TRACE METALS (Fe, Mn, Co, Cu and Zn) IN SURFACE SEDIMENTS OF MANDOVI ESTUARY-WEST COAST OF INDIA.

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SONAL DILIP JANKAR

Seat number: 21P058014

P.R. No: 201800632

Under the supervision of

Dr. VISHNU M. MATTA

School of Earth Ocean and Atmospheric Sciences

Department of Marine Sciences

GOA UNIVERSITY

April 2024

Examined by:

Seal of the School

DECLARATION BY STUDENT

I hereby declare that the data presented in this Dissertation report entitled **"Trace metals (Fe, Mn, Zn, Cu, and Co) in surface sediments of Mandovi estuary-West coast of India"** is based on the results of investigations carried out by me in the Marine Sciences Department at the **School of Earth Ocean and Atmospheric Sciences**, Goa University under the Supervision of **Dr. Vishnu. M. Matta** and the same have not been submitted elsewhere for the award of the degree or diploma by me. Further, I understand that Goa University or its authorities will be not responsible for the correctness of observation /experimental or other findings given the dissertation.

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Seat No.: 21P058014

Date:- 02/05/2024

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This is to certify that the dissertation report " **Trace metals in the surface sediments of Mandovi estuary-West coast of India"** is a bonafide work carried out by **Ms. Sonal Dilip Jankar** under my supervision in partial fulfillment of the requirements for the award of the degree of **MSc. In Environmental Science** in the Department of Marine Sciences at the School of Earth, Oceans and Atmospheric Sciences, Goa University.

Date: 02/05/2024

02/05/2024
Dr. Vishnu Murty.Matta
Guide
School of Earth, Ocean and Atmospheric Sciences

31/7/24
Sr. Prof. Sanjeev C. Ghadi
Senior Professor and Dean
School of Earth, Ocean and Atmospheric Sciences
Date: 02/05/2024
Place: Goa University
Goa-403206

SEOAS, GOA UNIVERSITY TALEIGAO PLATEAU GOA
School Stamp

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CHAPTER 1

INTRODUCTION

1.1 Introduction

An Estuary is a partially enclosed coastally body of brackish water with one or more rivers or streams flowing into it and with a free connection to the open sea. The word estuary is derived from the Latin word aestuarium meaning tidal inlet of the sea, which in itself is derived from the term aestus, meaning tide. There have been many definitions proposed to describe an estuary. The most widely accepted definition is "a semi-enclosed coastal body of water, which has a free connection with the open sea, and within which seawater is measurably diluted with freshwater derived from land drainage" However, this definition excludes a number of coastal water bodies such as coastal lagoons and brackish water. An estuary is a dynamic ecosystem having a connection to the open sea through which the sea water enters with the rhythm of the tides.

There are four different kinds of estuaries, each created a different way; **1) coastal plain estuaries: 2) tectonic estuaries; 3) bar-built estuaries; and 4) fjord estuaries.1)** Coastal plain estuaries are created when sea level rise and fill in an existing river valley. The Chesapeake Bay, on the east coast of the United States, is a coastal plain estuary. **2**) Tectonic activity, the shifting together and rifting apart of the earth's crust, creates tectonic estuaries. California's San Francisco Bay is a tectonic estuary. The San Francisco Bay lies at the junction of the San Andreas Fault and the Hayward fault. The complex tectonic activity in the areas has created earthquakes for thousands of years. The San Andreas fault is on the coastal side of the bay, where it meets the pacific oceans at a strait known as the Golden gate.**3)** bar-built estuary is when a lagoon or bay is protected from the oceans by a sandbar or barrier island, it is called a bar- built estuary.**4)** fjord estuary is a fourth type of estuary created by glaciers. They occur when glaciers carve out a deep, steep valley. Glaciers retreat and the oceans rushes into fill the narrow, deep depression.

Fairbridge(1980) defined an estuary as an inlet of the sea reaching into the river valley as far as the upper limit of tide rise, usually being divided into three sectors: 1) A marine or lower estuary in free connection with the open sea. 2) A middle estuary, subjected to strong salt water and fresh water mixing. 3) An upper or fluvial estuary characterized by fresh water but subjected to daily tidal actions. The limits between these sectors are variable and subjected to constant changes in the river discharges. An estuary can classified based on geomorphology, circulation pattern (salinity distribution) and tidal range. According to the geomorphology, the salinity profile of an estuary classifies the estuaries into 1. Salt-wedge estuaries, where the fresh water flow is higher than that of tidal flood, 2. Partially mixed estuary, where the tidal rise and fall is experienced and the seawater entering from the bottom starts low tide and getting submerged during high tide.

Estuaries form a transition zone between river environments and maritime environments. Estuaries are subject both to marine influences such as tides, waves, and the influx of saline water, and to fluvial influences such as flow of freshwater and sediments. Estuaries are quantitatively important in the modification of the supply of dissolved and solid materials from river to the ocean. Almost 85% of all the soluble and particulate weathered products are introduced into the coastal waters via estuaries. Estuaries are complex environments in which diverse processes Intervene. Nutrients are taken up by plants or recycled by sediments. Nutrients are controlled by inputs from land; plants biomass and tidal flow. Estuaries are important sites of nutrients recycling in the coastal environment. Estuaries have a continuous source of nutrients from their freshwater inputs.

Estuaries are major sites for accumulation of sediments along our coastline. Sediments are added to estuaries by rivers, by shore erosion, by primary production, by the sea, and by the atmosphere. An estuarine delta generally forms near the head of the estuary. The delta grows seaward, extending the realm of the river and expelling the intruding sea from the coastal basin. Lateral accretion by marshes may also play a major role, and in some estuaries deposition of marine sediments near the mouths is important. As a result of this processes, the estuarine basin is converted back into a river valley. Finally, the river reaches the sea through a depositional plain, and the transformation is complete. (Lauff, 1967; Schubel, 1971).

Recently with the increasing population and the rapid industrialization around the estuaries, they are becoming overloaded with more and more inorganic wastes. Many mining areas are situated on the estuaries.

Mining in Goa for Iron ore has been the most important economic activity contributing to the state revenue over the years. Many of the world's seaports are situated on the estuaries and this has resulted in customary sewage and other wastes to be disposed off directly into the estuary.

The metal distribution in the Mandovi estuary revealed preferential input through open-cast mining, industrial, fishing, and agricultural activities. The heavy riverine runoff associated with high rainfall associated with high rainfall influenced the distribution of Mn, Zn and Pb during monsoon. Mandovi River showed an increase in ammonia, PHc, Hg, etc. this river suggested contamination from domestic waste/organic matter, boat traffic and ship building activities. Though, jetty construction would disturb bed sediments and increase trace metals, micronutrients and organic load, increasing oxygen demand of riverine water.

Even disposal of wastes leads to contamination of rivers and lakes and also chronically affects the flora and fauna. Poorly planned human settlement in the coastal zone will lead to greater stresses on estuarine systems worldwide. Therefore there has been a great concern over the contamination of rivers e.g.: Minamata Bay episode, Jakarta Bay.

`The outbreak of a mysterious, non-infectious, neurological illness among the inhabitants living around the Minamata Bay in southwestern Kyushu Japan. The first case of an acute poisoning by heavy metal contamination in marine coastal area. The disease was caused by methyl mercury in fish. The source of methyl mercury was conversion of the inorganic mercury in the sediments by anaerobic methane synthesing bacteria.

Ore loading platforms are constructed along the bank of the river from where it is loaded on the barges and transported to harbor. Thus, the estuarine bed and associated mangroves located along the Mandovi are exposed to high influx of metal affluent from ferromanganese mining. Metals are introduced into the aquatic environment from different sources like geological weathering, industrial processing of ores and metals and use of metals and metal components, leaching of metals from garbage and solid waste dumps as well as animal and human excretions which contain heavy metal **(Forster and Wittmann.1979)**

The Mandovi estuarine system in Goa is perhaps the only river system in the country facing the ill effects of mining activity along the shoreline. Therefore the total production of iron, manganese, and ferromanganese ores comes from the mines located on the river basins. Domestic sewage, mining activities and industrial effluents are recognized as the most important problems in Goa. Goa has a vast potential for development of tourism because of its scenic beauty. All future developmental activities along this river basin will have impounding impact on the waters, which will naturally cause harmful effects to flora and fauna including man it is therefore very essential that the environment of Goa has to be maintained as clean as possible with simultaneous developments on all fronts.

1.2 LITERATURE REVIEW

Globally, studies on the distribution of heavy metals in the sediments have been carried out by a number of workers.

Study was done on the level of toxic metals (Mn,Zn,Pb,Cd,Co,Cu)was determined in sediment samples from Chenab River, Pakistan ., Heavy metal concentration in sediments of Ganga River was studied along a 37-km stretch by **Pandey(2016),** In Oshogbo- Township, SW-Nigeria studied the impact of untreated wastes discharge which showed trace metals in sediments. **Tijani (2005).**

India is rich of enormous bounding coastline and vast stretches of estuaries and backwaters. Major estuaries occur in the Bay of Bengal and west side estuaries are Mandovi and Zuari. The major estuaries on the east coast are Hoogly (Ganga), the Mahanadi, the Godavari, the Krishna and the Cauvery. The Mandovi and Zuari estuarine system receive greater attention because of the accessibility from the research organization nearby.

Tirumalairajan river estuary(2015), in the south coast of India has studied about the concentration of trace metals of only selected heavy metals. Most of metals were considered to be immobile due to the high availability in the residual fraction of heavy metals. They didn't pose any high ecological risk where it was proved that that the enrichment of heavy metals was related with geogenic and anthropogenic sources.

A study was carried out to examine heavy metals concentration in water as well as the sediments of upstream and downstream of the entry of the sewage to the **Tembi River, Iran(2014)**. The highest average concentration on downstream for Mn in sediments was 820.5ppm.

Ruth and Panda(2009) studied about the particle distribution, geochemical composition and sequential leaching of metals carried out in core sediments from the Brahmani and Nandira Rivers, India. There was a considerable variation in the concentration of heavy metals in Brahmani upstream, downstream as well as Nandira River sediments. Therefore this variation was due to the change in magnitude of industrial/mining waste and sewage being added to the river stretch at different locations. Zn, Cr, Ni and Mn were found.

Mustafakemalpasa stream located in the world's largest borate basin **(Turkey,2018)**Mining activities in addition to the geology of Mustafamalpasa catchment have for long been linked to its deteriorating water and sediment quality so a study was assessed to find out the contamination levels of heavy metals and other major elements. So the highest value was recorded for Cr, B, Ni, As and Zn this was due the nearby urban settlement and mining sites particularly of coal and chromium.

Mahanadi basin, India(2011) sequential extraction technique was used to study the mobility and dynamics of operationally determined chemical forms of heavy metals in the sediments and their ecological risk on the biotic species. The result revealed that there was a high environmental risk of Cd, Ni, Co and Pb which was due to higher availability in the exchangeable fraction which also poses an adverse impact on aquatic biota.

Sundararajan and Team (2017) they studied different types of indices which were used to assess the ecological risk of trace metal contamination in sediments on the basis of sediment quality. As sediments samples were collected from three sectors i.e. Pre-monsoon, Monsoon, and Post-monsoon. Trace metal concentration was higher in the inner sector during post-monsoon. This was due to the industrial discharge in Veraval Harbor but this Harbor is mostly affected by anthropogenic activities rather than natural process.

Banerjee, Senthilkumar (2012) studied about sedimentation and trace metal distribution in selected locations of Sundarbans mangroves and Hoogly estuary, Northeast coast of India. Cd, Pb, Co and Cu these Metals were highly enriched with other metals such as Zn, Ni, Cr and Mn showed no enrichment or depletion. Both Sundarbans mangroves and Hoogly estuary have been receiving considerable pollution loads from anthropogenic sources such as industrial, domestic and shipping activities in recent times.

Sankaranarayanan and Reddy (1973) studied the distribution of dissolved Cu in the inshore waters Goa coast. They attributed increased land discharge from natural and artificial sources for the increase in dissolved Cu in the inshore waters.

The Changjiang (Yangtze River) is one of the largest rivers in the world and featured by a large river- dominated delta and adjoining estuary. **Zhongfa and Fangliang (2019)** the study presents the concentrations and chemical speciation of eight heavy metals (Zn, Cu, Ni, Pb, Cr, Hg, As, Cd) in 34 surface sediment samples collected from the Changjiang (Yangtze River) estuarine area, which aims to investigate the potential sources and environmental risks of heavy metals. It is widely known that the bulk concentrations of heavy metals in terrigenous sediments are primarily determined by sediment source, chemical weathering, hydrodynamic sorting during sediment transport and depositional processes and post- depositional diagenetic alteration. Human activity is another major factor that can greatly enrich heavy metals in recently deposited sediments.

Alagarsamy (2006) studied about the concentration and distribution of selected trace metals in surface sediments of the Mandovi estuary to determine the extent of anthropogenic inputs from mining activities and the estimate the effects of the monsoon on geochemical processes in this tropical estuarine system. An important observation is that, in general, lowest metals concentrations are found during the monsoon, compared to pre and post monsoon. The enrichment of Fe and Mn reflects the intensity of anthropogenic inputs related to iron ore processing in the upstream region of the estuary. Mn showed higher values in the pre monsoon period in the upstream region of the estuary. Cu and Zn enrichment in the river mouth region, associated with high organic carbon contents, is indicative of the influence of organic wastes from municipal sewage entering the estuary.

Veerasingam, Fernandes (2015) studied about the concentration of seven trace metals (Fe, Mn, Cu, Cr, Co, Pb and Zn).all sediment core showed enrichment of trace metals in upper part of core sediments and decrease in concentration with depth. This was suggested to be by excess of anthropogenic loading including mining activities occurred during the recent past.

Metals (Cu, Zn, Pb, Cd, Ni, and Fe) contamination in sediments from a tropical estuary (Ebrie Lagoon, Ivory Coast) was assessed using pollution indices, and sediment quality guidelines (SQGs). The results demonstrate that increased input of the studied metals occurred over the past 6 years compared to that from 20 years ago, due to rapid population growth, along with the increase of industrial and agricultural activities in the vicinity of the estuary. Cluster analysis (CA) and principal component analysis (PCA) investigation revealed that Cu, Zn, Cd, and Co result mainly from anthropogenic sources while Pb, Ni, and Fe may be of natural origin. **(Trokourey &Bernard Soro 2015).**

The study reported an assessment of metal (Fe, Mn, Zn, Cr, Cu and Pb) contamination in surface sediments of a tropical estuary from Goa-the West coast of India. Surface sediments were collected along the 35km stretch of the Zuari estuary on monthly basis for a period of one year and sampled were analyzed for texture, organic carbon(OC) and metals. The contamination factor and Geo- accumulation index (I Geo) revealed moderate contamination of Pb and Cr. Factor analysis suggest role of Fe-Mn oxy-hydroxide, OC and textural variables in abundance of trace metals in sediments. An attempt was made to understand the impact of mining on the Zuary estuary by comparing the present data(during mining ban period) with earlier published reports(during extensive mining period). It revealed influence of mining on the concentrations of Fe and Mn in surface sediments, but had no impact on the concentration of Cu, Cr, Zn and Pb in the Zuary estuary. **(Gaonkar and Matta 2019)**

Gandhi , kanagaraj (2024)study done in puducherry and cuddalore coasts of tamil Nadu, India states that these studies have been carried out to investigate the impact of anthropogenic, industrial, and other influences on surface sediment. Heavy metals were absorbed by alluvial sands, silts, clays, and organic matter, which is also an indication of pollution in the environment. As a result, the metal content in pre-monsoon sediments is lower in puducherry coastal areas than in Cuddalore coastal areas.

It is evident from above, though some information is available on the distribution of metals, in sediments, in recent years there has been a great deal of concern over the magnitude and effects of mans impact on estuarine environment. As Mandovi and Zuari estuarine system in Goa is perhaps the only river system in the country facing ill effects of mining activity along their shoreline. And also majority of the industrial activities of the state are concentrated over this river basin. Hence, an attempt has been made to study the distribution of trace metals in surface sediments of Mandovi estuary with following objectives.

OBJECTIVES:-

- **To study the distribution pattern of trace metals (Fe, Mn, Co, Cu, Zn, and Ni) in surface sediments of Mandovi estuary.**
- **To study the spatial variation of trace metals in surface sediments of Mandovi estuary.**
- **To study the seasonal variation of trace metals in surface sediments of Mandovi estuary.**

CHAPTER 2

PHYSIOGRAPHY OF THE STUDY AREA AND SAMPLING TECHNIQUES

2.1PHYSIOGRAPHY OF THE STUDY AREA

The State of Goa

The smallest Indian state, Goa has the shortest coastline distance of 101km. It is a home to many captivating beaches worldwide. Goa is enveloped by the Indian state of Maharashtra and Karnataka, with the Arabian Sea composing its western coast. Goa encompasses an area of 3702km2(1.429 sq mi) it lies between the latitudes 14 ° 53′ 54″ N and 15 ° 40′00″ N and longitudes 73 ° 40′33″ E and 74 ° 20′13″ E. Nine rivers rise in the Ghats and flow towards the Arabian Sea. These are Terekhol, Chapora, Mandovi, Zuari, Sal, Saleri, Talpona, Loliem and Galgibaga. Out of which Mandovi and Zuari are the most important for the economy of the state. Both these rivers are interconnected by the Cumbarzua canal.

The Mandovi and the Zuari are the two primary rivers in the State of Goa. These two rivers are situated within 5km near Panaji. Mandovi joins with the Zuari at a common creek at Cabo Aguada, forming the Mormugao harbor. The mouths of the two rivers are funnels shaped and are separated from one another. The two estuaries though partially landlocked are exposed to constant flushing and flooding by the semidiurnal tides, which considerably affect the environmental features of the area.

Diurnal changes in the temperature , salinity, pH, oxygen in the Mandovi and Zuari estuaries in relation to flood , ebb of the semidiurnal tides show significant correlation with the seasonally changing fresh water drainage and the land precipitation in the two ecosystem and the atmospheric temperature. Goa being in the Torrid Zone and near the Arabian Sea has a hot and humid climate for most of the year. The month of May is usually the hottest, seeing daytime temperatures of over 35°C coupled with high humidity.

Minerals products are ferromanganese, bauxite and iron ore contributing substantially to the economy of the state through exports. Iron ore is the leading commodity in that area. The iron ore deposits are considerable in terms of their total tonnage. Goa had been exporting iron ore even before its merger with India and there are extensive deposits in the northern part of the state at Advalpal, Velguem Pale. Some of the important and productive mines are located in the northern and eastern parts of Goa.

The majority of Goa's land cover consists of laterite, which is rich in iron-aluminium oxides and reddish in colour. Further inland and along river banks, the soils are the mostly alluvial and loamy.

2.1.1 RIVER MANDOVI

Mandovi is the major river of Goa. The Mandovi formerly known as the **Rio de Goa** is a river described as the lifeline of the Indian state of Goa. The Mandovi and the Zuari are the two principal rivers in the state of Goa. Mandovi joins with the Zuari at a common creek at Cabo Aguada, forming the Mormugao harbor. The river is one the main West flowing rivers of Goa state. The river runs in the north- east direction for about 5km and then follows in the west ward direction. The Mandovi basin lies between north latitudes of 15 °15' to 15 °40' and east longitudes of 73 ° 15' to 73 °45' approximately.

The Mandovi River drains an area of 1550 sq km., which lies in Tiswadi, Bardez, Bicholim, Sanguem and Ponda Taluka of Goa State. The river has total length of 81 kilometers (50 miles) - 1km (0.62 miles) in Maharashtra, 35km (22 miles) in Karnataka, and 45 km (28 miles) in Goa. It originates from a cluster of 30 springs at Bhimgad in the Western Ghats of Belgaum district in Karnataka state. The river has total 2032 km2 catchment area are of which 1580 km2, 375 km2 and 77km2 catchments area are in Goa, Karnataka and Maharashtra respectively. With its cerulean waters, Dudhsagar falls and Varapoha falls, it is also known as the Gomati in a few places. The Mandovi enters Goa from the north via the Sattari Taluka and from Uttara Kannada district of Karnataka near the castle rock Rly. Stn. the Mandovi flows through Belagavi, Uttara Kannada in Karnataka and Cumbarjua, Divar and Chorao in Goa, eventually pouring into the Arabian Sea. The tributaries of Mandovi or Mhadei include Nerul River, St Inez creek, Rio de Ourem, Mapusa River, Vavanti River, Udnai River, Dudhsagar River, Ragada River and Kotrachi Nadi. The Cumbarjua Canal, which links both rivers, has made the interiors of the Mandovi accessible to ship carrying iron ore. Iron ore is Goa's prime mineral and it is mined in the eastern hills. Three large freshwater isles- Divar, Chorao and Vanxim are present in the Mandovi near the town of old Goa. Its post-monsoon and pre-monsoon flow is mainly dominated by the semi diurnal tides having a maximum range of 2.3m. it has a large tributary system and has a number of islands, sharp turns and shallow depths along its course.

The average rainfall in the Mandovi basin is 3484 mm. the lowest and highest temperatures recorded are 9.30 °C during January 1937 and 42.6 °C during March 1959 respectively. March to May is the hottest months of the year and December to January are the coldest months of the year.

2.1.2 GENERAL CLIMATOLOGY

The atmospheric temperature of Goa varies between 15 and 45, maximum being in April-May and minimum in December- January. There is a secondary peak in October-November and secondary minimum during June-August. In Goa, normally three seasons prevail in a calendar year depending on the influence of southwest monsoon. They are pre-monsoon, monsoon, and post-monsoon seasons. The pre-monsoon extends from February to May. This is the warmest period of the year and experiences occasional showers towards the end of the May. The average relative humidity is around 80%. This season is followed by the south-west monsoon season extending from June to September during which Goa receives most of its rainfall. The post-monsoon period extending from October to January is a fair and stable season.

2.1.3 STATION LOCATIONS

The area of investigation covers the Mandovi estuary in Goa (west coast of India). It comprises of 11sampling station each in Mandovi estuary. These stations cover from mouth of the river to the head (**fig.1.**). Sediment samples were collected at each station during Monsoon (June-July), Pre-Monsoon (April-May), Post-Monsoon (November-December).

The stations were named as **Me01, Me02, Me03, Me04, Me05, Me06, Me07, Me08, Me09, Me10,** and **Me11.**

2.1.4 SAMPLING PRETREATMENT PROCEDURES

This samples for the study were collected in three season, Monsoon (June-July), Post-Monsoon (November-December), Pre-Monsoon (April-May) during 2014 and 2015.

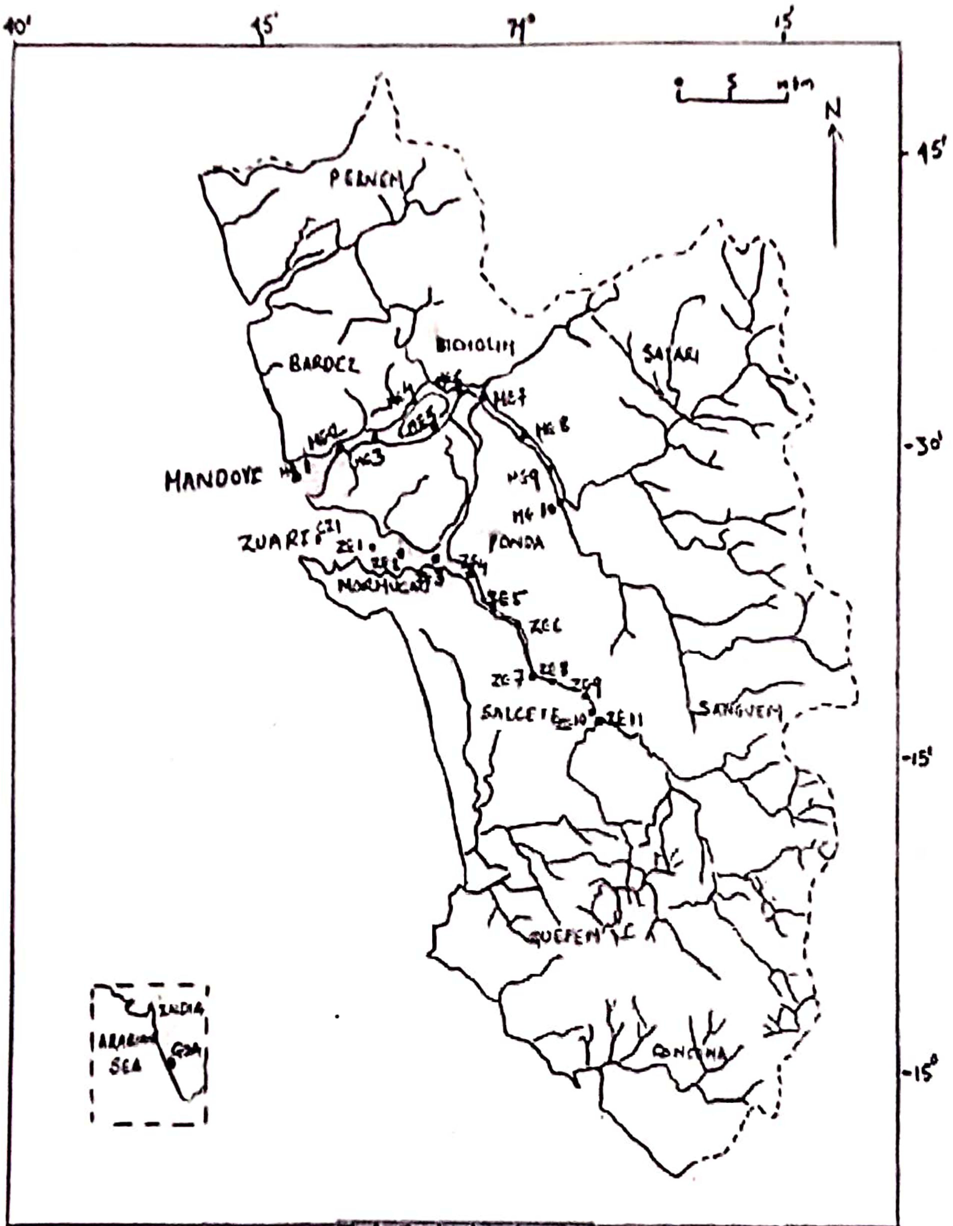


Fig 1. Station location map

Fig 1 Station Location map of Mandovi estuary

2.2. SAMPLING TECHNIQUES

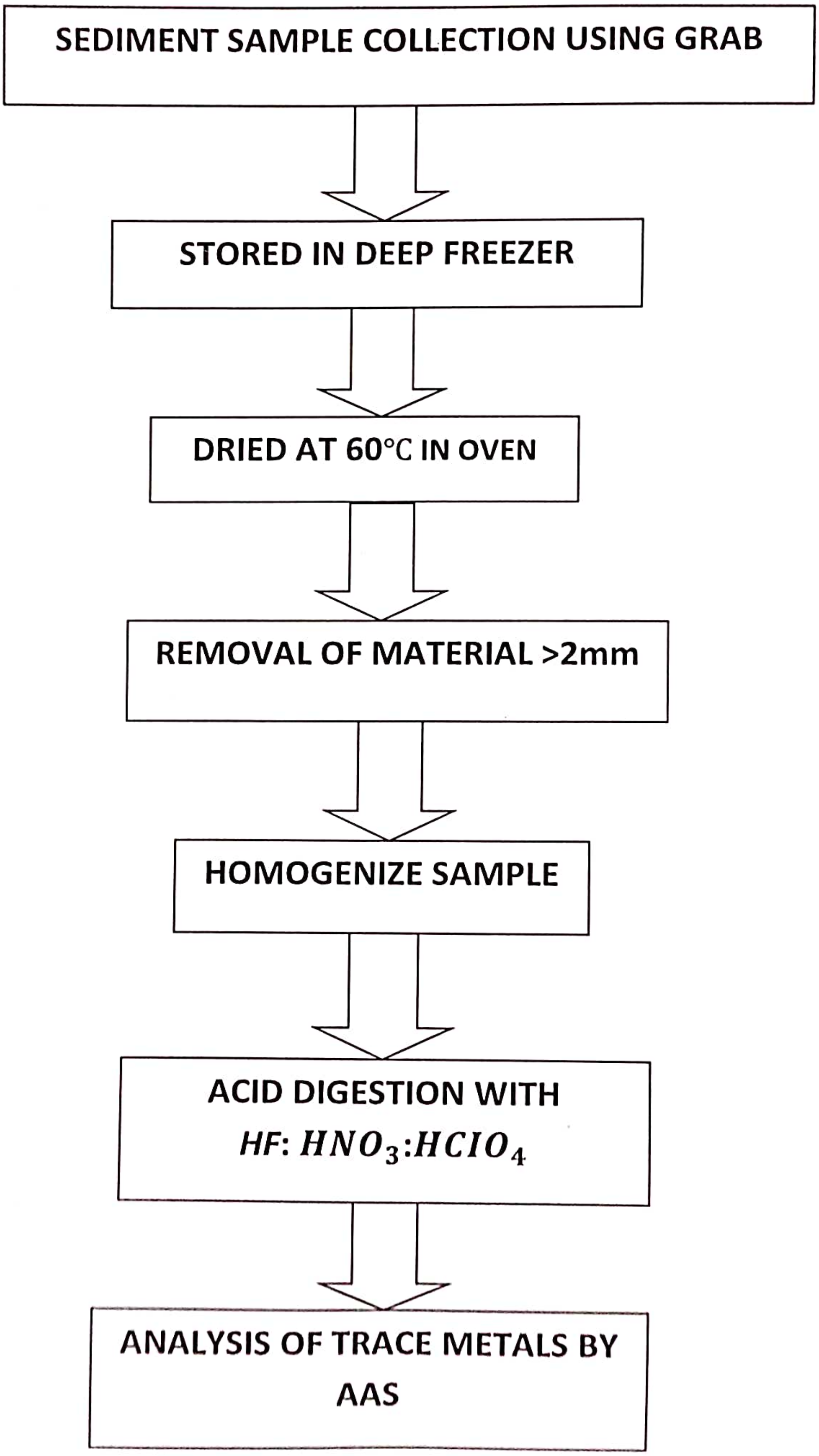
2.2.1 COLLECTION OF THE SEDIMENT SAMPLES

The surface sediment samples were collected using Petersons grab during pre-monsoon, monsoon, post-monsoon period. Collected samples were then transferred to clean polythene bags and kept in ice during transport. The samples were stored in deep freezer.

2.2.2 Digestion of sediments samples for trace metal analysis

Accurately weighed(0.3g) of finely grounded sample is transferred to Teflon beakers and is treated with 7:3:1 (HF:HNO3:HClO4) acid mixture and dried on dried on hot plate for 1hr, then 5ml of same mixture is added and dried again for 1hr. Then 2ml of HCL is added and dried completely. Then 10ml 1:1 HNO3 is added and warmed. The residue is filtered and diluted to 100ml with distilled water **(Loring and Rantal, 1992).**

Fig.2. ANALYTICAL PROCEDURE FOR ESTIMATION OF TRACE METALS FROM SEDIMENTS.



CHAPTER 3

ANALYTICAL METHODS

3.0 ANALYTICAL TECHNIQUES

All the measurement was carried using Atomic Absorption Spectrophotometer (AAS) with Air-acetylene fuel mixture for the determination of trace metals. The chemicals used in the analysis are analytical grade reagents. Milli Q water was used throughout the analysis.

3.1Trace Metals

Atomic Absorption Spectroscopy with or without flame is a versatile technique for the determination of trace metals. This technique is sufficiently accurate and free from interference, Hence this technique has been applied for determination of Fe, Mn, Co, Cu, Zn, and Ni. Standard stock solution of each metal was prepared using Merck solution with concentration of 1ml=1000ppm. Standard solutions were used to calibrate the instrument for direct reading using appropriate cathode lamps and wavelength (Table1). All instrumental setting was made for each metal as recommended in the operation manual of the instrument. The sample solution containing trace metals obtained after digestion process were aspired into AAS. The readings for each element were noted from the digital display.

Table 1: Optimum instrumental conditions for elemental analysis by AAS.

S.No.	Element	Wavelength	Fuel Mixture	Flame type	Range of standards.(ppm)
1	Fe	372.0	Air-acetylene	Oxidizing	2-9
2	Mn	279.5	Air-acetylene	Oxidizing	1-3.6
3	Zn	213.9	Air-acetylene	Oxidizing	0.4-1.5
4	Cu	324.7	Air-acetylene	Oxidizing	1-5
5	Co	240.7	Air-acetylene	Oxidizing	2.5-9
6	Ni	234	Air-acetylene	Oxidizing	1.8-8

Ox-Oxidizing Flame

The concentration of trace metals in sediments sample was computed using following equation:

C=A x D

D=V/weight of the sample

Where, A=AAS reading

d= dilution factor

V=volume of the solution after digestion

3.2 ACCURACY AND PRECESION

Accuracy is the degree of closeness of a measured or calculated quantity to its (true) value. Accuracy is closely related to precision, also called reproducibility or repeatability, the degree to which further measurement or calculations show the same or similar results. The precision and accuracy of the analytical procedure adopted and evaluated from replicate analysis and standard solution of known concentration.

Standard deviation and coefficient of variation of each constituent were evaluated using the following equation

Standard deviation (σ) = $\sqrt{(\mathrm{Xi} - \mathrm{X})2_{-n}}$

Where Xi = represents the determined value

X = arithmetic mean

N = number of determinations.

Coefficient of Variation (%) = σx100/X

The relevant data is incorporated in **Table 2**

Table 2: Statistical data for trace metals in sediments.

Elements	Quantity taken for analysis	Found	Standard deviation	Coefficient of variation
Fe	9	9.01	0.17	1.91
Mn	3.6	3.5	0.03	1.86
Co	9	9.18	0.18	1.28
Cu	4	4.002	0.11	2.95
Zn	1.5	1.51	0.02	1.43
Ni	1	0.98	0.052	5.31

CHAPTER 4

RESULTS AND DISCUSSSION

4.1 TRACE METALS IN SEDIMENTS

Estuarine sediments are major reservoirs for the metals. Metals get transported to the estuaries either in the form of suspended matters or dissolved ions, which are subsequently removed from water and are absorbed onto and finally incorporated into the sediments. Generally, the concentration of trace metals in river sediments reflect the occurrence and abundance of certain rocks or mineralized deposits in the drainage area of the river **W Salomons, AJ De Groot.**

Concentrations of trace metals in sediments are mainly influenced by the mineralogical and chemical composition of suspended matters, anthropogenic activities, enrichment by organism, and various physicochemical processes **(Singh et al.2005; Jain et al. 2007).**

The distribution of sedimentation in the estuary depends on several factors such as flocculation, coagulation, precipitation and Estuarine turbidity maximum (ETM). As a consequence of these dominating processes, the sediments are usually dominated by coarse- grained material in the lower estuary, and gravel in the upper estuary. **(Flemming and Hansom, 2011).**

An important industry in Goa is mining of iron and manganese ore. Active mining goes on at present at a number of locations distributed along a belt that stretches from north to south in the central part of the state. The iron ore from these sites is transported in open trucks to a number of nearby convenient locations on the banks of the Mandovi and Zuari estuaries. From these locations the ore is transferred to berges, which takes the ore to mormugao Port, from where it is shipped to others places. The mining operations and the process of transporting the ore generate dust that is then carried by winds to nearby areas. It is expected that some of the dust would settle in the waters of the two estuaries, leading to significant concentrations of dissolved and particulate trace metals. Raw sewage disposal into the Mandovi and Zuari estuaries has been a common practice throughout the history of the estuaries. Treatment of sewage from major cities like Panaji before its disposal into estuary is a recent development. With increasing population on the banks of the estuaries, the amount of sewage dumped in the estuary has also increased. Because of the high concentration of people along the coast and the increasing urbanization, coastal areas are under mounting pressure worldwide.

According to **Williams and Micallef (2009)**, an urban coast serves large populations with well-established public services such as schools, banks, restaurants, and a well- marked central business district. Marine ecosystem is being threatened by the discharge of untreated sewage wastes, industrial effluents like ores and minerals, leaching of metals from garbage and solid waste. Animal and human excretion contains heavy metals which ultimately affects the sustainability of living resources and public health. The accumulation of heavy metals eventually produces reactive oxygen species that can cause oxidative stress, which may lead to the production of various diseases. Metals induced neuronal toxicity, carcinogenicity, and perturbation to the endocrine system. Metals also cause serious instability to the transcriptomics, the proteomics, as well as to the metabolomics of the invertebrates used in toxicity test (Morgan et al., 2007).

4.1.1.1 Iron

Iron is the 4th most abundant element on earth and is found naturally in the water in diverse forms. Iron is essential trace element which is required by living things. Iron is found through Natural and Human related processes. Mining in Goa is finished by open cast strategy which required the evacuation of overburden overlying the iron ore formation. The normal yearly production of iron metal is about of 15-16 million tons. The main iron ore bearing zone is divided into four separate areas by major faults. These areas are: 1) Bicholim –Pale area, 2) Sancordem area, 3) Shigao-Kalay area, 4) Sanguem- Quepem area. The presence of Iron as a trace metal in its sediments can be influenced by various factors such as weathering of rock, industrial activity, and agricultural runoff. The metal distribution in Mandovi estuary revealed preferential input through open cast Iron Ore mining, Fishing etc. Data distribution of Iron (%) in sediment varied from12.19 to 3.5 during Pre-Monsoon (**Table 3**), from11.9 to3.4 during Monsoon (**Table 4**), from 11.5 to 3.22 during post-monsoon (**Table 5**).

Spatial variation of Iron **(Fig.3)** recorded higher concentration at station 8 and 10 during pre-monsoon season whereas; during monsoon and post-monsoon seasons higher values are recorded at 5 and station 2. Therefore through the spatial variation concentration of iron shows more at the head of the river. Therefore it shows high values from mid of estuarine system towards the head of the river. The enrichment of Fe and Mn reflects the intensity of anthropogenic inputs related to iron ore processing in the upstream region of the estuary, however, the highest enrichment levels were not found near the mouth region. There is detectable anthropogenic inputs to the Mandovi estuary.**(R. Alagarsamy 2006).** Also, **Mesquita and kaisary (2007)** reported higher concentration of Fe and Mn in the mid- estuarine region in addition to the upper estuarine region during 2002. The mining activity along the central portion of the state involved open cast mining largely for iron in the northern portion and iron and manganese in the southern portion. . The lower estuary near the mouth is subjected to the action of strong winds and tides as it is interconnected with the sea or ocean. strong tidal and wave energy is capable enough to carry finer sediments particles towards the upper estuarine region of the estuary **(Siraswar and Nayak, 2011).**

Further, solublization may also be the cause of the metal loss from the sediment. Solublization could result from the degradation of organic material in estuary sediments, which releases soluble organ metallic complexes into the estuarine water **(Muller, G., & Forstner, U., 1975).** It's possible that materials from an iron ore processing plant and ore spills at a loading point nearby are to blame for the higher concentrations that have been reported at some locations. Although iron ore mining is non-operational at present in Goa, the metal released and adsorbed onto the sediments of Mandovi- Zuari Estuary in the past is not permanently sequenced **(Huang et al., 2012)**, and therefore it can be mobilized.

Seasonal variation **(Fig.4)** in sediments collected from Mandovi Estuary region showed highest concentration Pre-Monsoon followed by Post-Monsoon. Lowest metal concentrations are found during monsoon compared to pre and post monsoon seasons. During pre monsoon period mining activities are very intensive. A large number of barges transport iron and manganese ores to the adjoining Mormugao harbor along the Mandovi River. In addition to these, high temperature favours decomposition of organic matter, by setting the trace metals in the bottom sediments which can be resuspended by tides (Martin and Whitfield, 1983). All these factors must have kept the concentration higher in pre- monsoon period. These combined effects might have resulted in higher concentration of metal during pre monsoon period. During monsoon, river discharge is very high and shipping while mining activities are very less compared to other seasons. Because of the rough weather at the mouth of the estuary, loading of iron ore is at its minimum. The dilution due to precipitation and reduced shipping and mining activities could have kept the concentration low.

Organic matter and Grain size are the main factors affecting the distribution of heavy metals in the sediments and these heavy metals become enriched in the sediments when its organic matter is higher and particle size is smaller. During the Pre-monsoon period, higher concentrations of iron are observed throughout the estuary, which may be attributed to high spillage during transportation of iron and ferromanganese ores down the estuary (Alagarsamy, 2006). Concentration of iron registered highest values during the premonsoon period followed by post monsoon and monsoon in the Mandovi River.

Due to its natural origin and prominence as one of the most prevalent elements in the earth's crust, Fe is one of the most abundant elements in the residual fraction and is therefore present in significant quantities.

Table 3: Data on variation of trace metals (Co, Cu, Zn, Fe, and Mn) in surface sediments of the Mandovi estuary, Goa during Pre-Monsoon season.

Station No.	Sample no.	Fe (%)	Mn (%)	Zn (ppm)	Cu (ppm)	Co (ppm)
1	Me01	3.50	0.13	230.7	2.775	42.68
2	Me02	4.74	0.66	58.66	16.79	58.91
3	Me03	8.93	0.44	49.26	11.18	55.02
4	Me04	6.04	0.27	53.12	7.18	51.6
5	Me05	11.29	0.37	48.49	16.36	58.88
6	Me06	9.33	0.27	41.13	8.09	56.97
7	Me07	6.18	0.1	56.33	5.89	53.1
8	Me08	12.19	0.32	45.94	14.41	65.01
9	Me09	9.81	0.19	33.92	7.35	60.01
10	Me10	11.61	0.23	36.63	7.83	63.07
11	Me11	10.78	0.63	46.94	13.88	67.46
	Average	8.581	0.3281	63.74	10.15	57.51
	Max	12.19	0.66	230.7	16.79	67.46
	Min	3.5	0.1	33.92	2.775	42.68
	Std dev	3.138	0.196	67.2	4.9	7.81

Table 4: Data on variation of trace Metals (Co, Cu, Zn, Fe, and Mn) in surface sediments of the Mandovi estuary, Goa during Monsoon season.

Station No.	Sample No.	Fe (%)	Mn (%)	Zn (ppm)	Cu (ppm)	Co (ppm)
1	Me01	3.40	0.1	8.68	2.66	61.95
2	Me02	9.94	0.57	22.31	4.15	74.91
3	Me03	7.32	0.27	24.87	3.47	73.95
4	Me04	7.74	0.28	20.13	1.29	72.25
5	Me05	11.9	0.35	26.82	4.13	78.31
6	Me06	5.5	0.22	32.89	5.68	81.34
7	Me07	7.36	0.2	16.3	0.12	71.75
8	Me08	6.76	0.10	12.76	0.78	70.29
9	Me09	7.71	0.09	15.25	1.1	73.36
10	Me10	8.54	0.24	15.09	0.82	74.86
11	Me11	6.15	0.02	7.6	1.03	71.38
	Average	7.483	0.2218	18.42	1.33	73.12
	Max	11.9	0.57	32.89	5.68	81.34
	Min	3.4	0.02	7.6	2.66	61.95
	Std dev	2.570	0.1737	8.47	2.85	5.76

Table 5: Data on variation of trace Metals (Co, Cu, Zn, Fe, and Mn) in surface sediments of the Mandovi estuary, Goa during Post-Monsoon.

Station No.	Sample No.	Fe (%)	Mn (%)	Zn(ppm)	Cu (ppm)	Co (ppm)
1	Me01	5.5	0.19	12.58	3.86	77.09
2	Me02	11.5	0.43	32.42	7.28	88.31
3	Me03	8.44	0.42	22.54	0.26	83.95
4	Me04	6.18	0.22	14.1	3.22	79.43
5	Me05	10.18	0.34	21.64	0.94	84.87
6	Me06	7.09	0.22	16.05	2.82	80.71
7	Me07	7.64	0.32	13.11	3.27	80.23
8	Me08	8.78	0.24	21.94	1.67	83.05
9	Me09	9.14	0.15	15.67	2.5	82.42
10	Me10	3.22	0.33	23.91	8.45	88.18
11	Me11	4.63	0.54	20.3	6.02	91.11
	Average	7.4818	0.3090	19.478	2.33	83.577
	Max	11.5	0.54	32.42	7.28	91.11
	Min	3.22	0.15	12.58	8.45	77.09
	Std dev	2.7058	0.1301	6.58	4.66	4.65

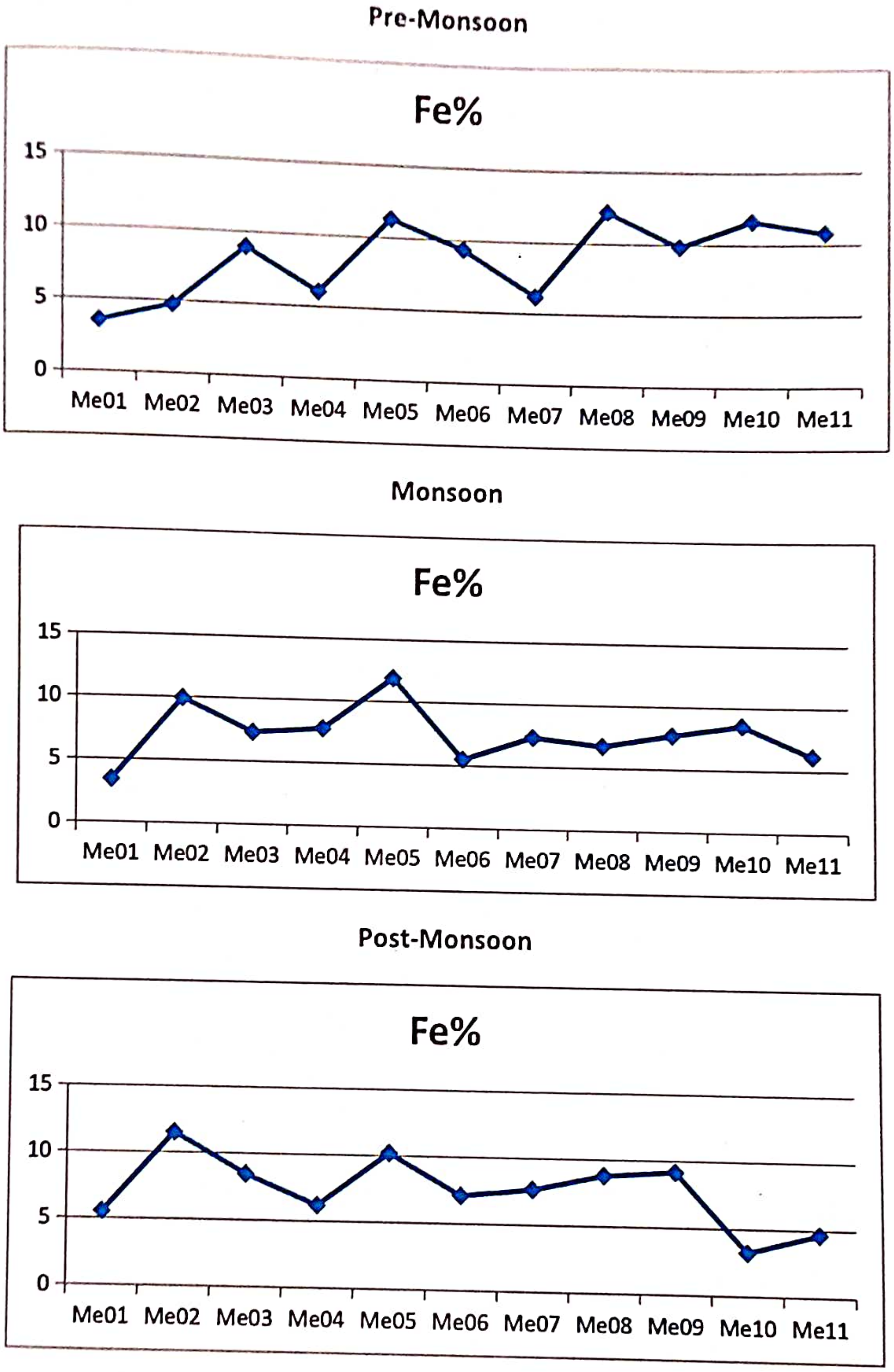


Fig.3. Spatial variation of Iron in surface sediments of Mandovi Estuary during Pre-Monsoon, Monsoon, Post-Monsoon.

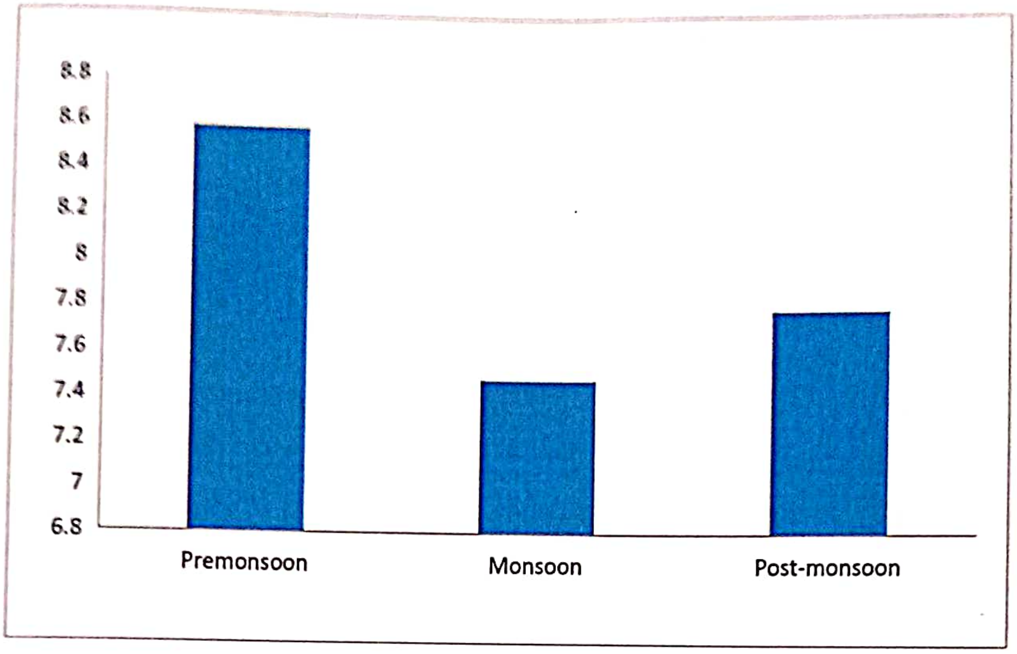


Fig.4: Seasonal variation of Iron in surface sediments of Mandovi Estuary.

4.1.2 Manganese

Manganese is a ferroalloy metal. It is hard, heavy, and silvery metal. It is exploited as ore as well as nodules on the deep seafloor. It is found that sediments from the immediate vicinity of river confluences, those of finer texture, and also those that are brownish in colour are generally more enriched in manganese. The mineralogy and geochemistry of manganese ores composed of higher oxides is especially complex, but pyrolusite, cryptomelane, romanechite, todorokite, and birnessite may be named as common representatives. Manganese occurs naturally in sediment, yet anthropogenic sources, such as industrial waste water and mining, increase Mn concentration. However, the environmental risk of bioavailable Mn is often overlooked and infrequently addressed.

Manganese ores are associated with iron ores and occur as pockets of various sizes in the form of concretionary pebbles in shale's. Iron and Manganese are belts extend from south-east to north-west of the state. Mn is used to produce a variety of important alloys and to deoxidize steel and desulfurize. It is also used in dry cell batteries, used as a black-brown pigments in paints and it an essential element for living creatures.

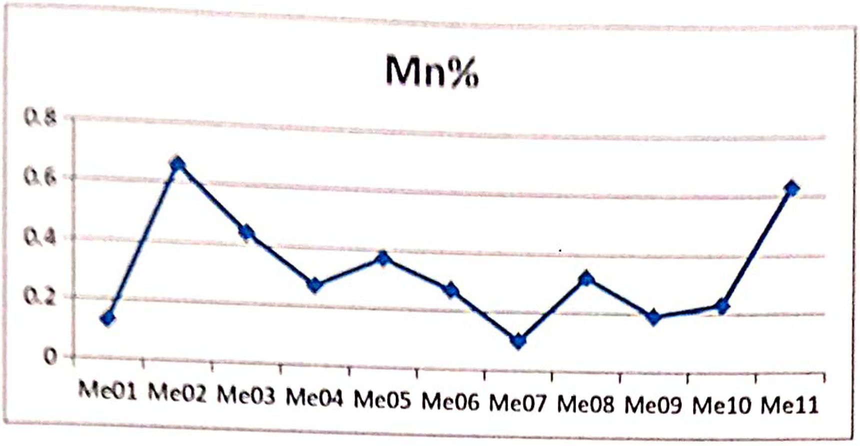
Data on variation of Manganese (%) in sediments varied from0.1 to 0.66 during Pre-monsoon **(Table 3)**, from 0.02 to 0.57 during Monsoon **(Table 4)**, and from 0.15 to 0.54 during Post-monsoon **(Table 5)**. The comparative analysis of trace metals revealed the Fe and Mn were highly enriched in the Mandovi Estuary compared to all other Indian Estuaries.

Spatial variation of manganese **(Fig.5)** recorded higher concentration at station 2 and 11during pre-monsoon where as in monsoon it was high at station 2 and lowest at station 11. In post-monsoon the highest value was recorded at station 11 and lowest at station 9. The high value at station 2 may be due to spillage of ore during loading may increase the concentration of manganese. An important observation is that, in general, lowest metal concentrations are found during the monsoon, compared to the pre and post monsoon. Manganese is mined in South Goa near Sanguem, therefore higher concentrations of Mn are found near head region. In addition, concentration of Mn Is found to be higher in lower middle estuary than upper middle estuary indicating lower middle estuary as favourable location for higher metal concentration. Reduced Mn concentration in the surface sediments might be due to dissolution and mobility of Mn ions which are easily removed from the pore water of sediments to the upper water columns through active diffusion and advection processes (Janaki-Raman et al., 2007).

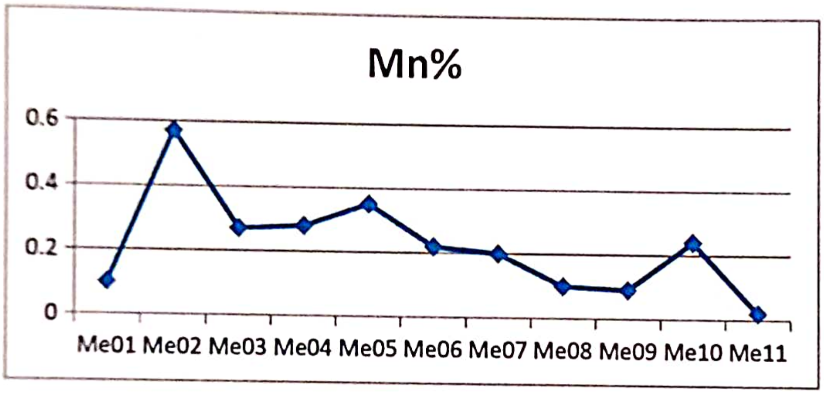
Seasonal variation of manganese **(Fig 6)** in sediments collected from Mandovi estuary shows highest concentration during pre-monsoon followed by post-monsoon. Metals released into the environment through human activities in substantial quantities end up as suspended materials in estuarine waters. The suspended matter acts as a scavenger for many trace metals (Burton and Liss, 1976). Increase in Mn concentration in sub surface layers in pre monsoon can be attributed to increased reduction of Mn oxyhydroxides which is microbially mediated (Lovely, 1995). Lower concentration of manganese is observed during monsoon season. This can be due to high energy conditions which are prevailed in the lower estuary/bay both during monsoon and pre monsoon because of consistent estuarine turbidity maximum (Rao et al., 2011).

This high concentration can be due to the anthropogenic sources which can be influenced by increasing urbanization along the coastal areas ,according to Williams and Micallef (2009), an urban coast serves large populations with well established public sectors such as schools, banks, restaurants, and a well marked central business district. Even mining plays a major role in increased Mn in surface sediments of Mandovi River. The heavy riverine runoff associated with high rainfall influenced the distribution of Mn during Monsoon Season.

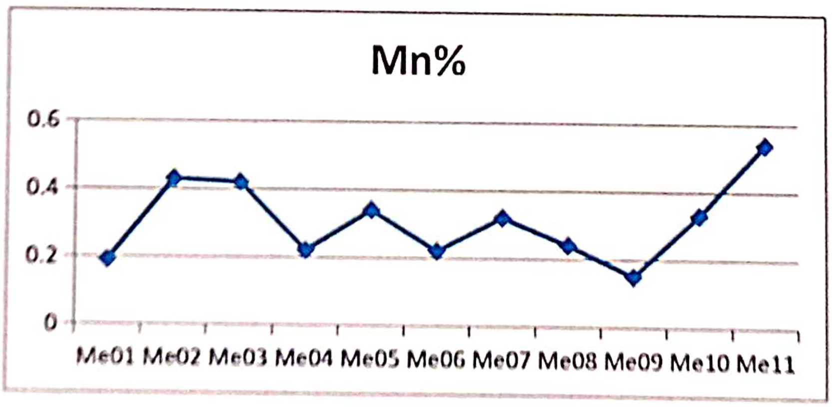
Pre-Monsoon



Monsoon



Post-Monsoon



g.5: Spatial variation of Manganese in surface sediments of Mandovi Estuary uring Pre-Monsoon, Monsoon, Post-Monsoon.

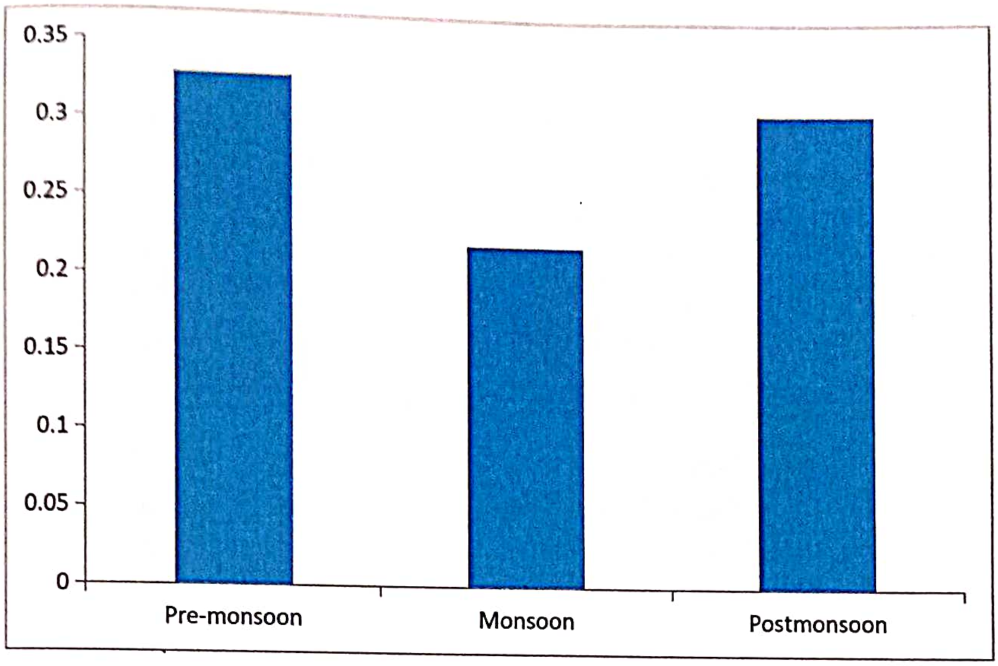


Fig.6: Seasonal variation of Manganese in surface sediments of Mandovi Estuary.

4.1.3 Cobalt

Cobalt is a shiny, gray, brittle metal that is best known for creating an intense blue color in glass and paints. Cobalt occurs naturally in soil, rock, air, water, plants, and animals. Most cobalt is mined as a byproduct of copper or nickel. Its concentration is high at the surface due to a major input from the atmosphere, and its concentration decreases with depth as dissolved cobalt is sorbed onto sinking particles and removed to the ocean sediments. Cobalt is obtained from the following three main type of ore deposits: 1)sediment- hosted stratiform copper deposits, such as those in the central African copper belt in the (DRC) and Zambia;2)magmatic nickel sulfide deposits, such those found at Sudbury, Canada, and Russia;3) nickel laterite deposits, which are found in tropical regions. Cobalt is also found in manganese nodules and crusts on the deep seafloor, but seafloor deposits are not currently being mined. Laterite deposits form in warm, humid, tropical or subtropical environments where igneous rocks with little silica are broken down by chemical weathering; in these types of deposits, cobalt is concentrated in the weathered rock. Cobalt and nickel are mostly found in dissolved form.

Globally, the leading use of cobalt is in rechargeable batteries to help increase battery life and stability and due to reduce corrosion. Cobalt also plays a vital role in human and animal health; it is an essential element in vitamin B12, which helps ensure proper brain function and aids in the formation of red blood cells.

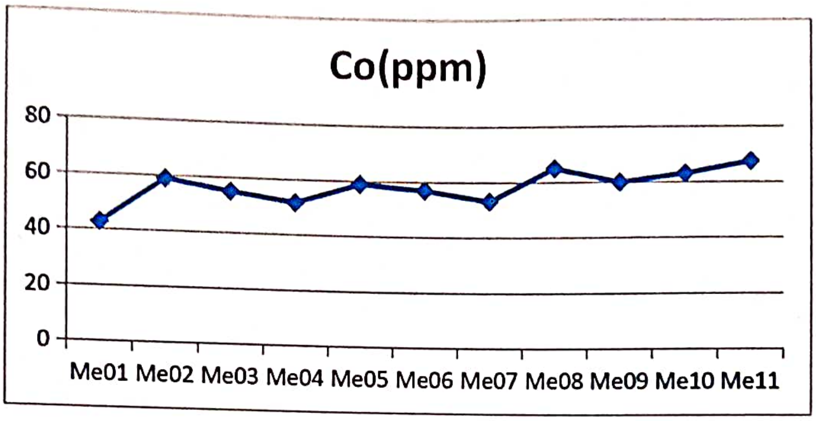
Data variation of Cobalt (ppm) in surface sediments of Mandovi varied from 42.6 to 6767.4 during pre-monsoon **(Table 3)**, from 61.9 to 81.3 during Monsoon **(Table 4)**, and 77.09 to 91.1 during Post-monsoon season **(Table 5)**.

Spatial variation of Cobalt **(Fig 7)** shows high concentration at station 11 during Pre-monsoon period that is in April and May. Whereas during monsoon and post-monsoon season the higher values are recorded from station 6 and station 11 respectively. However, comparatively higher values are recorded from the head and mouth region of the estuary. The heavy metals are added to the sediments in study area by two main pathways, via river run discharge and land runoff. The processes that influence the grain size variation of sediments are primarily supply or source of material and transportation, deposition and redistribution of sediments with in an estuary. In addition geomorphology of the estuary water moments owing to the tidal cycle also contributes to the distribution of sediment component.

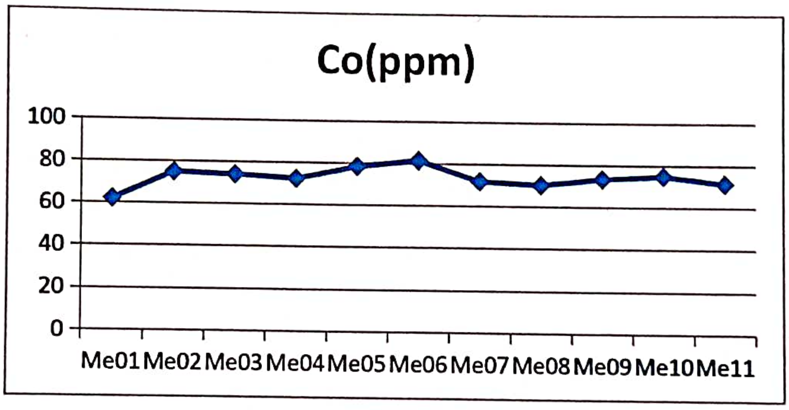
The spatial distribution of Cobalt in surface sediments of Mandovi shows a irregular trend from the head to the mouth region of the Mandovi estuary. The difference in the concentration of Co in sediments can be due to interplay of several factors such as drainage, adsorption, and dissorption from suspended matters. **(Veeransingam, Vethamany,2015)** sediments cores showed enrichment of trace metals in the upper part of the core sediments and decrease in concentration with depth, suggesting excess of anthropogenic loading(including mining activities) occurred during recent past. The anthropogenic sources of cobalt are derived from soils near deposits and ore smelting facilities and soils contaminated by airport traffic, highway traffic, or other industrial pollution source. Cobalt may enter aquatic environment via run off and leaching when rainwater washes through the substance containing cobalt.

Seasonal variation of cobalt **(Fig 8)** in sediments collected from Mandovi estuary shows highest values during post-monsoon season i.e. November and December followed by Monsoon season i.e. June and July. The lowest concentration was recorded during Pre-monsoon season. High concentration during Post- monsoon and Monsoon might be due to land runoff from mining area leading to an increase in the suspended load of rivers and transportation of ores. Additionally, during the post monsoon season , there can be an increase in biological productivity of the estuary, which can lead to an increase in the concentration of cobalt in the water column as it is taken up by phytoplankton and other organisms.

Pre-Monsoon



Monsoon



Post-Monsoon

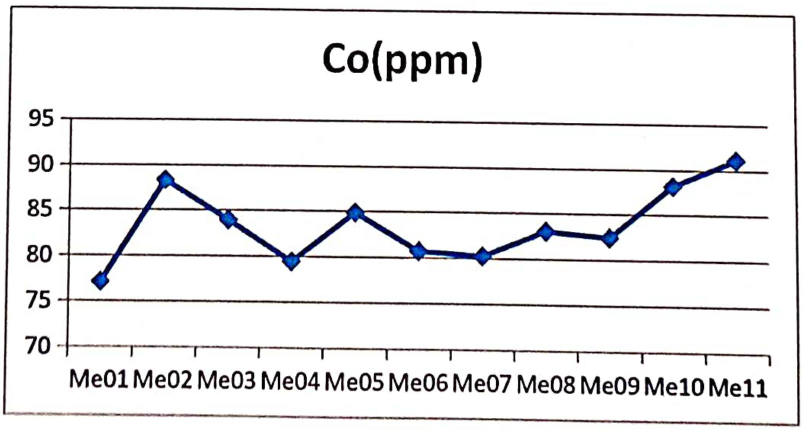


Fig.7: Spatial variation of Cobalt in surface sediments of Mandovi Estuary during Pre-Monsoon, Monsoon, Post-Monsoon.

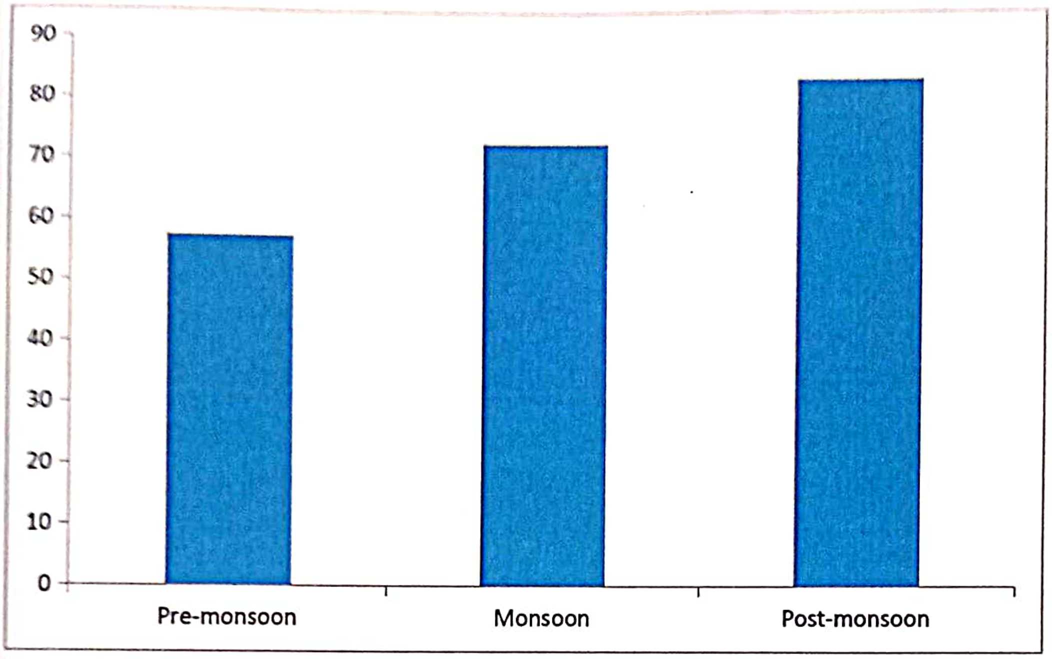


Fig.8: Seasonal variation of Cobalt in surface of Mandovi Estuary.

4.1.4 Copper

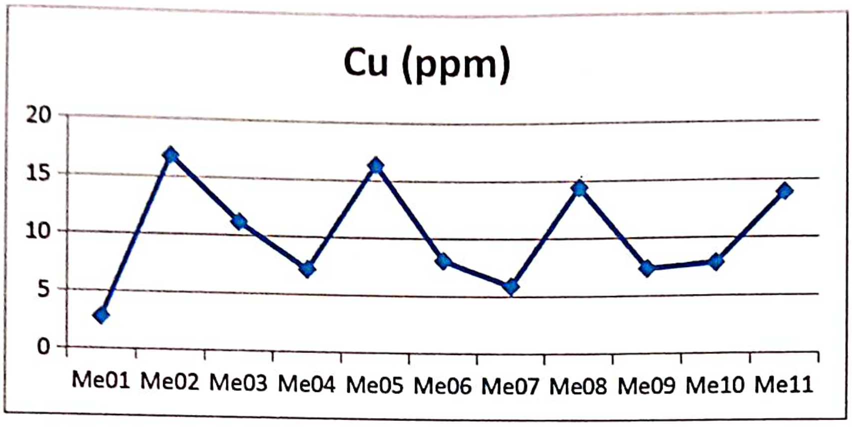
Copper is an essential trace nutrient that is required in small amounts (5-20ppm) by humans, other mammals, fish and shellfish for carbohydrates metabolism and the functioning of more than 30 enzymes. Copper is commonly found in aquatic system as a result of both natural and anthropogenic sources. Natural sources of copper in aquatic system include geological deposits, volcanic activity, and weathering and erosion of rocks and soils. Anthropogenic sources of copper include mining activities, agriculture, metal and electrical manufacturing, sludge from publicly owned treatment works etc. chronic exposure to copper can lead to adverse effects on survival, growth, reproduction. However, a copper concentration that exceeds 20ppm can be toxic. Copper is moderately soluble in water and binds easily to sediments and organic matter.

Concentration of copper (ppm) in surface sediments of Mandovi varied from 2.7 to 16.7 during Pre-monsoon **(Table 3)**, from 2.6 to 5.6 during Monsoon **(Table 4),** and from 8.4 to 7.2 during Post-monsoon season **(Table5).**

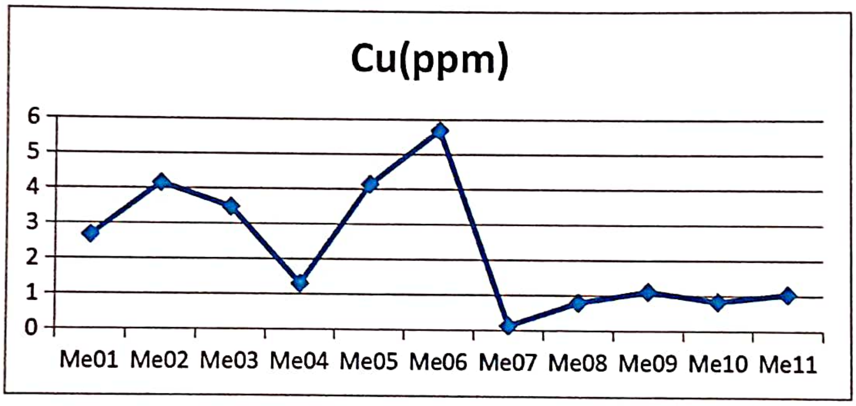
Spatial variation **(Fig 9)** of Copper recorded higher concentration at station 2 during Pre-monsoon and during monsoon it was recorded high at station 6. Whereas during post-monsoon season higher concentration of copper was recorded at station 10and lowest at station 3. Though spatial distribution of copper is not quite clear, it exhibits high concentration near mouth region. The higher concentration of copper is due to natural sources such as weathering of rocks and decomposition of biota detritus. (Badri and Aston, 1983).

Seasonal variation of copper **(Fig 10)** in sediments collected from Mandovi estuary showed highest during pre-monsoon followed by Post-monsoon and lowest during monsoon. High concentration of copper may be probably due to anthropogenic input during pre-monsoon. However, it showed low concentration during monsoon due to desorption of copper at lower salinities during monsoon season. The concentration of Cu is found to be highest during pre monsoon therefore according to Osterroht,(1988) dissolved organic copper exists in two forms i.e., one probably originating from humic acid being responsible for the constant background level of dissolved organic copper, while the other is formed from materials produced recently by the phytoplankton's resulting in the additional peak concentration of dissolved organic copper.

Pre-Monsoon



Monsoon



Post-Monsoon

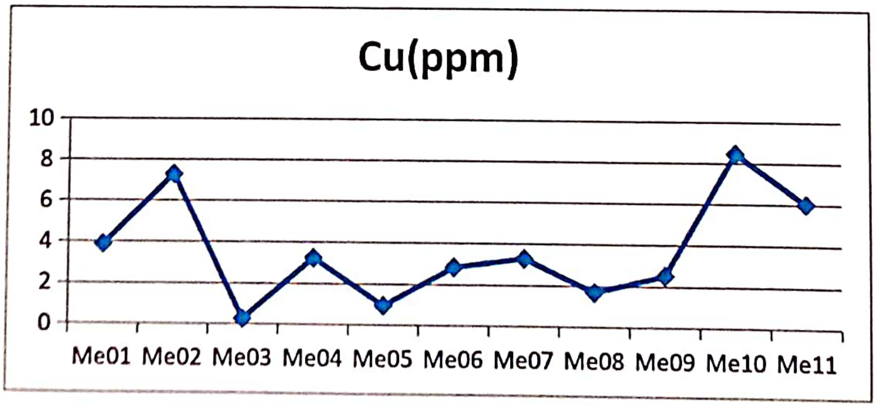


Fig.9: Spatial variation of Copper in surface sediments of Mandovi Estuary during Pre-Monsoon, Monsoon, Post-Monsoon.

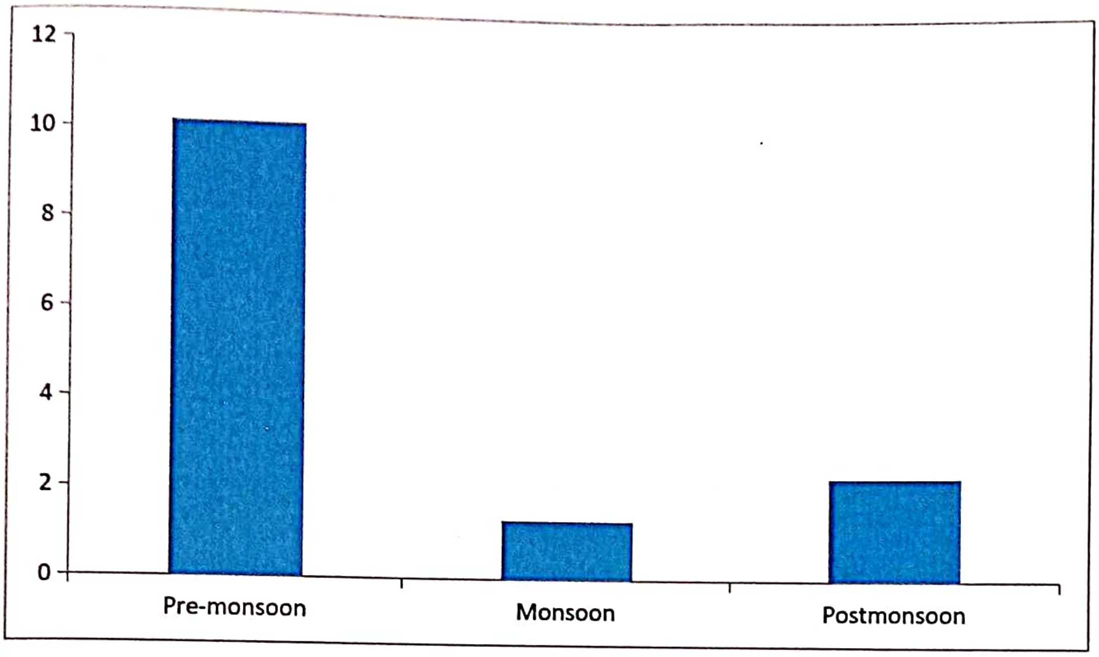


Fig.10: Seasonal variation of Copper in surface sediments of Mandovi Estuary.

4.1.5 Zinc

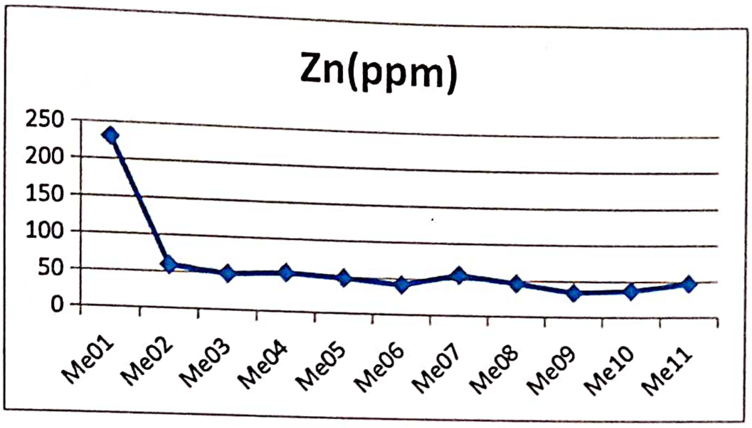
Zinc is one of the most mobile of the metals and is transported in natural water in both dissolved forms and associated with suspended particles **(Mance and Yates 1984)**. Zinc is an essential trace element for human, animals, plants and for microorganisms and is necessary for prenatal and postnatal development. Mostly zinc is added during industrial activities, such as mining, coal and waste combustion and steel processing. In river water, zinc is predominately present in the dissolved form. However, a small amount may remain either dissolved in water or as fine suspended particles. In turbidity maximum, zinc associated with suspended sediment will be deposited with flocculated particles where it can accumulate particularly in anaerobic sediments. In seawater, much of the zinc is found is dissolved form as inorganic and organic complexes.

Concentration of zinc (ppm) in surface sediments of Mandovi varied from 33.92 to 230.7 during Pre-monsoon **(Table 3)**, from 7.6 to 32.89 during monsoon **(Table 4)**, and from 12.5 to 32.4 during Post-monsoon **(Table 5)**.

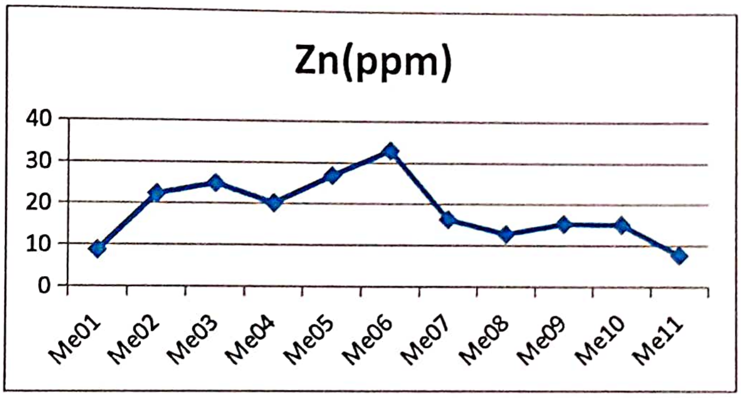
Spatial variation of Zn **(Fig. 11)** recorded high concentration at station 1 during Pre-monsoon, in monsoon station 6 recorded high concentration of Zn and station 2 showed high concentration of Zn in post-monsoon season. Though the spatial distribution of Zn in surface sediments of Mandovi is not clear, it exhibits higher concentration at station near upstream compared to mouth region, thus indicating terrigenous origin of Zn. Due to global population increase and rising industrial and agricultural production, large quantities of harmful chemicals, particularly heavy metals, have been dumped into rivers worldwide **(Shikazono et al., 2012, Liu et al., 2016)**.

Seasonal variation **(Fig.12)** of Zn in sediments of Mandovi showed higher concentration during pre-monsoon followed by Post-monsoon values during monsoon may be because of high influx of fresh water which is responsible for dilution of estuarine water.

Pre-Monsoon



Monsoon



Post-Monsoon

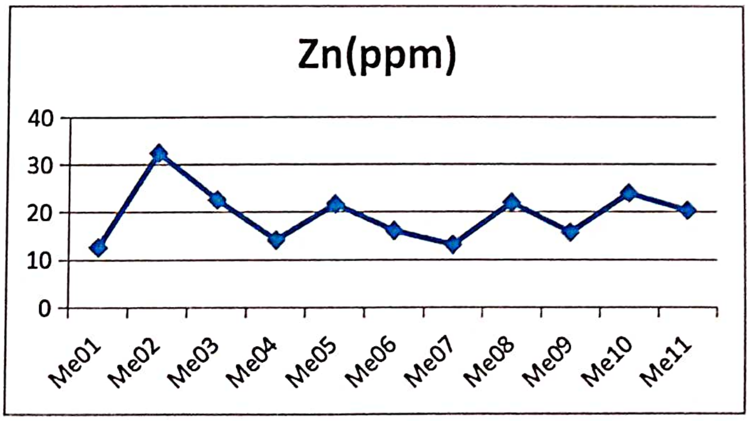


Fig.11: Spatial variation of Zinc in surface sediments of Mandovi Estuary during Pre-Monsoon, Monsoon, Post-Monsoon.

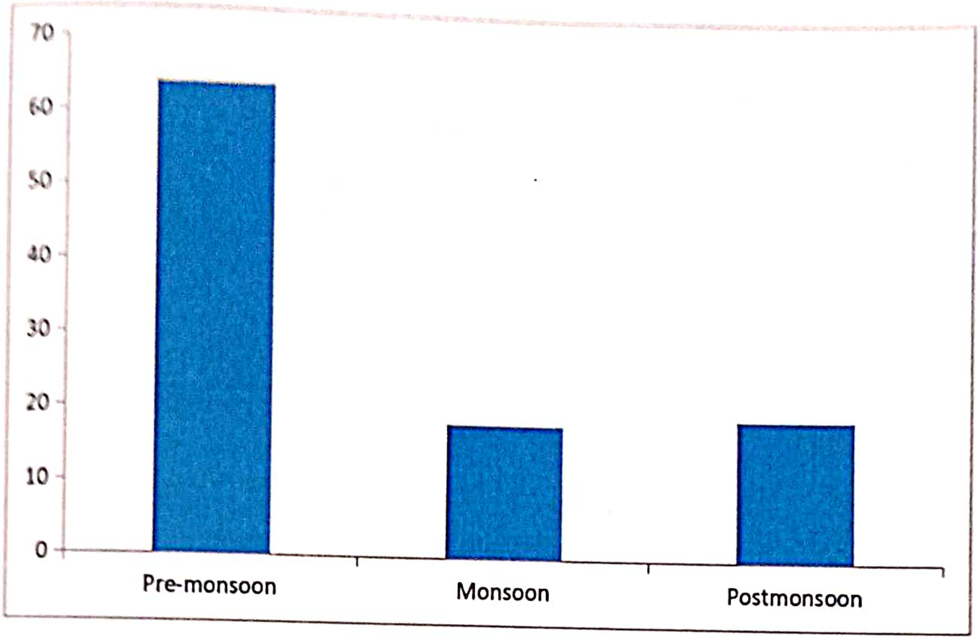


Fig.12: Seasonal variation of Zinc in surface sediments of Mandovi Estuary.

CHAPTER 5

SUMMARY AND CONCLUSION

5.0 Summary and conclusion

Civilization is often associated with rivers and coastal ecosystems from the past to the present. Specifically, estuaries are of global importance because they are viewed as highly productive zones and sustain unique plants and animal population. However, since past few years' developmental activities along the coast have increased the waste released in estuaries may contain trace metals and settle down at the bottom of the estuary by various physiochemical processes. Therefore with rising pollution of the fluvial and coastal ecosystem, the current scenario alarms humanity and marine life.

The Mandovi estuary system in Goa perhaps is the river system in country facing the ill effects of mining activity along the shoreline. About 2/3rd of the total production of iron , manganese and ferromanganese ores come from the mines located on this river the result of study revealed significant variation in metal concentration depending on the sampling sites within the Mandovi estuary. The range and average values obtained from the estuarine region of Mandovi River for the trace metals in sediments are in broad agreement with those in other Indian estuarine and coastal sediments. In general, all metals showed higher concentration during pre-monsoon followed by post-monsoon and monsoon season. During pre-monsoon, there is little or negligible precipitation and run off is almost absent. A good steady weather prevails, which increases the barge traffic along the river transporting iron ore to adjoining Mormugao harbor. Mining are also intensive during this period – factors like high temperature, light penetration, high nutrient availability are common during pre-monsoon season. These combined effects might have resulted in higher concentration of metals during pre-monsoon period. During Monsoon, river discharge is very high and shipping while mining activities are very less compared to other seasons because of the rough weather at the mouth of the estuary, loading of iron ore is at its minimum. Therefore it is observed that the concentrations of all the metals are low during monsoon season. Even Mandovi River has experienced increased levels of copper, cobalt and nickel contamination due to both anthropogenic activities and natural weathering processes. Anthropogenic sources include industrial discharge, agricultural runoff, and urban waste, while natural weathering of geological formations contributes to the release of these metals into the river.

Spatial variation of trace metals in sediments observed higher values from upper estuary region to the head region i.e station no. 6 and 11. In conclusion, this study presents a comprehensive analysis of trace metals concentration in sediments of Mondovi River. Our findings or research reveal a notable escalation in these levels compared to previous research, indicating a concerning trend of metals accumulation over time. The heightened values underscore the urgent need for enhanced environmental management strategies' to address the source and impact of these contaminants moving forward, continued monitoring and targeted remediation efforts are imperative to safe guard the health of the river ecosystem and mitigate potential risks to human population dependent on its resources. Therefore in adherence to safety protocols, the practice of mining in Goa has been suspended since the fiscal year 2012-13.

CHAPTER 6

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