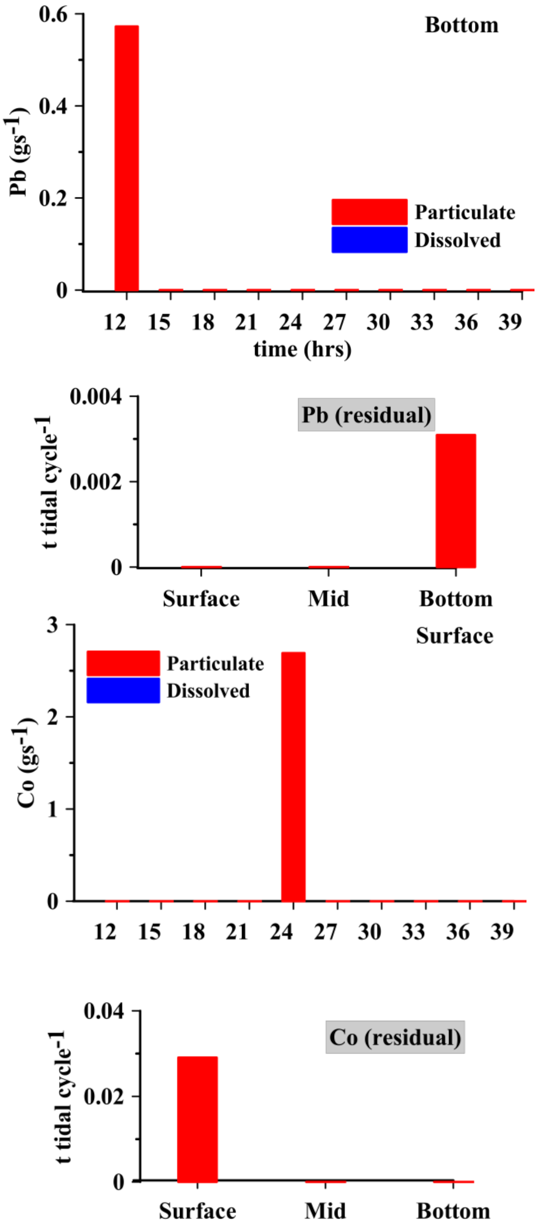

Fig 5.23**:** Pb and Co flux (gs^{-1}) for each 3 hour intervals and the residual flux (t/tidal cycle) through surface, mid and bottom water at Cochin inlet on 3rd-4th November 2015.

There was a reversal in the water flux at surface and mid depth, during flood at 27hr (-ve water flux) associated with increased turbidity (SPM). Elevated concentration of particulate Mn in the flood waters has probably resulted in an import flux at mid depth. However, the residual flux of particulate Mn showed an export of 0.102 & 1.747t/tidal cycle.

5.3.5.3 Net fluxes of trace metals

The net fluxes of trace metals through Cochin estuary is the difference in net riverine input and export at Cochin inlet.

Net flux = (net input fluxes through 6 major rivers) – (the export/residual fluxes through Cochin inlet).

The Cochin estuary showed a net export of 6.096Mm^3 water (per tidal cycle) during the observation period, which tuned to ~ 9.99% of fresh water input (Table 5.6). This difference in volume exchange (input-export) was well reflected in the trace metal transport across the Cochin inlet. The input and export fluxes of trace metals during the observational period are provided in Table 5.7. The net fluxes were computed based on the difference between the sum of inputs from 6 rivers and the transport through Cochin inlet. The result showed an average export of 246.39t Fe, 232.7t Mg, 1.90t Cr, 1.34t Zn, 1.25t Mn, 0.59t Ni, 0.029t Pb and 0.003t Pb respectively from the estuary during a tidal cycle on 3rd and 4th Nov-15 (Table 5.7), of which, ~ 68-99% was transported as particulate fraction. The dissolved metal fluxes were in the order Mg > Fe > Cr > Mn > Zn and particulate metal fluxes followed an order Fe > Mg > Cr > Zn > Mn > Ni > Co > Pb. The net transport of dissolved and particulate Cr was 45.9 and 5.67 times higher than their river input. Same was the case for Mg, in which, the net fluxes were 116.6 and 34.1 times higher than their riverine input. The net flux of Ni was 10.22 times in excess than its riverine input. Since the particulate Ni was absent in rivers whatever exported was excess contribution. The export fluxes of Fe (dissolved/particulate) were less (0.2 and 2.73 times of river discharge) compared to other metals. Considering the role of iron in oceanic productivity, this element plays an important role in the carbon cycle (Moffett et al., 2015). The net flux of particulate Zn was 11.02 times higher than its riverine input while the net flux of dissolved Zn was only 61.4% of the river discharge. The excess transported metals are the consequence of their anthropogenic sources into the estuary.

Table 5.7 Input (28th-30th Oct-15), export /residual at inlet (3rd-4th Nov-15) and net heavy metal flux (tons) through Cochin estuary during Oct-Nov 2015

Heavy metals	Net Input (td^{-1})	Export/ residual flux at the Cochin inlet (t/tidal cycle)	Net Flux through CE (t/tidal cycle)	Net flux D+ P (t/tidal cycle)
D Zn	0.09	0.15	-0.06	-1.34
P Zn	0.11	1.40	-1.29	
D Cr	0.01	0.51	-0.50	-1.90
P Cr	0.24	1.64	-1.40	
D Fe	2.70	3.27	-0.57	-246.39
P Fe	86.30	332.12	-245.82	
D Mn	0.00	0.10	-0.10	-1.25
P Mn	0.60	1.75	-1.14	
D NI	0.0004	0.00	0.00	-0.59
P Ni	0.00	0.59	-0.59	
D Mg	0.61	74.32	-73.71	-232.70
P Mg	4.48	163.47	-158.99	
P Pb	0.00	0.00	0.003	-0.003
P Co	0.00	0.03	-0.03	-0.03

‘D’ & ‘P’ represent dissolved and particulate fractions of metals: -ve sign represents seaward flux.

Suspended particles are the major carriers of trace metals and some of the binding sites on them (Fe and Mn oxides) are good scavengers capable of binding other elements to accumulate in sediments. Thus, Cochin estuary is a prominent depository of trace metals and one of the most impacted estuaries in the world (Balachandran et al., 2005). However, since SPM are finer particles, it may increase the export fluxes of trace metals especially during heavy run off periods (Shynu, et al., 2012). The present study supports this finding, as there was a net export of most of the heavy metals through the Cochin inlet.

Now, what could be the fate of these input/export fluxes is a question of great concern. The ultimate sink of these trace metals could be their deposition in coastal sediments (Pichaimani et al., 2008). The changes in redox conditions, pH, dissolved oxygen depletion etc. could be very crucial in the depositional environment where they are removed from the dissolved and particulate form to the sediments and vice versa (Machado et al., 2016). Thus, sediments can acts as both sink and source of metals under changing redox conditions. In the estuary, the deposition will be high, but there is a chance of their release back to the water as bioavailable and toxic form. The accumulation of trace metals in sediments is a long-term source of contamination to higher trophic level, as they are exposed to detrital and deposit-feeding organisms (Mendil and Uluozlu, 2007). The increased trace metal levels in suspended particles have adverse effect on the filter feeders.

In the coastal environment, oxygen deficient conditions may develop occasionally, when the bioavailable fractions of trace metals increase. This will definitely affect the health of marine organisms as well. There are several reports to show the impact of the deterioration in the Cochin Estuary and its adjoining coast (Jayakumar et al., 2001). Recent reports showed exceptionally high carbon uptake rates in the near shore and inner shelf waters of Cochin which is attributed to the export fluxes from the estuary (Bhavya et al., 2017). These also evidence the anthropogenic inputs in the region modulating the coastal biogeochemistry. However, sediment trace metals are found to undergo diagenesis and rapid chemical alterations (Nath et al, 2000). Increased supplies of trace metals are deposited in coastal sediments during monsoon, while they are effectively masked by incorporation onto clay or organic matter during the remaining period (Balchandran et al., 2003). Thus, these trace metals do not seem to constitute a threat to the coastal areas other than in estuaries. However, recent studies have shown that the coastal sediments of Cochin have increased trace metal levels and seem to be under stress (Sudhananth et al., 2011; Sreekanth et al., 2015).

The co-precipitation and adsorption of metals by Fe-Mn oxides is a major pathway of metal deposition (Fairbrother et al., 2007; Lu et al., 2014). Under reducing conditions, the hydroxides of Mn and Fe are destabilized and start releasing all other adsorbed and co-precipitated metals like Co, Ni, Cr, Cd, Cu, Pb and Zn (Zwolsman et al., 1993). This is accelerated by sulphate-metal interactions that increase their concentrations in pore or surface water (Du Laing et al., 2009). At even stronger reducing conditions, sulphate is reduced to sulphides, which form complexes with other metals and reduces their mobility and toxicity (Lu et al., 2014). In high saline conditions, the ionic interactions with carbonates, oxides, oxide-hydroxides, silicates and chloride can increase the metal adsorption on to sediments and vice versa (Fairbrother et al., 2007), whereas tidal activity can increase the sediment re-suspension

(Hawkins et al., 1996) to desorb metals from particles and pore waters (Lindberg et al., 1975).

The presence of deposit-feeders (polychaetes) also influences the deposition and remobilization of metals (Machado et al., 2016). Certain bacteria are found to solubilize heavy metals in sediment (Pillidge, 1985) and concentrate as extracellular polysaccharides (Aislabie and Loutit, 1986) facilitating its transfer to food chain (Bremer and Loutit, 1986). Therefore, a detailed study regarding the mobilization of metals is necessary to evaluate their ecotoxicological risk.

5.4 SUMMARY AND CONCLUSION

The present study shows that all the 6 major rivers contribute very low concentrations of trace metals, which are within the limits of Bureau of Indian Standards (BIS). Therefore, at present, there is no toxicity of trace metals (Fe, Zn, Mn, Cr, Ni, Co, Cu and Cd) from these rivers. Weathering and re-suspension are the major source of trace metals and Fe & Mg in the rivers. The present study showed that there were wide variations in the geochemical properties of all these rivers due the difference in the nature of alluvium in the catchment area.

The concentration of dissolved metals in the lower reaches of rivers (upper estuary) were below the permissible value of drinking water recommended by BIS-10500 (2012) and WHO, whereas particulate matter showed enriched heavy metals levels. Particulate Zn at Moolampilly and Ithipuzha were greater than the values reported in PAAS (85µg/g) and WRSPM (208µg/g). The concentration of Fe (dissolved and particulate) in

Kariyar and Cu in Purappillikkavu (particulate) were also high during the study period. Particulate Cr concentrations at Moolampilly, Purappillikkavu, Kariyar and Kumarakom were also higher than that in WRSPM (130µg/g) and PAAS (110µg/g). Particulate Pb at Purappillikkavu and Kumarakom was higher than that in PAAS (20µg/g) and WRSPM (61.1µg/g), while particulate Mn was lower than that of WRSPM (0.16%) and PAAS (0.08%).

The concentrations of trace metals like Zn, Cu, Cr and Pb in suspended matter showed an increase from the rivers to the estuary indicating their addition towards downstream. For other metals (Cr, Fe, Mn), a decreasing trend was noticed for Periyar and Muvattupuzha rivers, probably due to their deposition in the upper estuary. Thus, suspended particles play a vital role as a source and sink for trace metals. Bio-accumulation could also be a reason for the absence of Cr in both dissolved and particulate phases at Ithipuzha and Murinjupuzha. The present study showed that Murinjupuzha and Pallathuruthy were the least polluted among the regions studied, where heavy metals were generally absent.

The time series measurement at Cochin inlet on 3rd-4th November 2015 showed that the concentrations of dissolved Co, Cu and Pb were below measurable levels at the Cochin inlet, while dissolved Mg, Fe, Cr, Zn and Ni showed appreciable concentrations. Dissolved Mn and Cd were measured up to 10 and 3.3µg/L respectively, though it was non-detectable for most of the time. The metals Fe, Mg, Zn and Mn were mostly present in particle form, whereas dissolved Ni and Cr showed enrichment at higher salinity (bottom). The increase of heavy metals (Cr, Ni and Co) in turbid waters suggests that these metals are concentrated by suspended particulate matter. Some of the particulate heavy metals (Fe, Zn and Mg) showed strong inter relationship, while others did not show any correlation indicating the variable interaction among metals and with particles.

Increased river discharge naturally increases the suspended load, while tidal activity increases the re-suspension, both of which were evident during the present study. The enrichment of Fe in the upstream and its depletion towards the inlet could be due to the flocculation of Fe bound particles at high salinity. The non-conservative behavior of Fe could be due to its mobilization.

The observation that suspended particulates are the major carriers of trace metals to the Cochin estuary is in accordance with earlier studies. However, some metals like Zn and Ni behaved differently, as they were transported through Periyar and Muvattupuzha rivers. The poor adsorption sites of Zn and Ni or their better stability in dissolved state might be the reason for this. The present study also showed that partitioning of trace metals between the dissolved and particulate phases is controlled by river flow, nature of suspended particles, pH and salinity. The particulate concentrations of Cu and Fe during the present study were higher than the previous reports. However, particulate Mn was relatively lower than reported by Paul and Pillai, 1983, though it was higher than other reports. Dissolved fractions of all the metals were comparable with the earlier studies.

The average freshwater flow through the six rivers during 28-30th October 2015 was 58.559Mm^3d^{-1}, resulting in the net river input of 203.57, 604, 247.5, 0.4$kgd^{-1}$of Zn, Mn, Cr, Ni and, 89.0, 5.09$td^{-1}$of Fe and Mg respectively. The major contributor of Zn, Fe, Mn and Mg to the estuary was the River Achankoil following a high turbid condition. The major contibutor of Cr and Ni to the estuary was River Periyar. The results shows that the difference in the river geochemistry is principally controlled by its tributaries, land use pattern and soil type, whereas their downstream transport was regulated by the suspended particles and estuarine processes.

The exchange of water through the Cochin inlet (surface, mid and bottom) during 3- 4th November 2015 was 45.76, 29.44and -8.18Mm^3/tidal cycle respectively. The residual flux of 67.095Mm3/tidal cycle at the inlet was indicative of a net export from the estuary. The net water flux through the estuary (Input-Export) was 6.095Mm^3/tidal cycle directed seaward. It is estimated that about 9.99% of freshwater (6.095Mm^3) is getting exported in excess through Cochin inlet in a tidal cycle on 3- 4th Nov -15. This was also reflected in the trace metal transport across the inlet (246.39t Fe, 232.7t Mg, 1.90tCr, 1.34t Zn, 1.25tMn, 0.59t Ni, 0.029 t Co and 0.0031t Pb) per tidal cycle. Approximately 68 to 99% of this flux was associated with particles. The export fluxes can be attributed to the anthropogenic activities and internal processes within in the estuary

From the present study, it can be concluded that suspended particulate matter plays a major role in the geochemical cycling of elements in the Cochin estuary. The processes that affect the SPM dynamics leave significant impressions on the heavy metal distribution in the estuary. Moreover, the interactions of phytoplankton and filter feeders with particulate and dissolved materials also control the distribution of trace metals in the Cochin estuary. Scavenging by suspended particles has resulted in the removal of these trace metals on to estuarine sediments. Otherwise, the export fluxes would have been much larger than that observed today. The fate of these export fluxes is a matter of great concern as they are ultimately deposited along the coastal environment. The sediment texture, hydrological regime, salinity and organic matter were responsible for the mobility and release of these metals. Even though the fractionation study (chapter 3) indicates the fate of metals in the coastal sediments, which can be used for natural water management system; there are still uncertainties in the regulating mechanisms for metal mobility in coastal sediments. Therefore future studies should include the physical, chemical and biological mediated metal remobilization and microbial mediated mineralization in the estuarine and coastal marine environment.

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Chapter 6

SUMMARY AND CONCLUSION

Estuarine and coastal marine areas are highly complex and dynamic environments. Different kinds of physical, chemical, geological and biological interactions in the estuary during the mixing of freshwater and seawater can significantly regulate the transport and fate of materials (nutrients, trace metals and rare earth elements) from the estuary. Nutrients are the raw materials for the food chain, as they are essential to the primary production, while heavy elements are important due to their toxic effects, as well as their importance as micronutrients for many organisms. Rare earth elements are important tracers to understand the evolution of the earth's continental crust. They could also provide information regarding the depositional conditions of an environment. Sediments can represent sources and sinks of these materials in estuaries and the factors determining these pathways will largely be determined by quantifying the input, export and depositional processes in sediments.

The present study was mainly focused on the Cochin estuarine system, the largest tropical estuarine system along the south west of India which has significant influence on the biogeochemistry of the adjacent Arabian Sea. Although there are several studies delineating the environmental changes in the Cochin estuary caused by anthropogenic activities, there are only a few studies to quantify the material transport across the estuary and its fate on the adjacent coastal marine area. The major objective of the study was to understand the inter-tidal, intra-tidal, spatial and seasonal variations in the nutrient transports in the estuary and compute their respective fluxes to the adjacent coastal areas. To the best of our knowledge, this is the first attempt to quantify the fluxes of nutrients across the Cochin estuary. The magnitude of removal and addition for nutrients in the estuary are seasonally variable. Therefore, a series of time series measurements were carried out at different locations in the Cochin estuary for 3 different seasons to compute the input, export and net fluxes of nutrients.

Environmental impact of trace metal pollution in sediments depends not only on the total concentration of the metals, but the dominant state in which, each metal is associated in the sediment crystal or lattice. Therefore, fractionation studies were carried out to identify their mobility and availability in the sediments, which influences their deposition and availability to planktons and other organisms. Rare earth elements distribution and their chemical fractionation were also studied to access the geochemical variability and depositional condition affecting their fate and transport in the estuarine and coastal environment. The temporal and spatial variations of heavy metals in the rivers and estuary help to compute their fate, transport and transformations during estuarine mixing. These studies could provide a background of the processes that control the heavy metal cycling in the water, suspended particles and sediments of Cochin estuary and thereby its fluxes from rivers through estuary to the coastal region.

It is observed that rivers are the major source of the nutrients, nitrate and silicate in the estuary, while phosphate and ammonia are also added through non-point sources and re-suspension during estuarine mixing. Another observation is that the Cochin estuary maintains an oxidized water environment during all the three seasons. However, under-saturation in the dissolved oxygen levels recorded at the Cochin inlet during summer monsoon and post monsoon period was associated with coastal upwelling and incursion of hypoxic waters. These hypoxic waters were found to reach well inside the estuary, a finding reported for the first time. Moreover, there were significant inter-tidal, intra-tidal and seasonal variations in all the nutrients and dissolved oxygen during the study period. These variations are typical of an estuary when nutrient-rich fresh water mixes with nutrient deplete seawater on a varying degree depending upon the high/low (food/ebb flow), spring/neap (high amplitude/low amplitude) and seasons (variable fresh water flow).

The present study showed that despite a moderate utilization and sinking of nutrients, dissolved nutrients are exported from the Cochin estuary, especially during peak summer monsoon. Cochin estuary is a source of all nutrients during monsoon and a sink for SiO_4 during post-monsoon (spring and neap phase) and pre-monsoon (spring phase) period. The removal (15-20%) of SiO_4 during post-monsoon was coincided by a net addition of N and PO_4. During pre-monsoon spring 88.9% of NO_3 and 27.6% of SiO_4 were removed from the estuary due to biogeochemical processes. It has been estimated that approximately 148.6tons of NH_4 was retained in the estuary as an additional input from coastal region during pre-monsoon.

Thus, the Cochin estuary was a small source of nutrients to the adjacent coastal region during the study period. The present estimates of nutrient fluxes from Cochin estuary were higher than some estuaries (Chaliyar and Tapi estuary), but comparable with that of Hoogly and Meghna estuaries. The significance of this finding is that the export fluxes from the Cochin estuary could be a major factor sustaining the spectacular monsoon fishery along the south west coast of India.

The present study identified increased anthropogenic input of trace metals into the estuary and its impact on the coastal region. It was observed that the binding phases played a major role in the mobility of trace metals in the sediments. The exchangeable and bicarbonate phases were the important non-residual fractions for some metals (Zn, Cd and Mn). The enrichment of labile fractions of Cd and Mn with increase in their total metal content indicates that this would exacerbate the potential toxicity of these metals in the estuarine and coastal environment. The organic phase was the preferred phase for Pb, Cr and Ni in the estuarine sediments and Cr in coastal sediments. Inorganic precipitation though Fe-Mn oxyhydroxide was assumed to be the important depositional pathway for Zn, Ni, Pb, Cd, Mn and V in both estuarine and coastal sediments. The residual phase was the stable phase for all the metals (except Cd at some stations) in the estuarine and coastal sediments. Mn and Zn in residual fraction were higher than the value reported for adjacent source rock and was even higher than the standard sediment quality guidelines. The enrichment of these metals in the residual fraction could be due to the biogenic/diagenic transformation of non residual metals to stable residual forms under favourable conditions and thus making the pollutants less available to biota

A comparison with other fractionation studies in Cochin estuary showed that, an increase in the exchangeable Cd and Zn in the estuarine sediments prevails over the years. The concentrations of Mn, Cr, Pb, Ni and Cu in exchangeable/carbonate fractions have decreased over the years. The fractionation study explains the fate of metals under different environmental conditions, which can be used for natural water management system.

The present study is a first time attempt to carry out the fractionation of rare earths, thorium and uranium in the sediments of Cochin estuary and adjacent coastal region to understand the fate, transport and depositional characteristics of these elements. Rare earth element (REE) geochemistry of sediments from Cochin estuary and adjacent coastal stations showed that the light rare earth elements (LREE) are the more abundant compared to middle rare earth elements (MREE) and heavy rare earth elements (HREE). Cerium was markedly high in sediments of estuarine and coastal stations as it was the most abundant rare earth in earth crust. Lutetium was the least abundant rare earth present in the estuarine and coastal sediments.

Enrichment of rare earth elements (REE) in the north estuary (S_1, S_2) and a gradual decrease towards the central estuary (S_3, S_4, S_7, S_8) and to a lowest level near the Cochin inlet (S_5 & S_6) are some of the notable observations. The dynamic nature of the inlet may support swiping of finer particles leading to impoverishment of elements in the sediments. The coastal sediments showed high concentration of rare earths and the values were similar to the central estuary. This generally indicates the mobility of elements from riverine sources to downstream.

Shale normalized values of rare earths showed felsic source. A deviation in shale normalized pattern observed at northern estuary can be due to additional supply of REE into the estuary in addition to detritus. High thorium content in theses station too supports the external source. Positive Ce anomaly observed in the study region supports the terrigeneous origin. A slight negative Ce anomaly at northern station could be due to biological productivity. No anomaly or slightly positive Eu anomaly in both estuarine and coastal sediments supports its feldspar origin. Redox constraints like U/Th ratio and authigenic U supports the oxygenated conditions in both estuarine and coastal sediments.

The fractionation studies were carried out to understand the mechanism behind the deposition of REE, and actinides (Thorium and Uranium) in the Cochin estuary and adjacent coastal region. It was observed the residual phase was preferred by LREE, while organic phase was the major site for HREE in clayey sediments with high organic matter and residual phase was the major site for HREE in sandy sediments. The high thermodynamic stability of LREE in residual phase could be a reason for its enrichment in sediments. The stability of HREE in sediments depends upon the nature of organic compound to which it is associated. Sc showed deposition similar to LREEs and Y showed deposition similar to HREE due to their identical chemical properties. Thorium in the sediment was stabilized in the residual phases. The organic matter generally stabilized the Uranium in estuarine sediments, coastal sediments (with high organic matter) preferentially contained Uranium in residual phase. The bio-mineralization seems to be responsible for its accumulation in residual phase in the coastal environment. Thorium was mainly associated with residual phase in both estuarine and coastal sediments. Fe/Mn oxyhydroxides and exchangeable/carbonate phases of rare earths was relatively low compared to that in residual and organic phases. The present study thus highlights the major role of particle size and organic matter in controlling the deposition of REE in the estuarine and coastal environments.

The present study showed that suspended particles, which act both as a source as well as sink of trace metals, play a vital role in the distribution of trace metals in the estuary. The average river flow through the six rivers during 28th-30th October 2015 was 58.6Mm^{3}d^{-1}, resulting in net river input of 203.57kg Zn, 604kg Mn, 247.5kg Cr, 0.4kg Ni, 89t Fe and 5.09t Mg per day. The major contributor of Zn, Mn, Fe and Mg was river Achankoil following a turbid condition and the major contributor of Ni and Cr to the estuary was river Periyar. The concentration of Zn, Cu, Cr and Pb in suspended particles showed an increase from rivers to the estuary indicating their addition towards downstream. For other metals (Cr, Fe and Mn), a decreasing trend was noticed for Periyar and Muvattupuzha rivers, probably due to their deposition in the upper estuary. Bioaccumulation could also be a factor for the absence of Cr in the lower reaches of Muvattupuzha. At the Cochin inlet, the metals Fe, Mg, Zn and Mn were mostly present in particle form, whereas Ni and Cr showed dissolution at higher salinity.

Some of the metals (Fe, Zn, Mn) showed strong interrelationship, while some others did not show any correlation indicating the variable interaction among metals with particles. The enrichment of Fe in the upstream and its depletion towards the inlet could be due to the flocculation of Fe bound particles at higher salinity.

The observed estuarine flow through the Cochin inlet during 3rd- 4th November 2015 was 67.095Mm^3/tidal cycle (surface: 45.76Mm^3/tidal cycle; mid: 29.44Mm^3/tidal cycle; bottom: -8.18Mm^3/tidal cycle). Consequently the net water flux through the estuary (input-export) was 6.095Mm^3/tidal cycle directed seaward. This means that about 9.99% of the freshwater entering the estuary (through 6 major rivers) was getting exported in excess through the Cochin inlet in a tidal cycle on 3rd- 4th November-15. This difference in volume exchange was well reflected in the trace metal transport through Cochin estuary. The net metal flux (input-export) through the Cochin estuary on 3rd-4th November-15 was 246.39t Fe, 232.7tMg, 1.90t Cr, 1.34t Zn, 1.25t Mn, 0.59t Ni, 0.029t Co and 0.003t Pb in a tidal cycle and directed seaward. Approximately 68 to 99% of this flux was associated with particles. Similar to the results obtained from the nutrient flux studies, there was also a net export for most of the trace metals through the Cochin inlet as a consequence of anthropogenic sources, which ultimately could get deposited in coastal sediments. The sedimentation due to flow restrictions and flocculation processes in the estuary reduces the export of trace metals into the coastal sediments. Otherwise the export fluxes for all the trace metals would have been even larger than that observed for today.

The present study shows that the high run off through the rivers are capable of maintaining a better flushing of the estuary and regulate a balance in the nutrient and heavy metal levels to safe guard the estuary from intense eutrophication and pollution. The Cochin estuary seems to be a source of nutrients to the adjacent coastal areas even during dry season. The eutrophication in coastal waters to a certain extent increase the fishery production however as a consequence of monsoon upwelling, when the hypoxia intensify over the western India shelf, the pelagic and benthic fishes tend to the surface layers to avoid oxygen deficient waters. Thus controlling nutrient input from estuary is of important for achieving a healthy coastal environment.

Moreover, the fate of the export fluxes of trace metals is a matter of great concern as the ultimate sink could be their deposition in coastal sediments. The sediment texture, hydrological regime, salinity and organic matter were responsible for the mobility and release of these metals. Even though the fractionation study indicates the fate of metals in the coastal sediments, which can be used for natural water management system; there are still uncertainties in the regulating mechanisms for metal mobility in coastal sediments. Therefore future studies should include the physical, chemical and biological mediated metal remobilization and microbial mediated mineralization in the estuarine and coastal marine environment for proper estuarine and coastal management.

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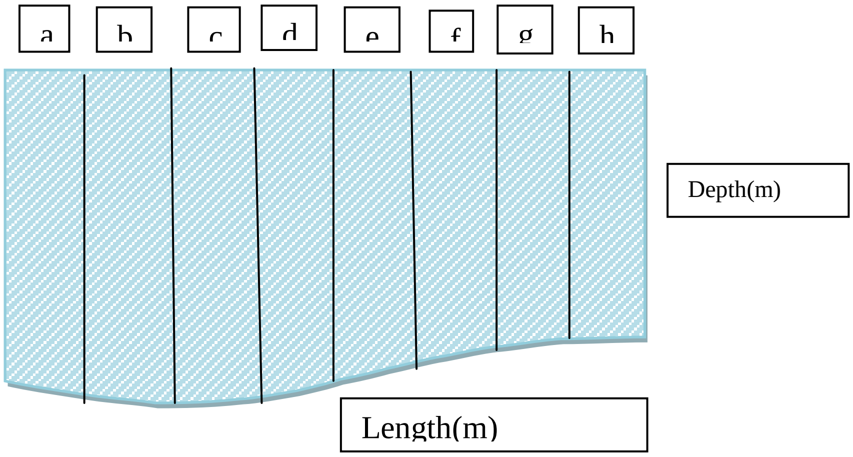
Appendix 1a:

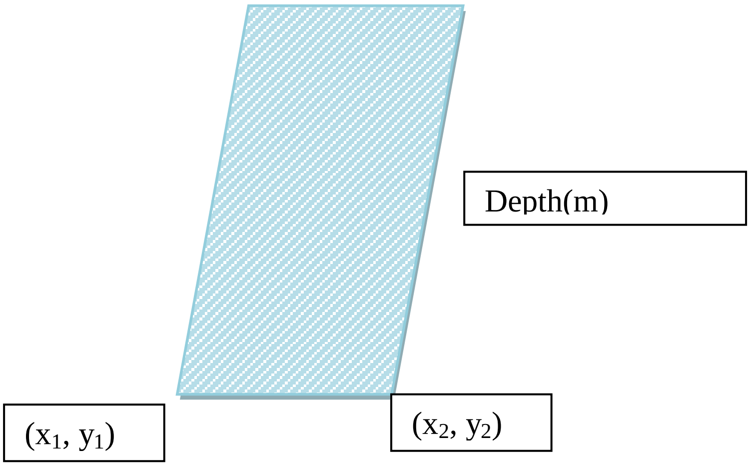
Calculation of cumulative area for nutient flux measurement using current meter records:

We can define the area by specifying the geographical position, width and depth of each locations (2 upstream and 2 inlet) of Cochin estuary. For that we can divide the area of each location into small different cross sections

The co ordinates of the area of one section is represented below

.





Calculation of section length:

Section length is calculated using the equation of a straight line,

$$\sqrt{(\mathrm{x1}-\mathrm{x2})^2+(\mathrm{y1}-\mathrm{y2})^2}$$

Where, x_1& x_2 are the longitudes and y_1 & y_2 are the latitudes of the area of interest.

Cumulative length = $\sum_{a}^{h} sectionlength$

Cross Section area= Section length* section depth

Cumulative Area = $\sum_{a}^{h} sectionarea$

The coordinates can be specified as degree decimals which we can to convert to kilometeres as 10,000 kilometers are there per 90 degree**.**

Cumulative area (in meteres)= (Cumulative area in degree decimals) *(111.11)* (1000).

Calculated cumulative area of the regions for computing nutrient fluxes.
Varapuzha =510m^2(max. depth= 3.5m)

Thanneermukkam = 2200m^2(max. depth= 4.87m)

(NB:The area of thanneermukkam bund is crossed out during calculation).
Cochin Barmouth= 5348.8m^2(max. depth= 15m)

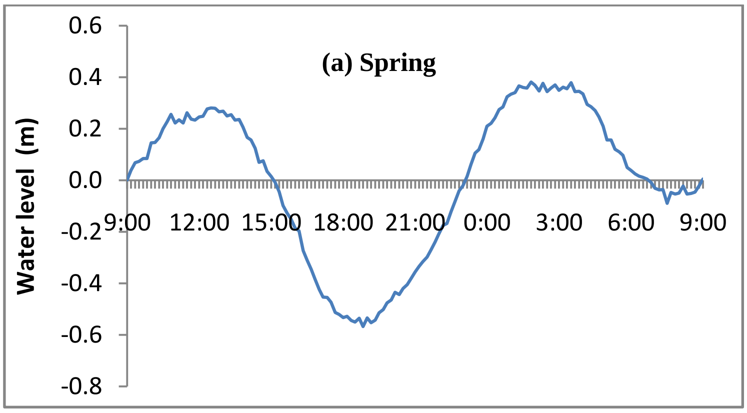
Munambam inlet = 203.63m^2(max depth=2m)

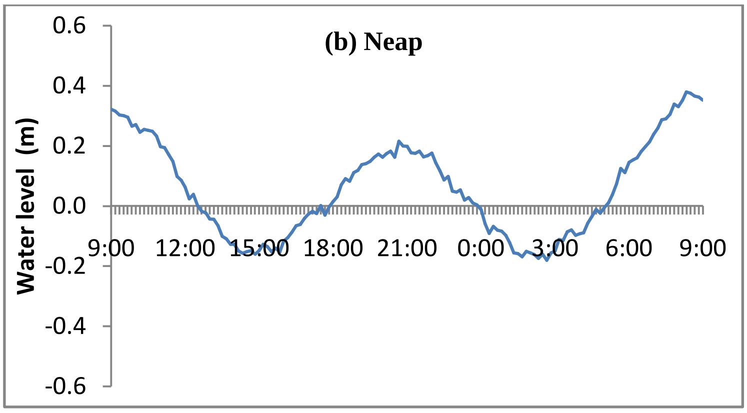
(NB: The drop or rise in water level were not considered during area computation)

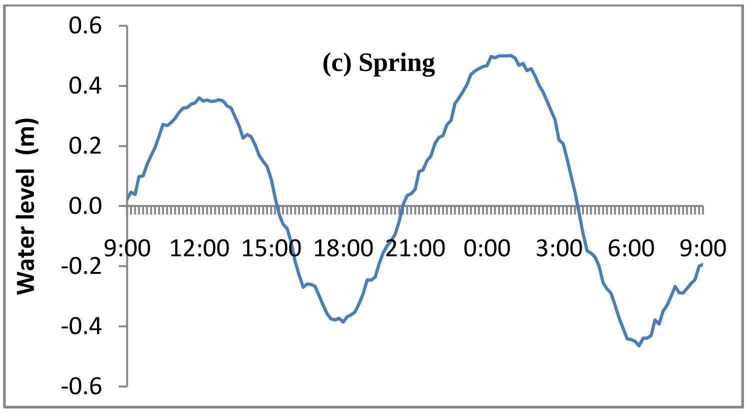
Appendix 16:

Water level variations at Cochin inlet during three different seasons (2009-2010).

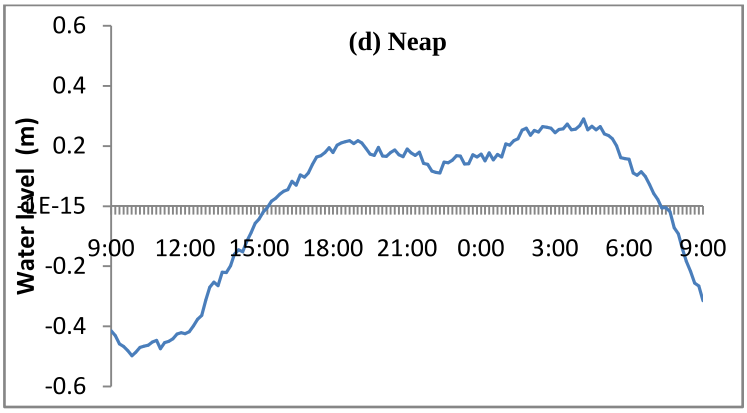
The selection of spring and neap phase observations are made based on the monthly variations in the water level at the Cochin inlet obtained from Indian Tide Tables. These are again checked during the simultaneous tidal measurements made at this location during the entire observational period, which is furnished below for three different seasons. (a) Post-monsoon spring; (b) Post-monsoon neap; (c) Pre-monsoon spring; (d) Pre-monsoon neap; (e) Peak summer monsoon spring; (f) Peak summer monsoon neap.



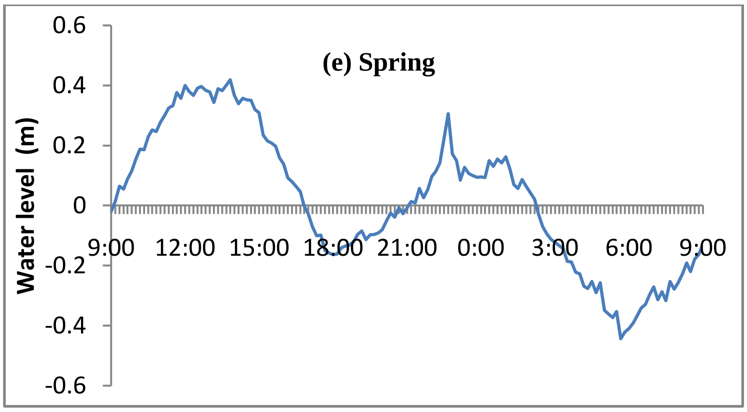




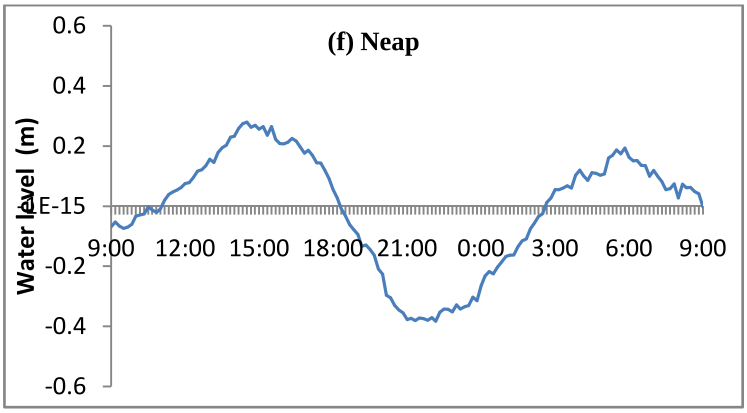
(c) Spring



(d) Neap



(e) Spring

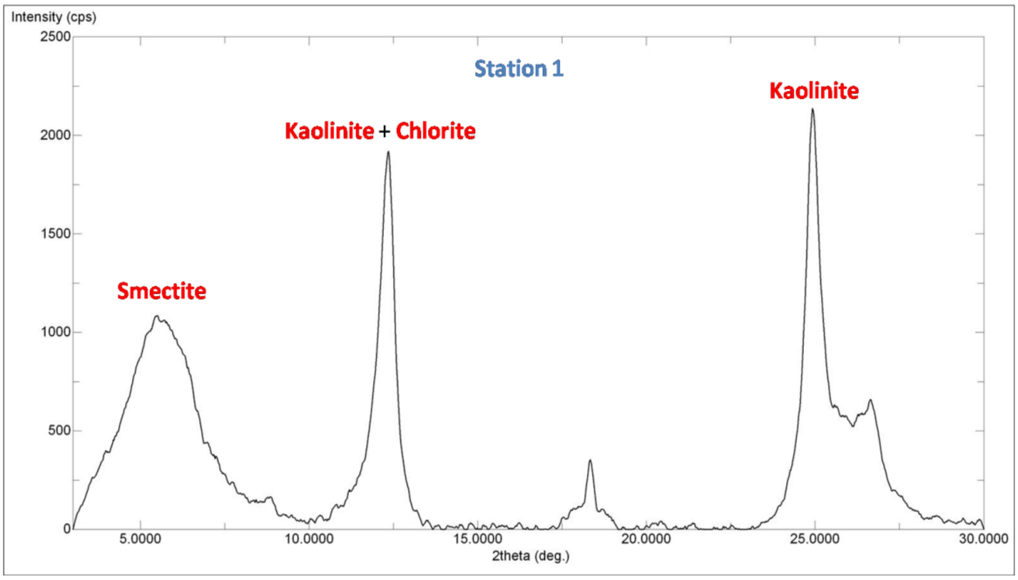

(f) Neap
Water level (m)
0.6
0.4
0.2
0E-15
-0.2
-0.4
-0.6
9:00
12:00
15:00
18:00
21:00
0:00
3:00
6:00
9:00

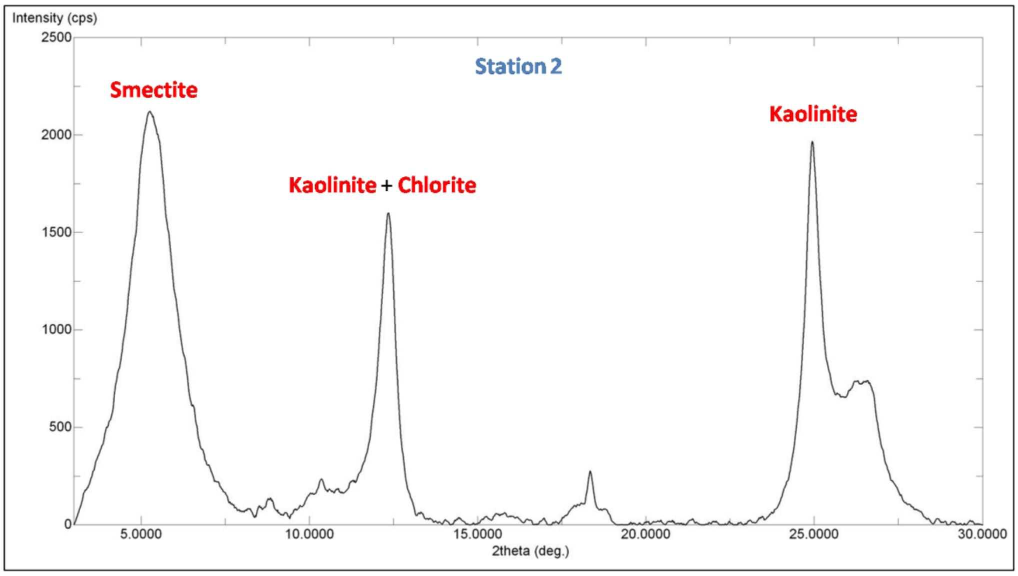
Appendix 2a

Water quality parameters (Metal fractionation studies - October 2011)

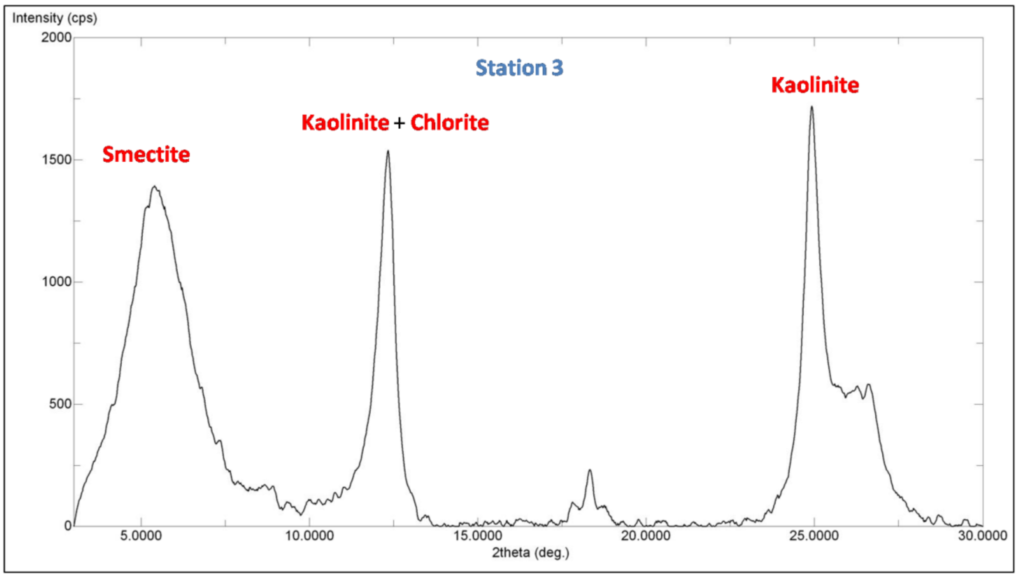
Stn	**pH**	**Salinity**	**DO (ml/l)**	**BOD ml/l**	**NO_3 (µM)**	**NO_2 (µM)**	**SiO_4 (µM)**	**PO_4 (µM)**	**NH_4 (µM)**
S_1	7.3	4.68	3.17	1.64	11.77	0.83	32.87	0.47	17.91
S_2	7.36	5.44	2.96	2.24	11.12	0.71	29.62	0.56	4.96
S_3	7.59	9.13	3.31	2.07	3.53	0.67	20.85	1.01	12.37
S_4	7.81	9.84	2.98	1.77	6.89	0.70	17.93	1.53	14.17
S_5	7.81	10.17	3.11	2.22	5.82	0.56	15.44	0.98	15.02
S_6	8.28	25.02	3.17	2.65	1.13	0.23	2.08	0.76	12.24
S_7	7.65	10.09	3.55	1.79	3.88	0.73	16.29	1.40	15.84
S_8	7.55	11.66	2.92	1.97	3.59	0.45	13.96	1.00	12.63
S_9	8.41	28.36	4.03	3.16	2.41	0.23	1.95	0.36	10.29
S_{10}	8.43	23.42	3.86	3.24	0.69	0.11	1.11	0.61	11.09
S_{11}	8.33	26.28	4.34	3.57	3.03	0.01	0.14	0.29	10.40
S_{12}	8.41	30.58	4.14	3.48	1.86	0.05	6.35	0.43	6.06

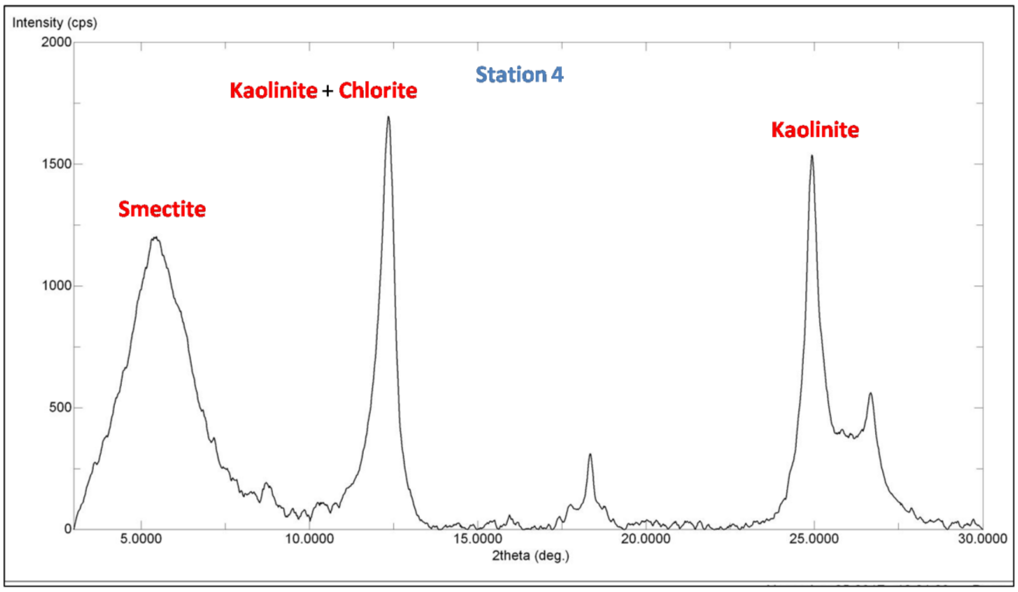
Appendix 26



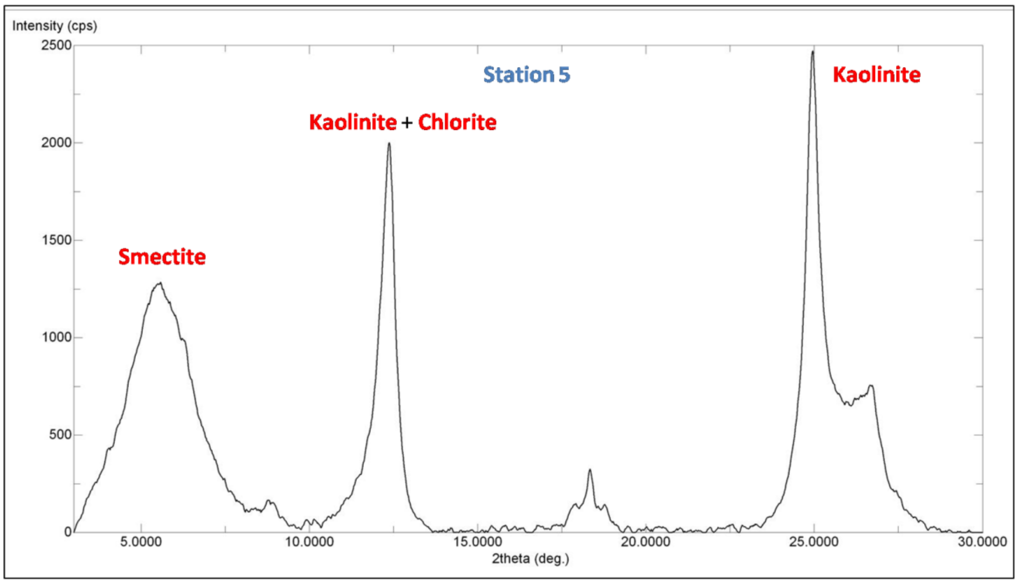


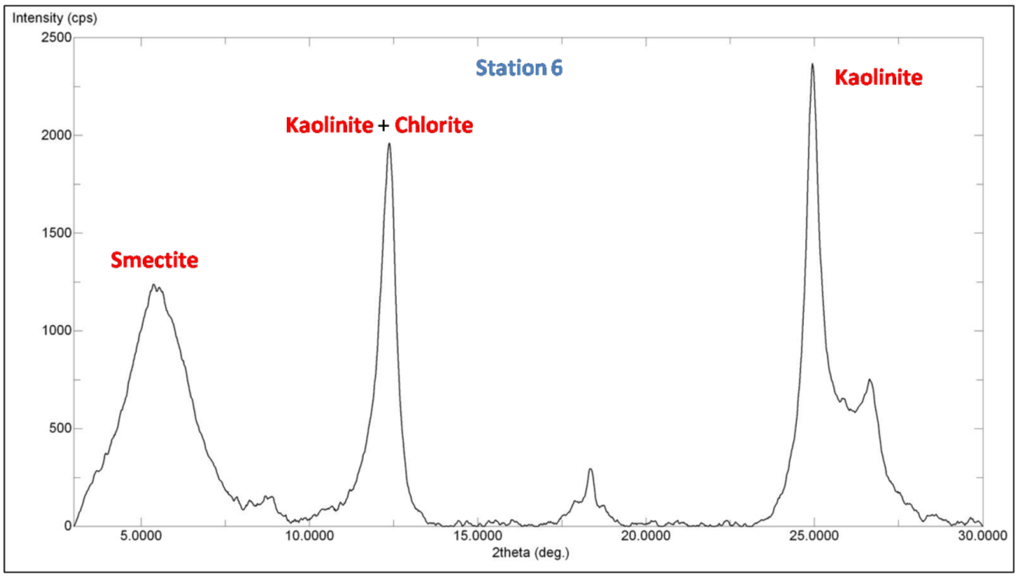
X-Ray Diffractograms of the estuarine sediments S_1 & S_2, during October 2011.



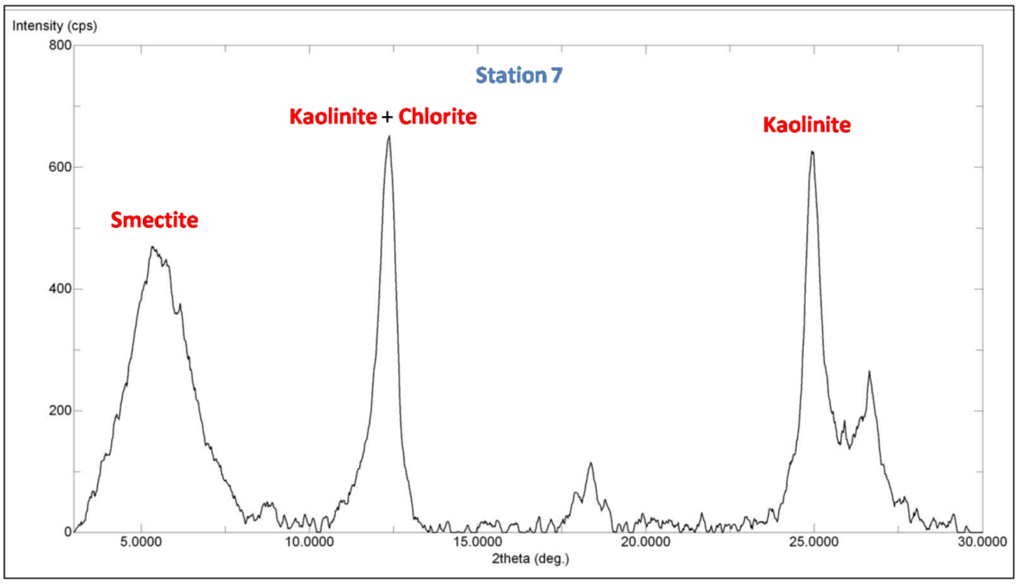


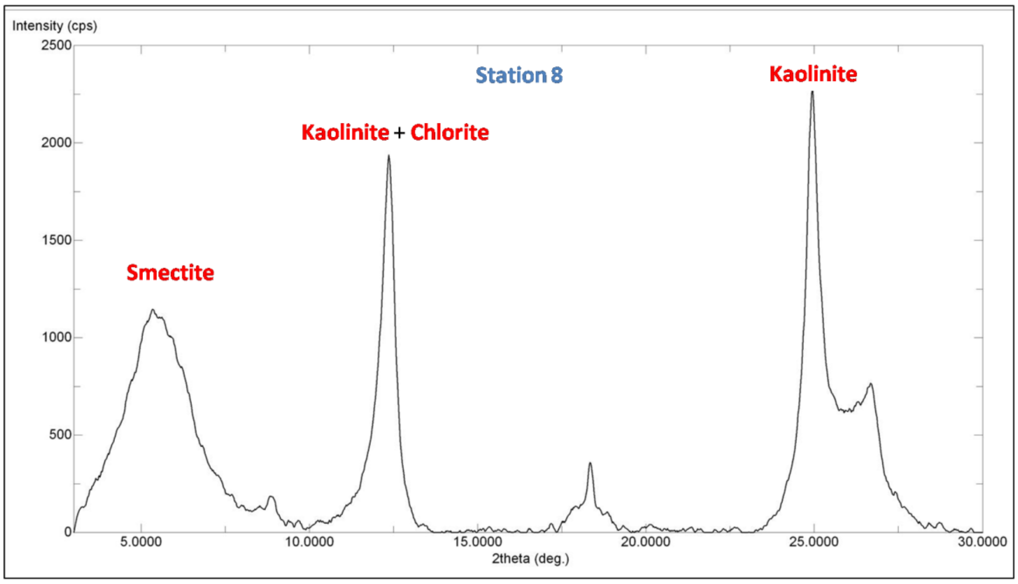
X-Ray Diffractograms of the estuarine sediments S_3 & S_4 during October 2011.



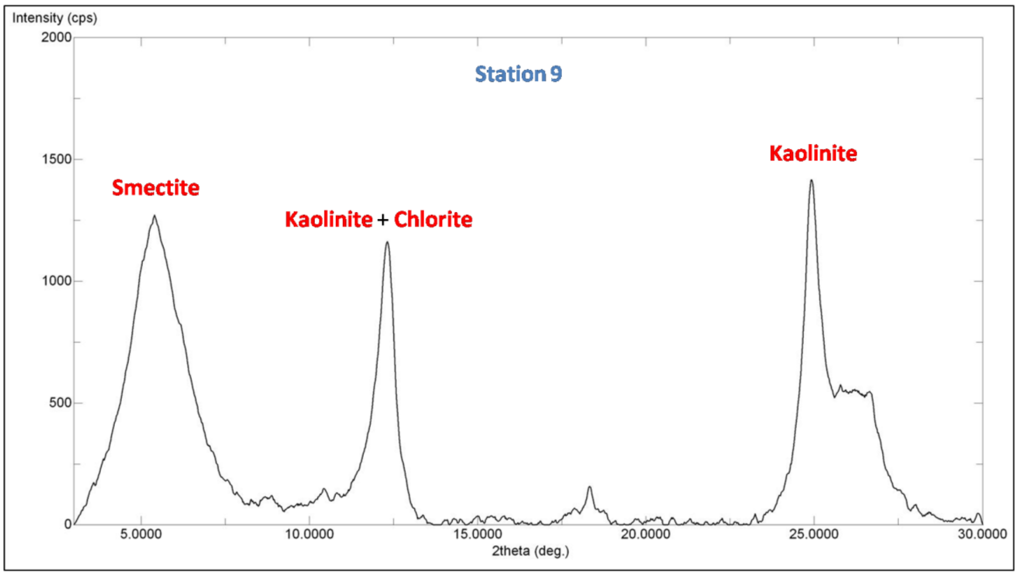


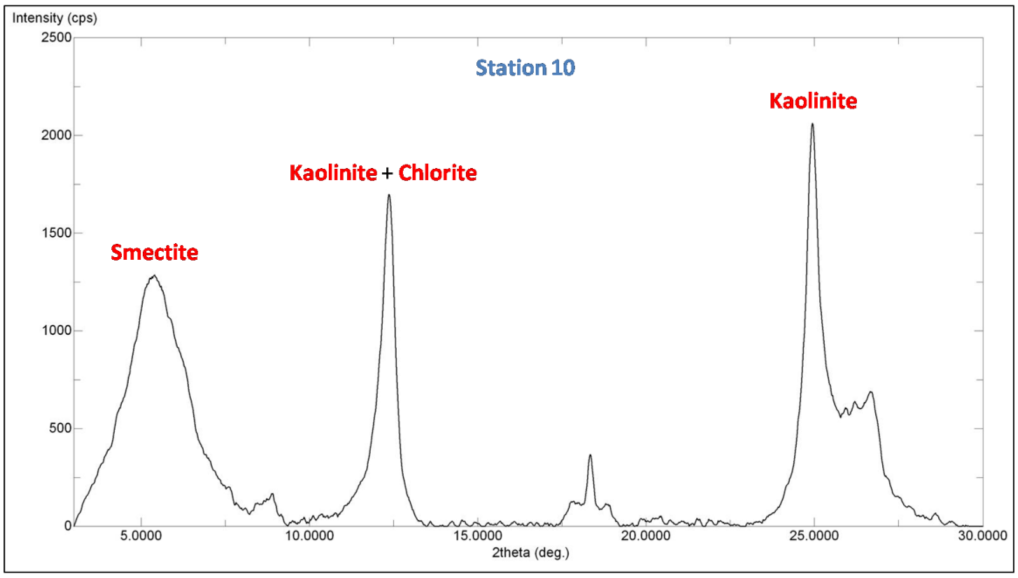
X-Ray Diffractograms of the estuarine sediments S_5 & S_6, during October 2011.



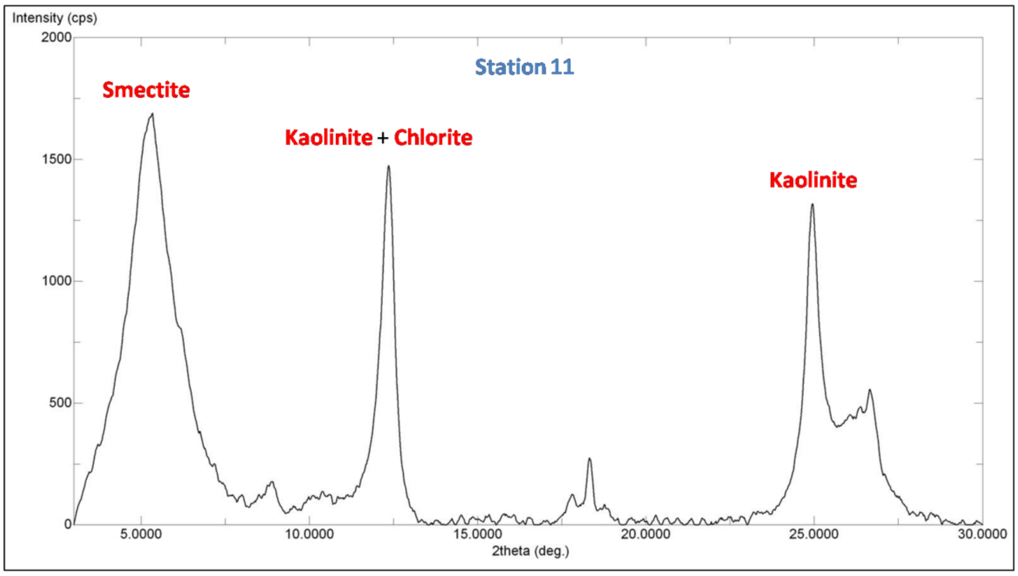


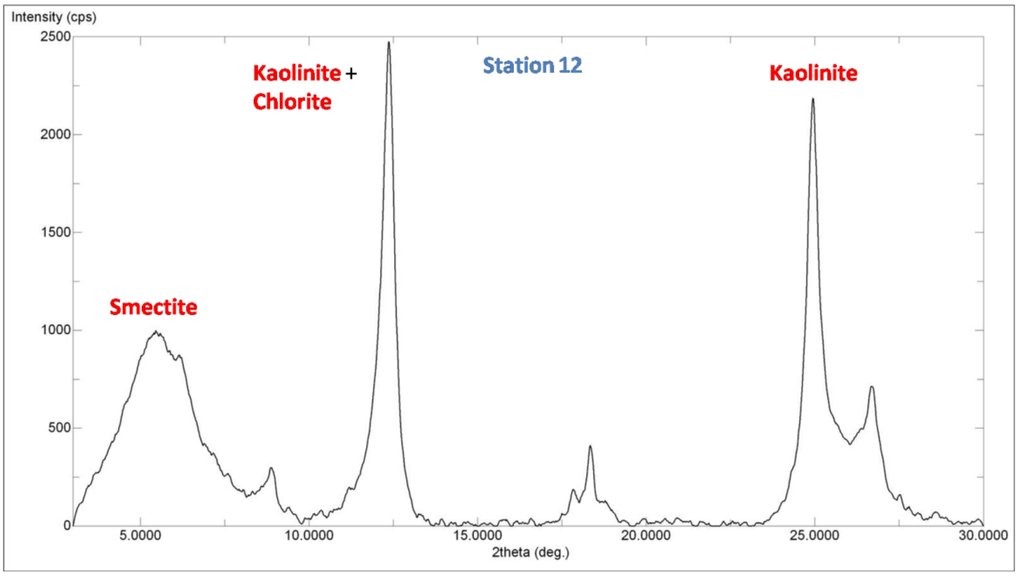
X-Ray Diffractograms of the estuarine sediments S_7 & S_8, during October 2011.





X-Ray Diffractograms of the estuarine sediments S_9 & S_{10}, during October 2011.





X-Ray Diffractograms of the estuarine sediments S_{11} & S_{12}, during October 2011.

Appendix 3

Pearson Correlation matrix for REE (Sc, Y, La), Clayminerals and SPM

Variables	S%	I%	K%	SPM	OC	Sc1	Sc2	Sc3	Sc4	TSc	Y1	Y2	Y3	Y4	TY	La1	La2	La3	La4	TLa
S%	**1.00**																			
I%	**-0.79**	**1.00**																		
K%	**-0.95**	0.56	**1.00**																	
SPM	-0.23	0.29	0.17	**1.00**																
OC	0.29	-0.04	-0.37	0.46	**1.00**															
Sc1	0.54	-0.36	-0.54	-0.28	0.48	**1.00**														
Sc2	0.46	-0.56	-0.34	-0.37	0.31	**0.71**	**1.00**													
Sc3	0.25	-0.37	-0.15	-0.51	-0.21	0.54	**0.77**	**1.00**												
Sc4	0.20	-0.09	-0.23	0.01	**0.71**	**0.76**	0.54	0.18	**1.00**											
TSc	0.28	-0.19	-0.28	-0.09	**0.66**	**0.83**	**0.70**	0.38	**0.98**	**1.00**										
Y1	0.51	-0.16	**-0.60**	-0.54	-0.06	**0.64**	0.28	0.52	0.19	0.29	**1.00**									
Y2	0.26	-0.40	-0.16	-0.15	0.54	0.51	**0.73**	0.42	**0.69**	**0.75**	0.04	**1.00**								
Y3	0.39	-0.06	-0.49	-0.08	**0.73**	**0.83**	0.54	0.26	**0.88**	**0.90**	0.52	**0.63**	**1.00**							
Y4	0.27	-0.33	-0.20	-0.47	0.22	0.48	**0.58**	0.42	0.44	0.50	0.30	**0.73**	0.51	**1.00**						
TY	0.24	-0.08	-0.28	-0.18	0.57	**0.61**	0.47	0.19	**0.85**	**0.84**	0.33	**0.74**	**0.87**	**0.70**	**1.00**					
La1	0.52	-0.15	**-0.62**	-0.52	-0.04	**0.64**	0.26	0.50	0.18	0.28	**1.00**	0.03	0.52	0.28	0.32	**1.00**				
La2	0.18	-0.39	-0.04	-0.31	0.30	0.46	**0.78**	**0.59**	0.56	**0.65**	0.07	**0.94**	0.49	**0.84**	**0.66**	0.05	**1.00**			
La3	0.33	-0.25	-0.32	-0.31	0.55	**0.71**	**0.77**	0.48	**0.80**	**0.87**	0.34	**0.88**	**0.84**	**0.81**	**0.89**	0.33	**0.86**	**1.00**		
La4	0.09	-0.19	-0.02	-0.47	0.09	0.17	0.35	0.20	0.31	0.34	0.13	**0.64**	0.34	**0.89**	**0.68**	0.11	**0.74**	**0.69**	**1.00**	
TLa	0.14	-0.17	-0.11	-0.38	0.24	0.28	0.44	0.27	0.43	0.47	0.18	**0.73**	0.49	**0.93**	**0.77**	0.15	**0.81**	**0.80**	**0.97**	**1.00**

Values in bold are different from 0 with a significance level alpha > 0.05 *XLSTAT 2014*

Pearson Correlation matrix for REE (Ce, Pr, Nd), Clayminerals, OC and SPM

Variables	S%	I%	K%	SPM	OC	Ce1	Ce2	Ce3	Ce4	TCe	Pr1	Pr2	Pr3	Pr4	TPr	Nd1	Nd2	Nd3	Nd4	TNd
S%	**1.00**																			
I%	**-0.79**	**1.00**																		
K%	**-0.95**	0.56	**1.00**																	
SPM	-0.23	0.29	0.17	**1.00**																
OC	0.29	-0.04	-0.37	0.46	**1.00**															
Ce1	0.53	-0.15	**-0.63**	-0.51	-0.03	**1.00**														
Ce2	0.26	-0.41	-0.14	-0.27	0.41	0.07	**1.00**													
Ce3	0.35	-0.25	-0.35	-0.13	0.57	0.42	**0.82**	**1.00**												
Ce4	0.31	-0.50	-0.17	-0.48	0.22	0.16	**0.92**	**0.70**	**1.00**											
TCe	0.35	-0.39	-0.28	-0.30	0.45	0.20	**0.94**	**0.84**	**0.95**	**1.00**										
Pr1	0.53	-0.15	**-0.63**	-0.51	-0.03	**1.00**	0.08	0.42	0.16	0.20	**1.00**									
Pr2	0.16	-0.40	-0.02	-0.28	0.32	-0.04	**0.99**	**0.74**	**0.92**	**0.90**	-0.03	**1.00**								
Pr3	0.24	-0.25	-0.20	-0.29	0.37	0.32	**0.90**	**0.94**	**0.78**	**0.85**	0.32	**0.86**	**1.00**							
Pr4	0.28	-0.48	-0.14	-0.45	0.14	0.06	**0.88**	**0.58**	**0.96**	**0.89**	0.07	**0.90**	**0.69**	**1.00**						
TPr	0.24	-0.38	-0.14	-0.37	0.30	0.10	**0.93**	**0.73**	**0.96**	**0.96**	0.11	**0.93**	**0.79**	**0.96**	**1.00**					
Nd1	0.53	-0.15	**-0.64**	-0.50	-0.03	**1.00**	0.07	0.42	0.15	0.20	**1.00**	-0.04	0.32	0.06	0.10	**1.00**				
Nd2	0.21	-0.31	-0.12	-0.06	**0.58**	-0.06	**0.96**	**0.81**	**0.80**	**0.88**	-0.05	**0.94**	**0.87**	**0.75**	**0.84**	-0.06	**1.00**			
Nd3	0.30	-0.24	-0.29	-0.06	**0.66**	0.22	**0.89**	**0.96**	**0.72**	**0.86**	0.23	**0.82**	**0.93**	**0.63**	**0.77**	0.22	**0.92**	**1.00**		
Nd4	0.13	-0.12	-0.11	-0.34	0.27	0.14	**0.73**	**0.58**	**0.74**	**0.79**	0.15	**0.74**	**0.64**	**0.77**	**0.87**	0.15	**0.66**	**0.63**	**1.00**	
TNd	0.21	-0.18	-0.20	-0.30	0.40	0.20	**0.83**	**0.74**	**0.80**	**0.88**	0.21	**0.82**	**0.78**	**0.80**	**0.92**	0.20	**0.79**	**0.79**	**0.97**	**1.00**

Values in bold are different from 0 with a significance level alpha > 0.05 *XLSTAT 2014*

Pearson Correlation matrix for REE (Sm,Eu, Gd), Clayminerals and SPM

Variables	S%	I%	K%	SPM	OC	Sm1	Sm2	Sm3	Sm4	TSm	Eu1	Eu2	Eu3	Eu4	TEu	Gd1	Gd2	Gd3	Gd4	TGd
S%	**1.00**																			
I%	**-0.79**	**1.00**																		
K%	**-0.95**	0.56	**1.00**																	
SPM	-0.23	0.29	0.17	**1.00**																
OC	0.29	-0.04	-0.37	0.46	**1.00**															
Sm1	0.53	-0.15	**-0.64**	-0.49	-0.01	**1.00**														
Sm2	0.12	-0.41	0.04	-0.24	0.29	-0.12	**1.00**													
Sm3	0.19	-0.22	-0.14	-0.44	0.17	0.34	**0.74**	**1.00**												
Sm4	0.10	-0.05	-0.11	-0.05	0.33	0.03	0.34	0.04	**1.00**											
TSm	0.24	-0.21	-0.22	-0.28	0.44	0.22	**0.74**	**0.61**	**0.80**	**1.00**										
Eu1	0.53	-0.14	**-0.65**	-0.48	-0.01	**1.00**	-0.17	0.30	-0.01	0.17	**1.00**									
Eu2	0.24	-0.46	-0.09	-0.13	0.46	-0.06	**0.94**	**0.75**	0.21	**0.66**	-0.09	**1.00**								
Eu3	0.36	-0.24	-0.36	-0.07	0.57	0.39	0.54	**0.82**	0.11	**0.58**	0.38	**0.69**	**1.00**							
Eu4	0.13	-0.27	-0.05	-0.36	-0.27	-0.12	0.33	-0.09	0.43	0.32	-0.16	0.12	-0.45	**1.00**						
TEu	0.34	-0.34	-0.29	-0.28	0.39	0.13	**0.69**	0.44	**0.80**	**0.92**	0.09	**0.64**	0.41	0.51	**1.00**					
Gd1	0.52	-0.15	**-0.63**	-0.50	-0.04	**1.00**	-0.14	0.32	0.00	0.19	**1.00**	-0.07	0.38	-0.15	0.11	**1.00**				
Gd2	0.20	-0.42	-0.07	-0.25	0.37	0.00	**0.99**	**0.80**	0.34	**0.78**	-0.04	**0.97**	**0.66**	0.24	**0.72**	-0.02	**1.00**			
Gd3	0.22	-0.13	-0.23	-0.22	0.48	0.34	**0.66**	**0.92**	0.16	**0.67**	0.31	**0.74**	**0.95**	-0.30	0.49	0.32	**0.76**	**1.00**		
Gd4	0.22	-0.31	-0.14	-0.31	0.16	0.08	**0.69**	0.33	**0.79**	**0.85**	0.02	0.51	0.15	**0.73**	**0.87**	0.04	**0.66**	0.26	**1.00**	
TGd	0.28	-0.25	-0.25	-0.26	0.52	0.23	**0.75**	**0.66**	**0.74**	**0.98**	0.19	**0.73**	**0.69**	0.19	**0.91**	0.21	**0.81**	**0.75**	**0.77**	**1.00**

Values in bold are different from 0 with a significance level alpha > 0.05 *XLSTAT 2014*

Pearson Correlation matrix for REE (Tb,Dy, Ho), Clayminerals,OC and SPM

Variables	S%	I%	K%	SPM	OC	Tb1	Tb2	Tb 3	Tb4	TTb	Dy1	Dy2	Dy3	Dy4	TDy	Ho1	Ho2	Ho3	Ho4	THo
S%	**1.00**																			
I%	**-0.79**	**1.00**																		
K%	**-0.95**	0.56	**1.00**																	
SPM	-0.23	0.29	0.17	**1.00**																
OC	0.29	-0.04	-0.37	0.46	**1.00**															
Tb1	0.52	-0.15	**-0.62**	-0.51	-0.05	**1.00**														
Tb2	0.23	-0.42	-0.10	-0.23	0.39	0.01	**1.00**													
Tb 3	0.42	-0.32	-0.40	-0.04	**0.59**	0.31	**0.68**	**1.00**												
Tb4	0.26	-0.29	-0.21	-0.26	0.26	0.00	**0.61**	0.25	**1.00**											
TTb	0.31	-0.27	-0.29	-0.19	0.58	0.20	**0.79**	**0.78**	**0.74**	**1.00**										
Dy1	0.52	-0.15	**-0.62**	-0.52	-0.06	**1.00**	0.01	0.31	0.00	0.20	**1.00**									
Dy2	0.22	-0.41	-0.09	-0.16	0.45	-0.04	**0.99**	**0.68**	0.56	**0.78**	-0.04	**1.00**								
Dy3	0.30	-0.17	-0.32	-0.25	0.51	0.41	**0.74**	**0.91**	0.22	**0.74**	0.41	**0.74**	**1.00**							
Dy4	0.21	-0.28	-0.14	-0.11	0.21	-0.09	0.49	0.13	**0.97**	**0.64**	-0.09	0.46	0.04	**1.00**						
TDy	0.32	-0.25	-0.31	-0.14	**0.62**	0.21	**0.76**	**0.81**	**0.69**	**1.00**	0.21	**0.76**	**0.75**	**0.60**	**1.00**					
Ho1	0.52	-0.15	**-0.62**	-0.54	-0.05	**0.99**	0.06	0.32	0.08	0.24	**0.99**	0.00	0.43	-0.01	0.25	**1.00**				
Ho2	0.06	-0.34	0.09	0.00	0.45	-0.32	**0.94**	0.57	0.54	**0.69**	-0.32	**0.96**	**0.59**	0.47	**0.67**	-0.28	**1.00**			
Ho3	0.37	-0.16	-0.41	-0.23	0.51	0.47	**0.63**	**0.92**	0.14	**0.70**	0.47	**0.63**	**0.98**	-0.03	**0.73**	0.47	0.47	**1.00**		
Ho4	0.29	-0.36	-0.21	-0.20	0.16	0.03	0.43	0.10	**0.93**	**0.61**	0.03	0.38	0.00	**0.97**	0.57	0.10	0.36	-0.07	**1.00**	
THo	0.31	-0.23	-0.30	-0.15	**0.61**	0.24	**0.74**	**0.82**	**0.64**	**0.99**	0.23	**0.74**	**0.77**	0.55	**1.00**	0.26	**0.64**	**0.75**	0.53	**1.00**

Values in bold are different from 0 with a significance level alpha > 0.05 *XLSTAT 2014*

Pearson Correlation matrix for REE (Er, Tm, Yb), Clayminerals, OC and SPM

Variables	S%	I%	K%	SPM	OC	Er1	Er2	Er3	Er4	TEr	Tm1	Tm2	Tm3	Tm4	TTm	Yb1	Yb2	Yb3	Yb4	TYb
S%	**1.00**																			
I%	**-0.79**	**1.00**																		
K%	**-0.95**	0.56	**1.00**																	
SPM	-0.23	0.29	0.17	**1.00**																
OC	0.29	-0.04	-0.37	0.46	**1.00**															
Er1	0.52	-0.15	**-0.63**	-0.53	-0.04	**1.00**														
Er2	0.07	-0.34	0.08	0.01	0.46	-0.27	**1.00**													
Er3	0.43	-0.23	-0.46	-0.22	0.48	0.52	0.42	**1.00**												
Er4	0.31	-0.33	-0.25	-0.27	0.23	0.16	0.38	0.07	**1.00**											
TEr	0.33	-0.23	-0.32	-0.18	**0.60**	0.32	**0.63**	**0.78**	**0.60**	**1.00**										
Tm1	0.51	-0.15	**-0.61**	-0.53	-0.07	**0.99**	-0.32	0.52	0.08	0.29	**1.00**									
Tm2	0.20	-0.41	-0.07	-0.24	0.38	0.05	**0.94**	**0.58**	0.50	**0.76**	0.00	**1.00**								
Tm3	0.32	-0.10	-0.39	-0.22	0.50	0.57	0.43	**0.97**	0.13	**0.82**	0.55	**0.61**	**1.00**							
Tm4	0.35	-0.36	-0.29	-0.39	0.19	0.29	0.33	0.14	**0.98**	**0.62**	0.21	0.50	0.20	**1.00**						
TTm	0.41	-0.27	-0.41	-0.31	0.52	0.51	0.52	**0.83**	**0.58**	**0.98**	0.47	**0.71**	**0.87**	**0.64**	**1.00**					
Yb1	0.51	-0.15	**-0.62**	-0.53	-0.06	**0.99**	-0.32	0.52	0.10	0.29	**1.00**	0.01	0.55	0.23	0.48	**1.00**				
Yb2	0.21	-0.40	-0.08	-0.28	0.36	0.09	**0.92**	0.57	0.52	**0.75**	0.03	**1.00**	**0.61**	0.52	**0.72**	0.04	**1.00**			
Yb3	0.42	-0.11	-0.51	0.08	**0.86**	0.32	0.48	**0.81**	0.21	**0.78**	0.30	0.54	**0.82**	0.23	**0.75**	0.31	0.53	**1.00**		
Yb4	-0.03	-0.23	0.15	-0.35	-0.22	0.10	0.24	0.16	0.57	0.50	0.08	0.37	0.21	**0.60**	0.50	0.08	0.37	-0.15	**1.00**	
TYb	0.35	-0.25	-0.34	-0.19	**0.61**	0.35	**0.62**	**0.83**	0.54	**1.00**	0.32	**0.75**	**0.86**	**0.58**	**0.98**	0.33	**0.75**	**0.80**	0.47	**1.00**

Values in bold are different from 0 with a significance level alpha > 0.05 *XLSTAT 2014*

Pearson Correlation matrix for Lu, Th, U, Clayminerals, OC and SPM

Variables	S%	I%	K%	SPM	OC	Lu1	Lu2	Lu3	Lu4	TLu	Th1	Th2	Th3	Th4	TTh	U1	U2	U3	U4	TU
S%	**1.00**																			
I%	**-0.79**	**1.00**																		
K%	**-0.95**	0.56	**1.00**																	
SPM	-0.23	0.29	0.17	**1.00**																
OC	0.29	-0.04	-0.37	0.46	**1.00**															
Lu1	0.51	-0.15	**-0.61**	-0.53	-0.07	**1.00**														
Lu2	0.20	-0.37	-0.09	-0.37	0.31	0.10	**1.00**													
Lu3	0.30	-0.14	-0.33	-0.05	0.57	0.30	**0.65**	**1.00**												
Lu4	0.26	-0.38	-0.16	-0.28	0.18	0.05	0.44	-0.03	**1.00**											
TLu	0.33	-0.25	-0.32	-0.24	0.58	0.33	**0.78**	**0.81**	0.48	**1.00**										
Th1	-0.36	0.31	0.33	-0.14	-0.01	0.06	0.16	0.36	-0.52	0.05	**1.00**									
Th2	0.07	-0.03	-0.07	-0.33	0.20	0.43	**0.73**	0.50	0.44	**0.64**	0.27	**1.00**								
Th3	0.23	-0.53	-0.05	-0.42	-0.14	0.16	**0.74**	0.41	0.11	0.38	0.08	0.35	**1.00**							
Th4	0.00	-0.11	0.06	-0.40	0.05	0.12	**0.74**	0.36	**0.59**	**0.58**	0.16	**0.86**	0.32	**1.00**						
TTh	0.02	-0.15	0.05	-0.43	0.05	0.14	**0.78**	0.39	**0.58**	**0.60**	0.17	**0.87**	0.39	**1.00**	**1.00**					
U1	0.11	-0.15	-0.07	**-0.68**	-0.29	0.45	0.53	0.16	0.51	0.37	0.11	**0.78**	0.33	**0.87**	**0.87**	**1.00**				
U2	0.04	-0.19	0.04	**-0.70**	-0.35	0.40	**0.64**	0.20	0.45	0.38	0.16	**0.78**	0.54	**0.85**	**0.87**	**0.96**	**1.00**			
U3	0.25	-0.24	-0.22	**-0.65**	-0.07	**0.59**	**0.76**	**0.59**	0.28	**0.65**	0.28	**0.84**	**0.61**	**0.78**	**0.81**	**0.84**	**0.89**	**1.00**		
U4	0.04	0.01	-0.06	0.23	**0.73**	-0.15	0.43	**0.64**	0.35	**0.79**	0.03	0.29	-0.07	0.35	0.34	-0.03	-0.07	0.15	**1.00**	
TU	0.22	-0.18	-0.20	-0.49	0.20	0.47	**0.81**	**0.72**	0.42	**0.85**	0.24	**0.86**	0.48	**0.83**	**0.85**	**0.76**	**0.77**	**0.93**	0.49	**1.00**

Values in bold are different from 0 with a significance level alpha > 0.05 *XLSTAT 2014*