STUDIES ON GEOCHEMISTRY OF SEDIMENT CORES WITH REFERENCE TO PAST MINING IN GOA, WEST-COAST OF INDIA

THESIS

SUBMITTED TO GOA UNIVERSITY FOR THE DEGREE OF

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IN

ENVIRONMENTAL SCIENCES

BY

NITA TRIMBAK RANE

Under the guidance of

PROF. VISHNU MURTY MATTA

SCHOOL OF EARTH, OCEAN AND ATMOSPHERIC SCIENCES

GOA UNIVERSITY

GOA-403 206

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DEDICATED TO MY FAMILY

STATEMENT

As required under the University Ordinance OB.9A, I state that the present thesis entitled "**STUDIES ON GEOCHEMISTRY OF SEDIMENT CORES WITH REFERENCE TO PAST MINING IN GOA, WEST-COAST OF INDIA",** is my original contribution and the same has not been submitted for any other previous occasion. To the best of my knowledge, the present study is the first comprehensive work of its kind from the area mentioned.

The literature related to the problem investigated has been cited. Due acknowledgements have been made wherever facilities and suggestions have been availed of.

Place: Goa University

January, 2020

NITA TRIMBAK RANE

CERTIFICATE

This is to certify that the Thesis entitled "**STUDIES ON GEOCHEMISTRY OF SEDIMENT CORES WITH REFERENCE TO PAST MINING IN GOA, WEST-COAST OF INDIA"** submitted by Ms. Nita Trimbak Rane for the award of the Degree of Doctor of Philosophy in Environmental Sciences is based on her original studies carried out by her under my supervision. The thesis or any part thereof has not been previously submitted for any other degree or diploma in any universities or institutions.

Place: Goa University
January, 2020

Prof. Vishnu Murty Matta
School of Earth, Ocean and Atmospheric Sciences
Goa University, Goa

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PREFACE

The mining of metal ore is a very important economic activity in many countries including India. Intensive iron ore mining activity has increased the prevalence and occurrence of heavy/trace metal contamination at the earth's surface. Open-cast mining generates a large amount of mine wastes which has a serious environmental impact on the quality of soil and surface water due to pollution. India is endowed with large reserves of iron ore. Goa is one of the highest iron and manganese producing state in India. Legal and illegal mining activities were concentrated in Bicholim, Sattari, Sanguem and Quepem talukas of Goa. Mining practice in Goa has been by open-cast method. Exhaustive mining activities have produced a large amount of hazardous wastes. The overburden produced to access the ore has posed a major problem in the handling of ore and its storage.

The run-off from the mining areas has caused the siltation of adjoining rivers, lakes, dams and agricultural fields. Mandovi and Zuari riverine system of Goa are heavily used to transport large quantities of ferromanganese ores from mines located in upstream to the unloading point at Mormugao harbor. Tremendous iron ore mining activities have resulted in threatening the ecology of the Mayem lake of Goa. Mining silt has been accumulating in the Mayem lake from the iron ore mining dumps that have been kept at an elevation unprotected and unstabilized. The mining activities have also affected the Selaulim dam on the Guleli river in Sanguem taluka, which supplies drinking water to the southern part of the state of Goa. More than 20 mines are operating in the vicinity of the dam. The Pollution due to high loads of pollutants, mainly from the mine wastes are devoid of plant growth and supportive nutrients and hence pose danger to agricultural soil. When brought into agricultural fields of Mayem and Sanvordem areas in the form of run-off caused siltation of it. Damage to the environment was mainly caused by the uncovered reject dump, pumping out waters from the working pits and slimes from the beneficiation plant.

In view of the extensive mining activities in Goa, an attempt has been made to understand **"Studies on the geochemistry of sediment cores with reference to past mining in Goa, West-coast of India"** with the following objectives: i) to study the effect of past mining on the rivers running through mine areas of Goa. ii) to study the influence of past mining on lake/dam of Goa and iii) to study the influence of past mining on agricultural fields of Goa

Chapter 1 Includes **Introduction**, wherein detailed information on mining and its impact on the sediment core and metal contamination from the different environment is provided. Mining, a very important economic activity in many countries today including India. Intensive iron ore mining activities have produced a large amount of hazardous wastes throughout the world causes significant environmental degradation. The main focus was on sediment cores from rivers, water reservoirs and agricultural fields affected due to past iron ore mining activities in Goa. Numerous studies on mining and its effects on soil, plants, and water have been carried out in several countries with limited studies undertaken in Goa. To understand the area and depth of investigations and possible gaps in research a detailed literature review on the topic of research was carried out. Literature on sediment components, organic carbon and their role in trapping of metals and pollution indices were reviewed which includes some studies carried out in the recent past in the other parts of the world depicting International scenario and the studies carried out in the recent past in the different parts of the country including Goa describes the National scenario.

.Chapter 2 provides **Physiography of the study area and sampling techniques** wherein it gives information about different areas chosen for the study namely 1. Rivers 2.Water reservoirs and 3. Agricultural fields. Sediment cores from river, lake and agricultural fields exhibit the characteristics of local environmental conditions hence ten sediment cores were collected representing rivers, water reservoirs and agricultural fields from Goa West-coast of India that includes five rivers namely Bicholim river (BR), Mandovi river (MR), Kushavati river (KR), Zuari river (ZR) and Terekhol river (TR); Two water reservoirs namely Mayem lake (ML) and Selaulim dam (SL) and Three agricultural fields namely Mayem agricultural field (MF), Sanvordem agricultural field (SF) and Pernem agricultural field (PF). The description of each station is given in detail. The color of the sediment core was recorded in order to understand the depositional environment of the sediment. The subsamples were digested by adopting standard procedures.

Chapter 3 Describes the **Methods** adopted in estimation of grain size (Folk, 1968), organic carbon (Loring and Rantala, 1992), total phosphorus (Murphy and Riley, 1962), Sediment digestion (Jarvis and Jarvis 1985) was carried out for estimation of major elements namely, Fe, Mn, Al, and Mg and trace metals namely, Cu, Zn, Pb, Ni, Cr and Co for the 10 sediment cores collected from three different environments. Trace metals were estimated by using Atomic Absorption Spectrophotometer (Model GBC 932 AA) and major elements by ICP-OES (Model: Agilent 710 series). The precision and accuracy of the analytical procedure adopted for several chemical parameters for sediments were evaluated for the replicate analysis of reference material Cody Shale (SCO-I), US Geological Survey.

Chapter 4 describes the **Results and Discussion** of various sedimentological and geochemical analysis carried out on 132 sediment core samples and the conclusion drawn from it have also been discussed. This chapter is sub-divided into three sections namely; sections I, II and III. **Section I** deals with the sediment texture (sand, silt and clay), OC, TP, major elements and trace metals in bulk sediments of five rivers namely Bicholim river (BR), Mandovi river (MR), Kushavati river (KR), Zuari river (ZR) and Terekhol river (TR). The results indicated that BR and KR cores recorded a high concentration of major elements and trace metals as compared to MR, ZR and TR sediment cores this is attributed to past mining in these regions. **Section II** deals with the sediment texture (sand, silt, and clay), OC, TP, major elements and trace metals in bulk sediments of two water reservoirs namely Mayem Lake (ML) and Selaulim dam (SL). The results revealed that ML and SL cores showed a high concentration of major elements and trace metals and is attributed to the run-off from the mining waste dumps. **Section III** deals with the sediment texture (sand, silt, and clay), OC, TP, major elements and trace metals in bulk sediments of three agricultural fields namely the Mayem agricultural field (MF), Sanvordem agricultural field (SF) and Pernem agricultural field. The results indicated that MF and SF cores recorded a high concentration of major elements as compared to PF core this may probably due be due to the location of these fields in the vicinity of the mining dumps. Statistical analysis like Pearson's correlation and Factor Analysis were employed to understand the association and metal input source. Pollution indices namely Enrichment Factor (EF), Contamination Factor (CF), Pollution Load Index (PLI) and Geo-accumulation Index (Igeo) were calculated for rivers, reservoirs and agricultural fields. The pollution indices studies indicated that among the five rivers Bicholim is the most polluted and Terekhol is the least polluted river. Similarly, both Mayem Lake and Selaulim Dam reservoirs and Mayem and Sanvordem agricultural fields are polluted. This is attributed to the impact of past mining in these regions.

Chapter 5 provides **Summary and Conclusion** drawn from this research study.

References they are listed in alphabetical order at the end of the Thesis.

1.1 Introduction

Exhaustive iron ore mining activities throughout the world have produced a large amount of hazardous wastes (**Modabberi *et al.,* 2013**). The erosion and transport of mine tailings may spread these elements in aquatic and terrestrial systems (**Anawar *et al.,* 2011**). A considerable amount of solid wastes piled in the form of huge overburden dumps caused destruction and degradation of forest and agricultural lands. Discharge of effluents from iron ore mines into nearby water-bodies are some of the associated problems with iron ore mining activities, that have an adverse impact on the environment (**Kandrika and Dwivedi, 2003**). The acid mine drainage in the waste deposits, agricultural lands, and aquatic ecosystems are controlled by the disposal practices of mining wastes, burial, and formation of secondary Fe, Mn, and Al oxy-hydroxide minerals. Environmental degradation is caused due to mining activities leading to contamination of water and soil, which ultimately results in biodiversity loss (**Luptakova *et al.,* 2012**).

Sediments in water systems are as a result of rock weathering and soil erosion. They reflect the characteristics of numerous sources such as geological matrix, natural and anthropogenic inputs. Sediments are one of the important carriers of contaminants/pollutants in rivers and other water systems (**Sekabira *et al.,* 2010**). Many earlier studies have reported that sediments from the river, estuary, and lake reveal the characteristics of local environmental conditions, which show difference in geochemical properties (**Robertson *et al.,* 2003**). Sediments from various water environments exhibit differences in hydrodynamic regime, redox potential, mineral components (**Wu *et al.,* 2007**). Riverine sediments are usually derived from ambient soils and road deposits (**Taylor and Owens, 2009**).

In an aquatic environment, trace elements are distributed between the dissolved phase, colloids, suspended matter, and sedimentary phases. Sediments and soils have a high storage capacity for contaminants. In the hydrological cycle, less than 0.1% of the metals are actually dissolved in the water, and more than 99.9% is stored in sediments (**Salomons, 1998**). Sediment-associated metals pose a direct risk to detrital and benthic organisms and may also act as a long-term sources of contamination to higher trophic levels (**Mendil and Uluözlü, 2007**). Sediments from the estuarine area receive the run-off, comprised of terrestrial and marine particulate. Lake sediments originate from surrounding river particles and riparian soils. These sediments show a relatively fine size due to a frequent wave sorting effect (**Bilali *et al.*, 2002**) and serve as archives of environmental changes through time (**Silva and Rezende, 2002**). However, anthropogenic inputs, distribution, and accumulation of trace metals are influenced by sediment texture, mineralogical composition, reduction/oxidation state, adsorption and desorption processes, and physical transport (**Buccolieri *et al.*, 2006 and Tang *et al.*, 2010**). The lake sediments are basic components of our environments as they provide nutrients for living organisms. Bottom sediments of the lake are sensitive indicators for monitoring contaminants as they act as a sink and also a carrier for pollutants in the aquatic environments (**Bai *et al.*, 2011**). Thus, lake sediment analysis plays an important role in evaluating the pollution status in the aquatic environment (**Suresh *et al.*, 2012**).

In freshwater bodies, there is always a presence of some amount of heavy metals derived mostly from the mineralogy and weathering (**Samarghandi *et al.*, 2007 and Karbassi *et al.*, 2008**). However, anthropogenic activities such as mining, long-term disposal of untreated and partially treated effluents containing metals as well as metal chelates, indiscriminate use of heavy metal-containing fertilizers and pesticides in agriculture fields, wet and dry fallout of atmospheric particulate matter, urban run-off and direct solid waste dumping (**Kraft *et al.*, 2006 and Krywult *et al.*, 2008**) can accelerate the rate at which these heavy metals are added to the water bodies. Lakes and water bodies are one of the linkages that are necessary for sustainable ecology. They provide a linkage between land and water resources. The quality of the lakes and wetlands depends directly on the integrity of the watershed. In recent two decades anthropogenic activities have altered the Lake Ecosystems all over the world. Sediments are innate and indivisible parts of the aquatic ecosystem. They play a key role in physicochemical and ecological dynamics in aquatic ecosystems. Contaminated lake sediments threaten organisms in the lake ecosystem (**Toolahalli and Sham Sundar, 2018**).

Sediments and soils have a high storage capacity for contaminants. Increased heavy metal contaminants are particularly harmful because they are toxic and remain in environment over a long period of time (**Sheng, *et al.*, 2012**). Physical and chemical processes (leaching and oxidation) can cause heavy metals to accumulate in the soil that is released, which eventually will enter water bodies and later will be taken up by the crops (**Hossain, *et al.*, 2008 and Janos et *al.*, 2010**). Some metals like Cu, Fe, Mn, Zn are required for the growth of crop plants but prove to be fatal when present beyond their permissible limit (**Cai and Zhuang, 1999; Freitas *et al.*, 2010 and Nunes *et al.*, 2010**).

Anthropogenic activities such as mining and smelting of metal ores have increased the prevalence and occurrence of heavy/trace metal contamination at the earth's surface. Opencast mining generates large amounts of sulfide-rich tailings (**Bhattacharya *et al*., 2006**) that have a serious environmental impact on the quality of soils and surface water leading to pollution. In general, mined soils are mechanically, physically, chemically and biologically deficient and characterized by instability and limited cohesion, with low contents of nutrients and organic matter and high levels of heavy metals. Apart from the local disturbance of the physical properties, toxic metals can also cause a more widespread contamination of soil, sediments and food crops leading eventually to a loss of biodiversity in the vicinity of the mining areas (**Lee *et al*., 2001; Zhang *et al*., 2012 and Galan *et al*., 2003**).

Iron ore mining alters the natural landscape of the area and discharges large volumes of mine wastes, tailings that pose serious pollution hazards to human health, to agriculture and ultimately the environment (**Festin *et al.*, 2019**). The contamination of soils by heavy metals from different sources has received great attention worldwide in recent years. Heavy metals in soil are of great concern as they do not degrade naturally and are retained in the soil for a longer period. Heavy metals are either leached into ground or surface water and thereafter enter into the food crops **(Janos *et al.*, 2010).**

Several reports documented earlier have shown that various human activities are a major cause for heavy metal contamination of the soil and water ecosystem (**Al-Khashman and Shawabkeh, 2006; Banat *et al.*, 2005 and Kasassi, 2008**). It includes iron ore mining processes, iron and steel industries, transportation of the ore, open disposal of mine wastes (**Hansen *et al.*, 2002 and Lado *et al.*, 2008**). Soil is considered as the major sink for airborne metals as vehicular pollution participates in heavy metal pollution (**Chahal *et al.*, 2014**). Mining negatively impacts on agriculture because of the wastes which become part of the ecosystem when carried by the rains as a run-off and causing its siltation. With rapid industrialization, there has been an increase of heavy metals in our environment, heavy metal distribution and accumulation in the agricultural soils and their presence in food crops (**Matthews–Amune and Kakulu, 2012**). The highest risk of contamination has been reported for soils around mining operations (**Zhuang *et al.,* 2009**).

The contamination of agricultural soil by toxic elements such as heavy metals attracts the interest of people not only because metals can build up in the soil but also because metals can be accumulated in crops, where they cause significant potential risk to human health (**Huang *et al.,* 2007 and Nguessan *et al.,* 2009**). Heavy metals contamination in the environment may cause detrimental effects to both plants and animals including human beings. Food crops may be exposed to heavy metal through contaminated soil or atmospheric dispersal of such metals from industrial areas (**Machiwa, 2010**). Heavy metals such as copper, iron, manganese and zinc are considered to be useful micro-nutrients to plants when present in amounts that facilitate the physical growth and development of plants (**Aziz *et al.,* 2015**) but when these metals exceed maximum acceptable limits they become toxic to the plants (**Satpathy, 2014**). Crops such as rice that are grown in submerged conditions are even more exposed to heavy metal sources both from the soil and water. Rice being the second most consumed crop in the world may, in turn, expose the majority of its consumers to heavy metals (**Emumejaye, 2014**).

Metal mining is a very important economic activity in many countries including India. It causes significant environmental degradation. India is endowed with fairly large reserves of iron ore of moderate to good quality for its domestic requirement as well as for export. Goa is one of the highest iron and manganese ore producing state in India. The prospecting of Fe and Mn ore started in Goa as early as 1905, and the regular export commenced in 1947. During1971–1980, Goa accounted for 32% of the country’s total iron ore production and 55% of its export (**Swaminathan, 1982**). The iron ore is predominantly mined by open cast mining throughout Goa. Removal of overburden to access the ore can pose major problems in its storage, handling, and reclamation. The stripping ratio (waste-to-ore ratio) for surface mining in Goa generally ranges from 3:1 to 5:1 depending on site-specific local conditions (**IBM, 2002**).

In the state of Goa to obtain around 1 million tones of iron and manganese ore, approximately 2.5 million tones of overburden including wastes has to be excavated which resulted in problems of storage of dumps in the past (**Arondekar and Murthy, 2017**). The accumulated silt from the waste dumps enters the fields during heavy monsoons making the lands unfit for cultivation due to siltation. Iron ore mining industry requires water in huge quantities for the backwashing of the ore which is ultimately brought into the water bodies. Mining is one of the major concerns causing land degradation (**TERI 2012**). The physical and chemical composition of these wastes varies considerably according to the substance mined and the nature of the geological formation containing the deposit. This consequently leads to sub-surface and groundwater pollution due to high loads of pollutants, mainly from heavy metals present and the possible generation of acidic drainage from these dumps. A study by **Juwarkar *et al.*, (2004)** on mine wastes revealed that these mine wastes are devoid of plant growth nutrients and hence pose danger when they are mixed with the agricultural soil. Fe and Mn, and also associated trace metals are released into the environment (**Ratha and Venkataraman, 1995**). Trace metals in coastal and estuarine sediments are incorporated into the aquatic food webs through primary producers and then bio-magnified at higher tropic levels (**Veerasingam *et al.*, 2012**)

Goa is crisscrossed by eleven rivers, of which Mandovi and Zuari are the major drainage systems. The Mandovi estuary is one of the tropical estuaries along the west coast of India. Mandovi and Zuari River are heavily used to transport large quantities of ferromanganese ores from iron ore mines located upstream to the Mormugao harbor. Iron ore mining associated activities such as ore loading, transportation of ore to platforms, effluents from beneficiation plants and barge-building activity were taking place along the two river basins. All these activities associated with mining contribute a large quantity of material in the Mandovi estuary. Within the estuary, sediments are the major repositories of metals (**Dessai *et al.*, 2009**).

Iron ore mines act as important sources of major metals. The temporal variations in sediment cores reflect the geochemical history of a given region, including any anthropogenic impact (**Venkatachalapathy *et al.*, 2011a, b and Veerasingam *et al.*, 2014**). Though the impacts of iron ore processing on the surface sediments of the Mandovi estuary have been documented earlier (**Alagarsamy, 2006; Shynu *et al.*,**

2012 and Kessarkar *et al.*, 2015). **Priyanath, (1999**) reported a decline in agriculture due to mining activities in the areas of operation. The four talukas: Bicholim and Sattari in North Goa and Sanguem and Quepem in South Goa largely fall in the mining belt. This accounts for almost 1/5th of the area of Goa i.e, approximately 700 km^2. The inhabitants in these areas were largely dependent on agriculture for their livelihoods.

Mining activities on a large scale has resulted in threatening the ecology and environment of the lake of Goa. Mayem Lake is Located around two km away from Bicholim town of Bicholim Taluka of Goa, It is a tourist destination, a decade ago with the active operation of mining leases within a radius of kilometer has accounted in declining the water level in the lake. Mining silt has been accumulating in the lake from the mining dumps that have been kept open and unstabilized (**Girap, 1997**). Iron ore mining has also affected the Selaulim dam on the Guleli River in Sangeum taluka of Goa, which supplies drinking water to half the state's population, besides providing water for irrigation and industries. Over 20 iron ore mines are operating in the vicinity of the dam. Heavy silt has settled in the dam/ reservoir due to mining activities brought in by heavy monsoon.

1.2 Review of literature:

Numerous studies on iron ore mining and its effects on soil, plants and water have been carried out in several countries with limited studies undertaken in Goa. To understand the area and depth of investigations and possible gaps in research a detailed literature review on the topic of research was carried out.

1.2.1 International Scenario

Table 1.2.1 Literature surveys of the studies carried out in the recent past in the other parts of the world

Authors	Parameters analyzed	Observations
Amor *et al.*, (2019)	The concentration of heavy metals and speciation	The total concentration and the speciation of heavy metals (Pb, Cd, Cu, Zn, Ni, and Cr) in surface sediments of Rades-Hamam Lif coast off the Mediterranean Sea were carried out. The geochemical indices were used to assess the risk of contamination and the environmental risks of heavy metals on surface sediments. The concentrations of these heavy metals are influenced by runoff, industrial, and urban wastewater. Cd, Pb, Zn, and Ni are affected by anthropogenic sources,
Cheng *et al.*, (2018)	Levels of trace elements and their spatial distribution, main sources of risk element pollution.	Agricultural soils from the Dongchuan copper mining area were sampled and analyzed to determine the concentrations of selected trace elements, namely As, Cd, Cr, Cu, Hg, Ni, Pb and Zn. Values of As, Cu and Zn in the soils were significantly higher. The most serious threat to the ecosystem and human health was represented by Cd. The main sources of Cu and As were identified mining activities, airborne particulates from smelters and the weathering of tailings, and partly also fertilizers. The major source of Cd in agricultural soils was from agricultural fertilizers and partly sources associated with mining and smelting activities.

Khan *et al.*, (2017)	Trace metals	Surficial sediments were studied to establish their concentration on the Bengal coast. It was revealed that the majority of the trace elements have been introduced into the Bengal marine sediments from the riverine inflows that are also affected by the impact of industrial, ship breaking yard, gas production plant, and urban wastes.
Wu *et al.*, (2016)	Heavy metals and the potential hazards and possible sources of these metals.	This study investigated 82 samples for the concentrations of six heavy metals in Shenzhen's agricultural lands and examined the potential hazards and possible sources of these metals. Agricultural topsoil was collected. The potential ecological risk index was used to calculate the potential risk of heavy metals. Shenzhen's soils, particularly the surface topsoil, are enriched with six heavy metals (Cu, Zn, Pb, Ni, Cd, and Cr) than in the past. The heavy metal Cd was the main contributor to the pollution in agricultural land during the study period. The high potential risk is closely related to industrial pollution and transportation
Yao and Xue, (2016)	Heavy metals and source	Two short sedimentary cores were collected in 2012 from Chihu Lake in the middle Yangtze River Basin. Heavy metals, including Pb, Cu, Zn, Cd, Cr, Co, Ni and Mn, and major elements, including Al, Fe, K, Mg, and Ti, were measured. The Mn enrichment in the sediments of the two cores did not significantly influence the distribution of the heavy metals. The Pb, Cu, Zn, Cd, Co and Ni contents have increased over the past 30 to 40 years. The heavy metal enrichment at Chihu sediment was high overall because of the mining waste discharge.

Anawar, (2015)	Heavy metals and remediation processes of mining wastes	The study of Global Acis Rock Drainage reports at School of Earth and Environment (M087), The University of Western Australia revealed that the minerals release extremely acidic leachate, sulfate and potentially toxic elements e.g., As, Ag, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Th, U, Zn, etc. from different mine tailings and waste dumps. For the sustainable rehabilitation and disposal of mining waste, the sources and mechanisms of contaminant generation, recent insights in mechanisms of oxidation of sulfidic minerals, environmental contamination by mining waste, and remediation and rehabilitation techniques, and then developed the GEMTEC conceptual model/guide [(bio)-geochemistrymine typeemineralogy- geological texture-ore extraction process-climatic knowledge)] to provide the new scientific approach and knowledge for remediation of mining wastes and acid mine drainage and effective and integrated management of mining waste and acid mine drainage.
García and Muñoz-Vera, (2015)	Metals	The study was undertaken to examine the influence of metal mining activities on the composition of sediments of a Mediterranean coastal lagoon, named Mar Menor. Grain size, mineralogy, geochemistry and organic matter of sediments of this coastal lagoon, was investigated with variation along space and time. The study included minerals and metals coming from the mining area, such as greenalite, pyrite, Pb, Zn, Fe, and S. It was observed that Sedimentation dynamics are ruling clearly the grain size

		predominant in each area of the MarMenor coastal lagoon, determining the existence of entrainment, transport and sedimentation areas. For minerals, elements and organic matter, sedimentation dynamics are also determining their distribution.
Kayastha, (2014)	Heavy metals	The study was carried out to assess heavy metals (Cu, Zn, Pb, Cd,) in soils of the Bhaktapur District (Manohara, Nagadesh, Bode, Hanumanghat, Sipadol, Tathali and Gundu). The geo-accumulation class (Igeo) indicates that the agricultural soil of Hanumanghat, Manohara, Nagadesh and Bode are moderately contaminated of Cd. study has generated data on heavy metal concentration in soil. The soil is a long term sink for the group of potentially toxic elements often referred to as heavy metals, including zinc, copper, lead, cadmium, arsenic and mercury. The high contamination of heavy metals found in soil were closely related to the pollutants in irrigation water, agricultural soil fertilizers, and dusts. It showed highest concentration of zinc.
Ameh, (2013)	Heavy metals, CF, EF and Igeo	A study on Twelve stream sediment samples along River PomPom were collected and analysed for heavy metals. Contamination factor (CF), index of geo-accumulation (Igeo) and enrichment factor (EF) indices used recorded the same order of enrichment / contamination among the heavy metals was studied Fe, Cu, Pb and Ni have contaminated the sediments.
Yacoub *et al.*, (2012)	Heavy metal contamination	Examination of heavy metal pollution in sediments close to two mine sites in the upper part of the Jequetepeque River Basin, Peru. Sediment concentrations of Al, As, Cd, Cu, Cr, Fe, Hg, Ni,

		Pb, Sb, Sn, and Zn were analyzed. The sediment samples analyzed showed that potential ecological risk is caused frequently at both sites by As, Cd, Cu, Hg, Pb, and Zn. The long-term influence of sediment metals in the environment is also assessed by sequential extraction scheme analysis (SES). The availability of metals in sediments is assessed, and it is considered a significant threat to the environment for As, Cd, and Sb close to one mine site and Cr and Hg close to the other mine site. A tentative relationship between pollution sources and possible ecological risk was established.
Rahman *et al.*, (2012)	Heavy metal concentration	The present work assessed the heavy metal contamination of agricultural soil in the close vicinity of the Dhaka Export Processing Zone (DEPZ) in both dry and wet seasons using different pollution indices were studied. Samples were collected from the surface layer of soil and analyzed. The study area was strongly and moderately contaminated with As and Hg in the dry and wet seasons respectively. Soil was classified as moderately contaminated with Zn, Cr, Pb and Ni, considerably contaminated with Cu and highly contaminated with As and Hg. The main sources of metals included effluents from wastewater treatment plants, treated and untreated wastewater from surrounding industrial establishments as well as agricultural activities.
Leopold *et al.*, (2012)	Trace metals, CF, Igeo and PCA	The study was carried out on sediment cores collected from the Municipal Lake of Yaounde, Cameroon.It revealed that the sediment cores are contaminated with Pb, Cd, Cu, Zn and Cr. CF and

		I-geo values showed that the lake is moderately to very strongly polluted with trace metals. Pearson's correlation indicated their possible common sources. PCA of the data revealed that heavy metal (Pb, Cd, Cu, Zn and Cr) input is anthropogenic Whereas Ni and Mn were controlled by natural inputs
Yin *et al.*, (2011)	Total phosphorus and heavy metals	Concentration of heavy metals, its source in the sediments from Lake Taihu were studied. Results showed that the measured heavy metals had varied spatial distribution patterns, indicating that they had complex origins and controlling factors. Total phosphorus was positively correlated with the measured metals except Cd. Pb probably might be from domestic sewage and industrial wastewater. Sediment from Wuli Lake, Gonghu Bay and the Northwest Area suffered high pollution, whereas other areas of Lake Taihu were moderately polluted. Lake Taihu suffered from different anthropogenic effects.

1.2.2 National Scenario

Table 1.2.2 Literature surveys of the studies carried out in the recent past in the other parts of the country.

Fernandes *et al.*, (2019)	Grain size, OC and metals	Study was carried out on the four minor rivers namely Terekhol, Chapora, Sal, Talpona. In all 70 Surface water and bottom sediment samples were studied. The sediment texture fluctuated only slightly over the seasons. It was observed that particulate-metal concentrations was highest during the

		monsoon. The enrichment factor (EF) for Mn was high in suspended matter than the bottom sediments. The Geo-accumulation index (Igeo) values for all metals showed class 0 (unpolluted to polluted).
Ratnakar and Shikha, (2018)	Metals and contamination	The soil samples from agricultural areas in and around Lucknow city, Uttar Pradesh, India were studied to assess contamination due to heavy metals. Wastewater irrigation practices lead to the accumulation of heavy metals like nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd), iron (Fe) and lead (Pb) in the soil and chronic exposure to heavy metals can lead to their accumulation in plant parts affecting plant growth and ground cover.
Showqi *et al.*, (2018)	Trace metals	The study on sediment samples collected from the Anchar lake in the north-west of Srinagar city showed higher concentration of trace metals Zn, Cu, Ni, Cr, Cd and Pb at S1, S3 and S4 stations. This could be attributed to enhanced anthropogenic activities.
Renjan *et al.*, (2017)	Major elements and trace metals in suspended sediments	A study on metals (major elements Al, Fe, Mn and trace metals Cr, Pb, Cu, Ni, Zn and Co) in sediments of the Mandovi and Zuari rivers showed higher concentrations. Mn showed significant pollution in these rivers. A strong correlation of the metals was observed with Fe and Mn indicating their association with spillage during transportation of Fe-Mn ore material.

Nasnodkar and Nayak, (2015)	Grain size OC and metals	The study was carried out to investigate the processes and factors which determine the distribution of grain size, organic carbon and metals in mudflat sediment cores collected from lower regions of three tropical estuaries, viz., Mandovi, Sharavathi and Gurupur. The data revealed, increase in finer sediments, organic carbon and metals in the recent years in Mandovi and Sharavathi estuaries, while the data revealed decrease in the Gurupur estuary. The increase in finer sediments in Mandovi and Sharavathi estuaries was attributed to catchment area activities role of finer sediments and organic carbon in distribution of metals. However, in Gurupur estuary, dilution of metal concentration is observed by input of coarser sediments in the recent years. The distribution of metals is largely regulated by Fe oxide. In addition, metals showed difference in their associations with Fe and/or Mn oxide within cores collected from Mandovi and Sharavathi estuaries.
Veersingam *et al.*, (2015)	Grain size and metals	The study was carried out on estimation of concentration of metals from 3 sediment cores of Mandovi river, West coast of India and also to study the depositional trends and its contamination level in the sediment cores. The sediment cores was enriched with trace metals. The Igeo values indicated that Mandovi river is moderately polluted (class 2) with Pb, and unpolluted to moderately polluted (class 1) with Fe, Mn, Cu, Cr, Co and Zn.

Prajith *et al.*, (2015)	Metal concentration, Enrichment factor, Igeo	Seven sediment cores of the Mandovi estuary, western India were studied to understand the concentration of Fe and Mn their provenance and pollution. Fe and Mn in sediments registered high values. The EF and Igeo values of Fe and Mn showed that the sediments from the upper/middle estuary are strongly polluted.
Lokhande *et al.*, 2014	Trace metals	The study was carried out to evaluate the water quality of the water resources and soil contamination by trace metals in the area located at iron ore mines Rawghat, in the state of Chhattisgarh, India. Iron ore mining activities can be seen through the concentration of iron which was substantially higher and was noted to be 218, 2568 and 5284 mg/kg in red ore and black ore soil samples.
Siraswar and Nayak, (2011)	Gain size, Metals	The study revealed that hydrodynamic conditions are the main factors regulating the distribution of metals n mudflats in the recent past along Mandovi Estuary. It revealed that sand percentage is the highest in the mudflat situated near the mouth and finer sediments are higher in lower and upper-middle regions of the estuary.
Sundararajan and Natesan, (2010)	Grain size, OC and metals	Sediment cores from Calimere along the southeast coast of Vedaranyam, India were analyzed for grain size carbonates, organic carbon to study the environmental conditions near point It showed a high concentration of sand in the core. No significant variation was shown in the values of OC. Mn concentration was high. The distribution pattern of various

		trace elements in the core is shown as Pb > Cu > Co > Zn > Ni > Mn > Cr. Core samples show a relatively very low degree of alteration in sediments.
Dessai *et al.*, (2009)	Grain size, OC and metals	In this study surface, sediment samples, as well as near-surface and near-bottom water samples from 18 selected stations from Zuari estuary in three different seasons, were collected. It is observed that the size of the sediment (clay) plays an important role in binding metals in the sediments. During monsoon, a significant correlation with the clay content was observed indicating the role of finer sediments in the distribution of metals in this season.
Yellishetty *et al.*, (2009)	Metals	Studied the environmental impacts of mining activities in the State of Goa, India, water–soil interactions occurring in the mining area. Mine and mineral processing wastes (tailings) from the Codli mining area were examined for their metal concentrations. And it was found that these wastes contain several metals such as Cr, Zn, Pb, Cd, Ni, Mn, Fe, and Cu. Among the various metals present, iron and manganese are very high in concentration. The pyretic minerals that are present in the mine wastes that are capable of producing acid mine drainage. Wastes generated from these mining sites have a considerable concentration of heavy metals.

Kandrika and Dwivedi, (2003)	Spatial erosion - deposition	The database study was carried out in Bicholim and Sattari taluka of Goa that consists of IRS-1C LISS-III and PAN data that showed an increase in the overburden material from mining areas in the catchment. The parameters were then used to run the USPED model to retrieve erosion-deposition zones in a GIS domain. The study indicated that mining leads not only to pollution of surface and groundwater but also accelerates erosion by water which, in turn, results in the deposition of the mining wastes in agricultural fields which may affect the growth and yield of agricultural crops.
Girap *et.al.*, (1994)	Grain size and Organic carbon	The study was carried out on surface sediments and three sediment core samples from Mayem lake of Goa during the monsoon seasons and it was used to understand their size distribution in the lake. It is studied that the major part of the sediment falls in a very fine grained category (silt and clay). Seasonal variation occur in the sediment characters and there is a definite relation between the sediment distribuition and organic carbon. Organic carbon content in the sediments of Mayem lake is higher (Av. 8.79%). This high concentration may be due to large scale supply of organic matter from the catchment areas along with water and sediments.

It is evident from the above that numerous studies on mining and its effects on soil, plants and water have been carried out in several countries with limited studies undertaken in Goa. Although some work has been carried on the impact of mining on the Mandovi and Zuari river systems, but information with reference to past mining on agricultural lands and water reservoirs of Goa is poorly understood. The long term contamination history of metals and impact of mining activities in estuarine sediments are sparsely understood. Considering the long term contamination history of heavy metals, an attempt has been made to understand the impact of past mining in different environments of Goa with the following objectives.

1.3 Objectives

i) To study the effect of past mining on the rivers running through mine areas of Goa.
ii) To study the influence of past mining on lake / dam of Goa and
iii) To study the influence of past mining on agricultural fields of Goa

2.1 Physiography of the study area: The state of Goa

Goa is the twenty-fifth state of the Indian Union with an area of about 3, 65,563 hectares. Out of which 65,400 hectares were leased out for mining. The majority of mining leased was in the forest areas. 55% of iron ore export was from Goan deposits. Sattari (14.7%), Bicholim (46.12%) in North district and Sanguem (35.83%) and Quepem (14.7%) in the South district of Goa are on the iron ore belt and were mined for iron. Among all the four talukas Bicholim taluka was mined the most causing damage to the ecosystem. Minerals like manganese, bauxite, silica sand constituted a small part of the total minerals mined (**Singh and Kamal Kant, 2015).**

Goa is the smallest state of India with scenic beauty sustained by 11 rivers, Terekhol, Mandre, Harmal, Sal, Saleri, Colvale, Baga, Mandovi, Zuari, Talpona and Galjibag along with 42 tributaries. These rivers are lifeline which has supported the human settlements. The rise in the ghats and discharge towards the Arabian Sea (**Singh, 2000**). These rivers are not only the source of economy and potable water, but they support also the Goan eco-systems.

Mandovi and Zuari are the two River basins of the state of Goa. These rivers flow through mining areas and end up in the Arabian Sea. About 2/3rd of the total production of iron, manganese and ferromanganese ores comes from the mines located on these two river basins (**Satyanarayana and Sen Gupta, 1996 and Singh, 2000**).

Goa had 90 operational iron ore mines spread along the Western Ghats. Most of the legal and illegal iron ore mines are in forest areas and basically in four talukas of Goa namely Sattari, Bicholim, Sanguem and Quepem. Iron ore mining practice in Goa has been by the open-cast method. It is carried out by making systematic benches on the hilltop and also along hill slopes in these areas. The pits are laterally extended in stages in all directions with increasing depth of the mine. Mining has degraded the environment and it is a matter of concern. Damage to the environment was mainly caused by the uncovered reject dum, pumping out waters from the working pits and slimes from the beneficiation plant.

The overburden of topsoil and laterite scrapped off during open cast mining is dumped on hillsides, riversides that were exposed to erosion during monsoon. The damage is more evident where the rainwater carries the run-off from the waste dumps to the adjoining rivers, low-lying agricultural fields and water bodies such as lakes and dams. The slimes and silts enter the agricultural field during the monsoon are of such character that they get hardened on drying in the post-monsoon season. The washed-out material from the dumps and the flow of slimes from the beneficial plants besides polluting the water causes siltation of water-bodies, especially during monsoon. Such silting of water-bodies over the years may trigger even flooding of the adjacent fields and inhabited areas, especially during monsoon season.

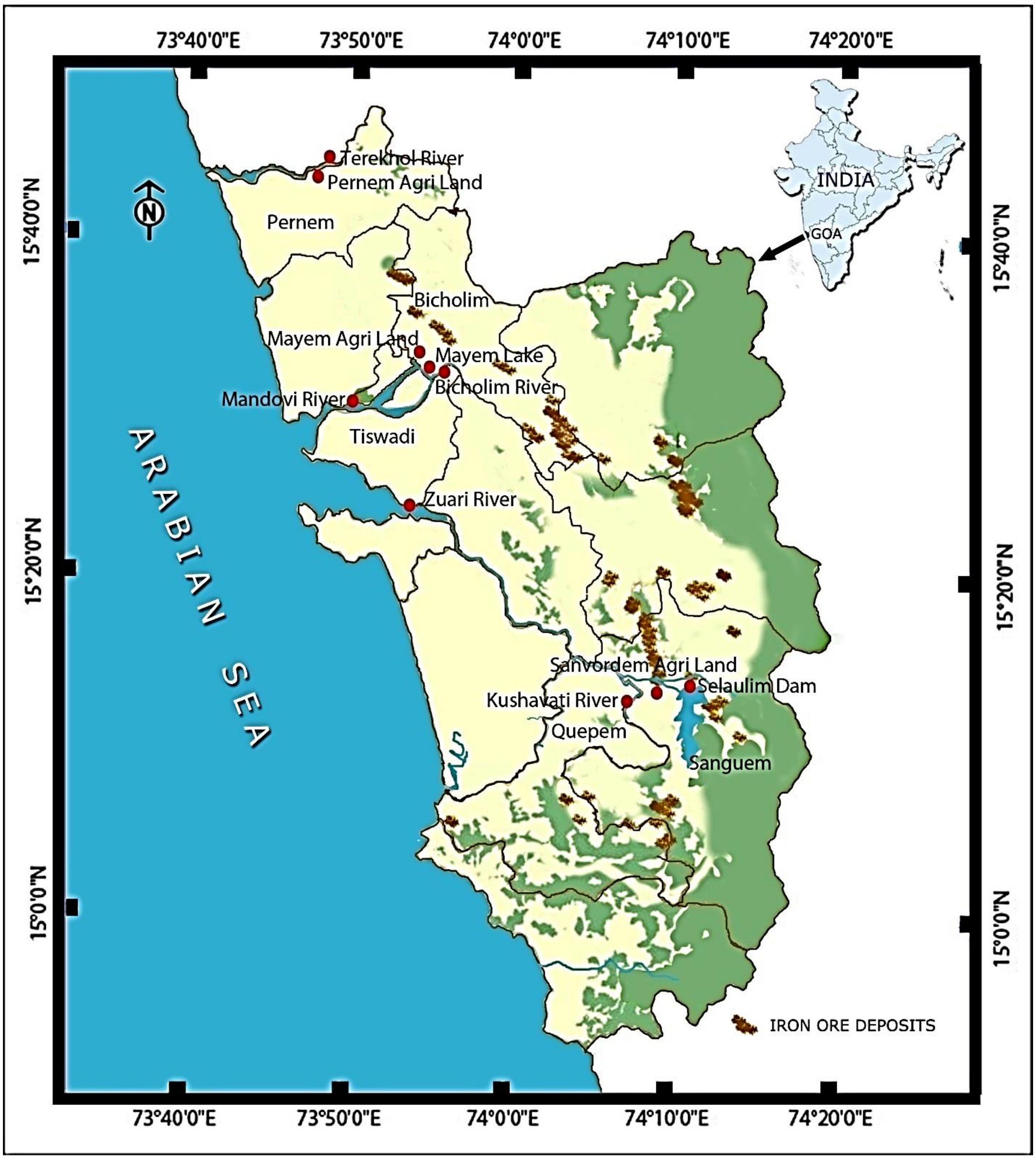


Fig. 2.1 Station location map

2.1.1 Station locations

Sediment cores were collected from three different environments namely 1. Rivers, 2. Lake/Dam and 3. Agricultural fields. The latitude and longitude of the stations are placed in the table (**Table 2.1.)**

Table 2.1. Latitude and longitude of stations.

Sr. No	Environment	Stations	Latitude	Longitude
1	**Rivers**	Bicholim River (BR)	15° 34' 583'	073°57' 198'
2		Mandovi River (MR)	15°30'.329	73°49'.953
3		Kushavati River (KR)	15°10'989'	074°06'046'
4		Zuari River (ZR)	15°25'.101	73°54'.922
5		Terekhol River (TR)	15°44'207'	073°48'285'
6	**Lake/Dam**	Mayem Lake (ML)	15°34' 662'	073° 56' 411'
7		Selaulim Dam (SL)	15° 12' 588'	074°10' 615'
8	**Agricultural Fields**	Mayem Agricultural Field (MF)	15° 35' 127'	073°54' 510'
9		Sanvordem Agricultural Field (SF)	15° 11' 966'	074°05'905'
10		Pernem Agricultural Field (PF)	15°43'038'	073°47'380'

2.1.2 Riverine stations

a. Bicholim River (BR): Bicholim River, is a tributary of Mandovi River (**Fig. 2.1**) that flows SW to its confluence with Mandovi River at Sarmanas village (**Chaulya *et al.,* 1999**). The mining area comprises of five continuous leases covering an area of 498.10 hacters. These leases are situated on SE-NE oriented upland. The hill is gently sloping on the SE and SW sides of Bicholim River due to which it receives a large amount of run-off from the mining dump sites. It is a tributary of Mandovi River that flows through an iron-ore affected area located in Bicholim taluka of North Goa (**Rane and Matta, 2019**).

b. **Mandovi River (MR):** Mandovi river is one of the main river of Goa which originates from the Parwa ghat of the Karnataka which is a part of the Sahyadri Hills. It is a tropical estuary on the West coast of India (**Fig. 2.1**) which is fed by monsoon precipitation, and discharges from a catchment area of about 1530km^2. Its basin area is about 1530km^2 (**Singh, 2000**). There were 27 large operational mines which generate about 1500-6000 tones of rejects per day per mine, which is carried to this river during the monsoon as run-off **(NIO 1979)**. The estuarine channel of the Mandovi river was used for transportation of barges carrying large quantities of iron and ferromanganese ores from loading points at Sarmanas to Marmugao harbor (Arabian Sea) an unloading point throughout the year (**Algarsamy, 2006**). As it is the monsoonal estuary that receives run-off and sediment discharge only during the monsoon season. (**Kessarkar *et al.*, 2015**).

c. Kushavati River (KR): The Kushavati river flows through Quepem taluka of the state of Goa (**Fig. 2.1**). It is the major source of drinking water supply for the people living in the villages of Sanguem and Quepem taluka. Over the last few years, due to mining activities in this manganese-rich belt have resulted in contamination of the river due to run-off from the dumping site along its banks during monsoon season. The river faces siltation and pollution from iron and manganese mines. The wastes from the mining pits, which flow into the Kushavati River has caused siltation of it and also has affected its flow.

d. Zuari River (ZR): River Zuari within the state of Goa is one of the dynamic tropical estuaries along the central west coast of India (**Fig. 2.1**). It originates from the Digi ghat of the Karnataka (part of the Sahyadri hills) which after flowing through a stretch of 67 km joins the Arabian Sea (**Singh, 2000**). It is geomorphologically classified as Drowned River Valley Estuary (**Murty *et al.*, 1976**). The river is largely fed by monsoon-precipitation and receives a large volume of land runoff from the catchment area of 550 sq km of the Zuari estuary basin. Kushavati is one of the major tributaries of the Zuari River. There are 10 large mines in its basin which generates 1000-4000 tones of rejects per day per mine (**NIO 1979**). Many mining associated activities such as transportation of ore to platforms, ore loading, effluents from beneficiation plants and barge-building activity within the river basin do take place. All these activities associated with mining contribute a large quantity of material into the Zuari estuary (**Dessai *et al*., 2009**)

e. **Terekhol River (TR)**: It is the river that flows along Pernem taluka (**Fig. 2.1**). Basically known for sand mining in its catchment area. In the upper reaches it is known as the Banda River and as the Terekhol in the lower reaches. It also forms the boundary between the Sindhudurg district (Maharashtra state) and the North Goa district (Goa state) for some distance. The Terekhol rises in the Manohargad in the Western Ghats and flows in a south-western direction to meet the Arabian Sea. The two rivers which decide the boundary of Pernem taluka are Terekhol River and the Chapora River (**EIA/EMP 2012**).

2.1.3. Water Reservoir Stations

a. **Mayem Lake (ML):** It is located around two km away from Bicholim town and is situated between hill ranges which attain the maximum elevation of about 120m above sea level. During monsoon season the rainwater received by the catchment area flows in the form of surface run-off into the lake basin (**Girap *et al.,* 1994**). Operation of iron ore mining leases within its periphery has resulted in declining of water level in the lake due to the accumulation of mining silt in the catchment area of the lake from the mining waste dumps which have been kept uncovered, unprotected and unsterilized (**Fig. 2.1**).

b. Selaulim Dam / Reservoir (SL): The Selaulim dam is located on the Guleli river, which is a tributary of the Zuari river in Uguem village in the Sanguem taluka, of Goa (**Fig. 2.1**). Selaulim Dam is an integral part of the Selaulim Irrigation project, the largest water reservoir which facilitates work on the development of irrigation and supply of drinking water to the majority of areas i.e to about to 55% of Goa's population (**Annual Report 2013-14**). There were illegal iron ore mining operations in the catchment areas of the Selaulim Dam, endangering the reservoir and rapidly increasing its siltation rate. Sanguem taluka is the largest taluka of the state of Goa having 295 mining leases with a forest area of 578 sq km.

2.1.4 Agricultural Field Stations

a. Mayem Agricultural Field (MF):

Mayem agricultural field lies in Bicholim Taluka of Goa, which largely falls in the mining belt (**Fig. 2.1**). The residents in these areas were totally dependent on agriculture for their livelihoods. But with mining activities in the adjoining areas, there was a complete change in the occupational structure. In iron ore production, Bicholim contributes almost 60% of the value of total minerals exported (**Arondekar and Murthy, 2017**). The average annual rainfall of the order of 3714 mm and 3690 mm has been recorded in Bicholim taluka, which receives mostly from south-west monsoon **(Kandrika and Dwivedi, 2003**). Due to the steep slopes of dumps at the mining dump sites and the unconsolidated nature of their constituents, the low-lying agricultural lands get filled up with the dump materials that get washed down the slope thereby causing the siltation of the agricultural land and transforming it into uncultivable land (**Swaminathan, 1982**).

b. **Sanvordem Agricultural Field (SF)**: Sanvordem sgricultural field lies in Sanvordem area of Quepem Taluka in the South District of Goa State (**Fig. 2.1**). Mining is one of the major activities of Sanvordem. A lot of trucks carry the iron ore from loading point to unloading point by roadways. The spillage of the ore during the transportation on the roads enters the agricultural fields in the adjoining areas during monsoon season.

c. **Pernem Agricultural Field (PF)**: Pernem agricultural field lies in Pernem taluka. It is the northernmost subdivision of Goa (**Fig. 2.1)** which touches the Maharashtra border (Sindhudurg). Most inhabitants in this area survive on the local land for farming for the cultivation of rice and other staple food.

2.2 Sampling Techniques

2.2.1. Collection of core samples and preservation

The core samples were collected manually using gravity corer / using PVC/ acrylic pipes about 50cm long, and having a diameter of 4.5cm. The sampling was carried out in July and August month of 2014. The outer portion of every core was removed to eliminate the possible contamination by mass transport from one layer to another one during the insertion of the tube in the sediment. The cores were sub-sampled into 2cm each. These sub-samples were then transferred into clean plastic bags and stored in the refrigerator at a temperature of 4-6^{o}C. further, the wet samples were for overnight at temperature < 60^{o}C in the oven to remove the interstitial water, then crushed to a fine powder using an agate mortar and kept in pre-cleaned vials till their analysis.

2.2.2 Field observation of Sediment cores

The color of a mine wastes or weathered mine soil reveal about its weathering history, chemical properties, and physical make up. The sediment core MR, ZR, PF and TR showed grey color (**Table 2.2**). Grey colors in rocks, mine wastes and soils usually indicate a lack of oxidation and leaching and these materials which tend to be higher in pH and fertility (**Daniels *et al.*, 2004**). Whereas, sediment core collected from MF and SF showed yellowish brown/ Brown. Bright red and brown colors in mine wastes and soils generally indicate that the material has been oxidized and leached to some degree. These materials tend to be lower in pH and free of salts, less fertile, low in pyrites, and more susceptible to physical weathering than darker colored materials (**Daniels *et al.*, 2004**).

Red-brown spots indicated the presence of Fe-hydroxides partly reduced (**Zwolsman *et al.*, 1993**). This layer is produced due to the fluctuating water table and periodic shifts from oxidizing to reducing conditions during tidal inundation.

A grey layer with no mottling indicates the presence of Fe sulfides and consequently more reducing conditions of organic matter.

Table 2.2. Details of sediment core samples collected at selected stations.

Sr. No	Station Name	Length of Core	Color of core	Date of Sampling
1	Bicholim River (BR)	16 cm	Yellow to brown	31/7/2014
2	Mandovi River (MR)	42 cm	Dark grey	3/8/2014
3	Kushavati River (KR)	28 cm	Brown	2/8/2014
4	Zuari River (ZR)	36 cm	Grey	3/8/2014
5	Terekhol River (TR)	38 cm	Grey	4/8/2014
6	Mayem Lake (ML)	28 cm	Yellow to brown	31/7/2014
7	Selaulim Dam (SL)	22 cm	Dark brown	2/8/2014
8	Mayem Agricultural Field (MF)	18 cm	Dark yellow	31/7/2014
9	Sanvordem Agricultural Field (SF)	18 cm	Dark brown	2/8/2014
10	Pernem Agricultural Field (PF)	18 cm	Grey	4/8/2014

2.2.3 Sample preparatory

All sediment samples were analyzed for sediment grain size, organic carbon, total phosphorus and major elements (Fe, Mn, Al, and Mg) and trace metals (Cu, Zn, Pb, Ni, Cr and Co).

The report carries information about grain size analysis and texture of different cores collected from different stations. A known amount of dried powdered sediment was preserved to carry out grain size analysis.

2.2.3.1 Sediment Digestion

0.3g of finely ground sediment sample was transferred into a clean acid-washed Teflon beaker. To this, a mixture of 10ml of HF, HNO_3 and $HClO_4$ (7:3:1) was added slowly to avoid excessive frothing and was completely dried on the hot plate at 150^oC. After drying, again 5ml of the above mixture was added and dried on the hot plate for 1hr and then 1ml of concentrated HCl was added and dried completely. The final residue obtained was then dissolved in a 1:1 HNO_3 solution. After the complete digestion (clear solution) of the sediment sample, the content from the Teflon beakers was then transferred into the pre acid-washed volumetric flasks and the solution was made up to 100ml with Milli Q water (**Jarvis and Jarvis, 1985**). The solution is aspirated into AAS for the analysis of metals.

3.0 Methodology

All the chemicals, acids and solvents used in the present study were of guaranteed reagent grade/Analytical grade. Deionized water used for all experiments. The analysis was carried out by using Atomic Absorption Spectrophotometer (Model: GBC 932 AA) & ICP OES (Model: Agilent 710 series). All glassware used for the experiments was washed, soaked in 1N nitric acid, washed with water and rinsed with deionized water.

3.1 Sediment analysis

In the laboratory, part of the samples was oven-dried at $60^{o}C$ as analytical measurements are based on constant dry weights, finely powdered using an agate mortar and kept in pre-cleaned vials till their analysis. These samples were used to carry out the estimation of organic carbon and major elements and trace metal analysis. An aliquot of dried un-powdered sediment was preserved to carry out Grain Size Analysis.

3.2 Grain Size Analysis (sand: silt: clay)

Pipette Analysis was carried out to determine the sand: silt: clay ratio. Pipette Analysis is based on Stokes Law. According to which, when the sediment is allowed to settle in a vertical column of water, it settles with constant velocity called Settling or Terminal Velocity, which is directly proportional to the square of the particle diameter. It settles with constant velocity because the gravitational pull it gets is balanced by the Fluid Resistance (Viscosity) and Particle Drag Coefficient. The relation between all these parameters is expressed as follows.

$Vs = d_2(Xs - X)g/18j$

Where;

Vs = settling velocity

d = particle diameter

Xs = particle density

X = water density

g = acceleration due to gravity

j = dynamic viscosity

A 10gm sediment sample was taken in a 1000ml beaker. Distilled water is added to the sample and stirred. The sediment is allowed to settle. Next day water is siphoned out using a pipe. Then 10ml of 10% sodium hexametaphosphate is added to dissolve clay particles. On the next day, 5ml of 30% H_2O_2 is added in order to oxidize the organic matter. The content of the beaker is sieved over a 63micron (230 mesh) sieve. The filtrate is collected in a 1000ml measuring cylinder. The contents of the sieve are washed until the solution becomes clear. The volume is made up to the mark with distilled water and stirred using a stirrer for 1 minute. Then it is kept undisturbed for a period of time, which depends on the room temperature (**Table 3**). A pipette was inserted to a depth of 10cm into the cylinder and 25ml was pipetted out into the pre-weighed beakers and dried in an oven at 60^{o}C overnight. The beaker is then weighed again after drying. This gives the weight of clay. The fraction over 63 microns sieve is dried and weighed and it gives the weight of sand. The difference between the total weight of a sample and the weight of sand+clay gives the weight of silt (**Folk, 1968**).

% of sand, silt and clay were calculated as follows.

% of clay = (weight of clay/total weight) x 100

% of sand = (weight of sand/total weight) x 100

% of silt = [weight of silt- (weight of sand + weight of clay)]

Table 3.1 Time schedule to be used for Pipette Analysis

Size	**Depth to which pipette is inserted**	**Time after which water is to be pipetted out Hours:Minutes: Seconds**				
		28^{o}	29^{o}	30^{o}	31^{o}	32^{o}
4	20	0:00:48	0:00:46	0:00:46	0:00:44	0:00:44
5	10	0:01:36	0:01:34	0:01:32	0:01:29	0:01:28
6	10	0:06:25	0:06:15	0:06:06	0:06:57	0:05:52
7	10	0:25:40	0:25:02	0:24:25	0:24:49	0:23:27
8	10	1:42:45	1:40:13	0:37:42	1:37:15	0:33:51
9	10	6:30:00	6:40:40	6:32:50	6:32:10	6:11:30
10	10	27:06:00	26:30:00			

3.3 Organic Carbon (OC):

In this method, a finely powdered sediment sample of 0.5gm was treated with a known volume of standard dichromate solution. This was followed by the addition of concentrated H_2SO_4 with Ag_2SO_4 and mixture was allowed to stand for 30 minutes. Ag_2SO_4 was further added in order to prevent oxidation of chloride ions. After 30 minutes it was then diluted with distilled water. Then H_3PO_4 and NaF were added to it and shaken well. The excess dichromate was then back titrated with ferrous ammonium sulfate using diphenylamine as an indicator. (**Loring and Rantala, 1992**).

3.4 Total Phosphorus (TP):

The method is based on the reaction of orthophosphate ions with acidified molybdate reagent (**Murphy & Riley, 1962**) resulting in the formation of phosphomolybdenum complex, which on reduction gives blue color molybdenum compound.

5ml of digested sediment sample was taken and diluted to 50 ml with distilled water followed by the addition of 1ml acid molybdenum reagent (mixed reagent) and 1ml ascorbic acid. Using a 1cm cell, Absorbance was measured at 880 nm after 15minutes against Reagent Blank. The amount of phosphorus was estimated by constructing a calibration graph with known standards.

3.5.a Atomic Absorption Spectrophotometer (AAS).

The calibration of metals was done by using a multi-element standard (23 elements, Merck Germany). While analyzing, the instrument sensitivity and accuracy were frequently monitored with respect to mixed standard solutions.

The digested sediment sample for total metal analysis for various selected trace metals was done on Atomic Absorption Spectrophotometer (AAS Model GBC 932 AA). Atomic Absorption spectrophotometry is one of the most versatile techniques for the determination of trace metals. It is fast, accurate and free from interference. It is mainly based on the measurement of the light absorbed by the unexcited atoms of the wavelength of one of its resonance radiation. Standard stock solutions were obtained from E Merck with 1ml=1000ppm. The appropriate wavelength, flame type and cathode lamps were selected for each element and are presented in table (**Table 3.2)**. Statistical data for metal analysis was obtained from the replicate analysis of reference standard namely Cody Shale (SCO-I).

Table 3.2 Optimum instrumental conditions for elemental analysis by AAS

Element	**Wavelength(nm)**	**Fuel mixture**	**Flame type**	**Concentration of standard(µg/ml)**
Cu	324.7	Air-acetylene	Oxidizing	1-5
Zn	213.9	Air-acetylene	Oxidizing	0.4-1.5
Pb	217.0	Air-acetylene	Oxidizing	2.5-20
Ni	340.2	Air-acetylene	Oxidizing	1.2-3.0
Cr	357.9	Air-acetylene	Highly reducing	2-15
Co	240.7	Air-acetylene	Oxidizing	2.5-9

The standard solution was used to calibrate the instrument for direct readout using appropriate cathode lamps and wavelengths.

Instrument settings were made for each metal as recommended in the operation manual. Aliquots of the sample after the total decomposition step were aspirated into AAS. The readings of the solution were noted from the digital display. The concentration of the trace metals was calculated from the calibration curves constructed in standard metal-free waters. The concentration of trace metals in sediment was computed using the following equation:

$C=A\times D/W$

Where C= concentration of the element.

A = AAS response

W = weight of the sediment sample

V = volume of the solution in which the sediment the

D = dilution factor

The dilution factor ‘D’ is calculated using the equation

$D = V1\times V2/V1$

Where V1 = ml of a digested sample taken

V2 = ml deionized water added

3.5.b Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) Fe, Mn, Al and Mg were analyzed by using ICP-OES (Model: Agilent 710 series). ICP-OES is a trace-level, elemental analysis technique that uses the emission spectra of a sample to identify and quantify the elements present. The instrument sensitivity and accuracy was frequently monitored with respect to mixed standard solutions (Merck 23 elements), Germany in addition to multi-element calibration standards were run after every 10 samples, to check on the short term fluctuations in the ionization efficiency of the plasma source. Blank solutions were analyzed along with the samples. The calibration blank was prepared from > 18 MW/cm3 deionized water in 1% v/v HNO3 and 5% v/v HCl (both Merck Ultrapur). The optimum instrumental conditions for elemental analysis are as follows:

Element	Wavelength	View
Fe	258.588	Radial
Mn	257.610	Radial
Al	308.215	Radial
Mg	279.800	Radial

3.6 Accuracy and precision

The precision and accuracy of the analytical procedure adopted for several chemical parameters for sediment were evaluated from replicate analysis of standard solutions of known concentrations. Statistical data for trace metal in sediment were also obtained from replicate analysis of Cody Shale SCO-I (reference standard material)

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

Standard deviation (σ) = (xi-x)/n-1

Where xi = arithmetic mean

n = number of determination

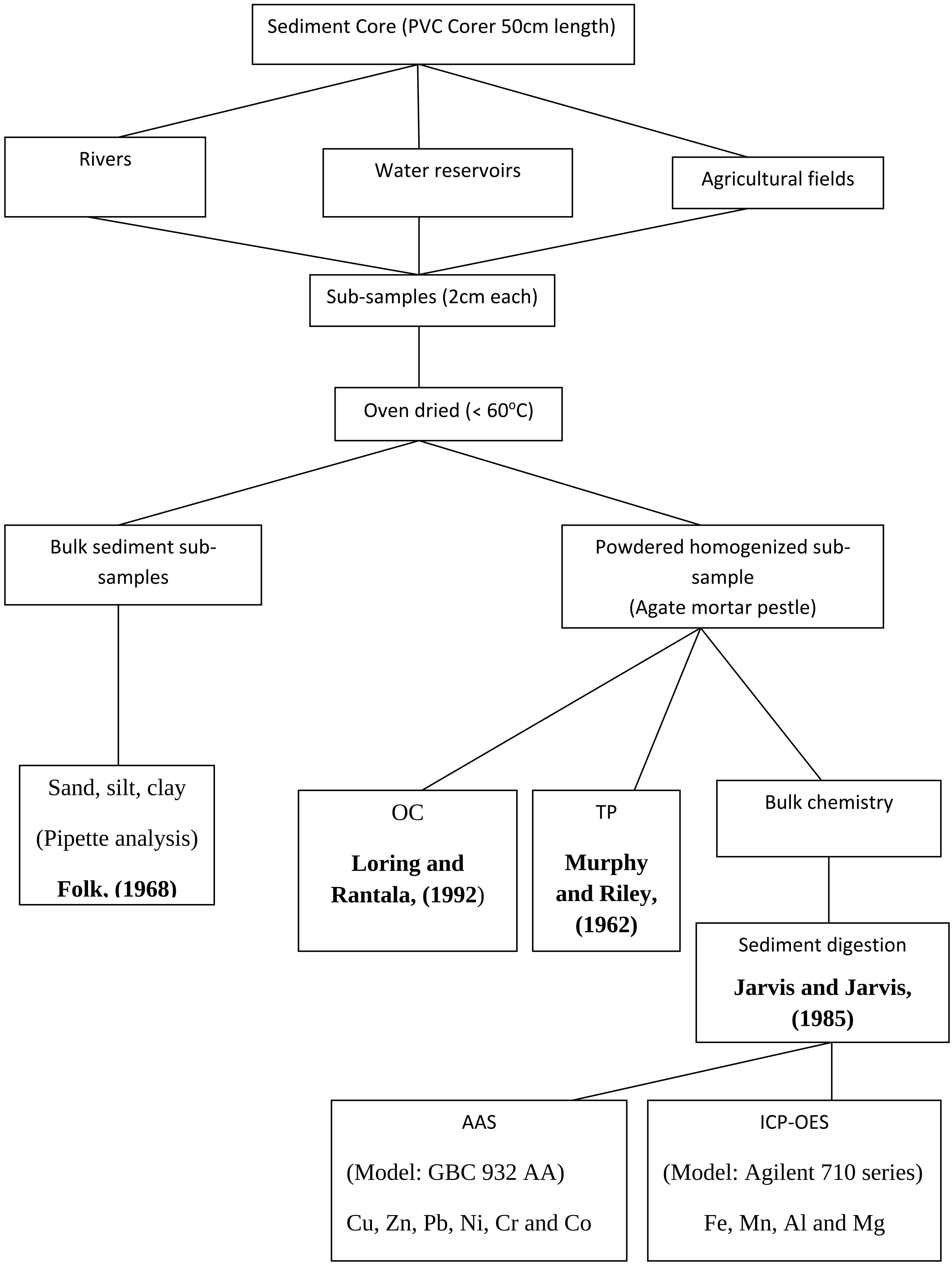
Coefficient of variation (%) = ×100/x

The relevant data is incorporated into the table (**Table 3.3)**

Table 3.3 Results of replicate Analysis of Cody Shale (SCO-I) Reference Standard.

Ref. Material	**Element**	**Certified value**	**Found**	**Standard deviation σ**	**Coefficient variation (%)**	**Recovery (%)**
SCO-I	Fe(%)	2.93±0.19	2.58	0.51661	0.122437	88.05
	Mn(%)	410±30	390.90	2.48	0.006	95.19
	Al(%)	6.52±0.21	5.32	0.6	11.27	81.6
	Mg(%)	4.44±0.2	3.8	0.32	8.42	85.6
	Cu(ppm)	29±2	24.33	1.04	0.017	81.11
	Zn(ppm)	100±8	90.57	0.99	0.11	91.64
	Pb(ppm)	31±3	25.74	0.91	0.035	83.03
	Ni(ppm)	27±3	25.09	0.89	0.08	90.02
	Cr(ppm)	30 ± 5	27.8	1.0	3.88	92.8
	Co(ppm)	11 ± 0.8	9.32	0.84	9	85.7

3.7 Analytical Procedures



3.8 Data Processing

3.8.1 Statistical Analysis

Software's like MS, Excel and Grapher 7 were used for computation and plotting of different parameters. The data were subjected to different analyses for studying large and cumbersome data. Statistica 7 software was used to obtain Factor analysis and Pearson's correlation between different parameters.

3.8.2 Pollution Indices

The following statistical parameters were used to indicate the pollution trend.

3.8.2a Enrichment Factor (EF)

Enrichment factor is one of the pollution indices used to compute the sedimentary metal source contributed by anthropogenic input or by natural sources (**Valdes *et al.*, 2005; Bastami *et al.*, 2012 and Landsberger *et al.*, 1982**). The metals are either normalized with Fe or Al to minimize the variations (**Loring, 1991 and Wedepohl, 1995**). It was calculated by using the formula given in the table (**Table 3.4**). If EF values range between 0.5 to 1.5, it indicates the natural input and if EF values are > 1.5 then it is anthropogenic input.

3.8.2b Contamination Factor (CF)

The level of contamination in the sediment core was known by its contamination factor (CF), which is calculated using trace metal data and metal concentration of world shale average (**Wedepohl, 1971**) as the background value. The contamination factor (CF) was calculated by following the formula shown in the table (**Table 3.4**).

3.8.2c Index of Geo-accumulation (Igeo)

Geo-accumulation Index (Igeo) was calculated (**Muller, 1979**) to ascertain and define metal contamination in sediment samples by comparing the present concentrations with pre-industrial levels. Factor 1.5 in this formula allows for natural fluctuations in the content of a given substance in the environment with very small anthropogenic influences. Six classes of the geochemical index were distinguished. The Index of Geo-accumulation (Igeo) was computed using the formula given in the table (**Table 3.4**). Igeo is used for the quantification of metal accumulation in the study area. Igeo classes in the study area vary from metal to metal and also from site to site (across metals and sites) (**Rabee *et al*., 2011**)

3.8.2d Pollution Load Index (PLI)

This index is a quick tool in order to compare the pollution status of different places (**Adebowale *et al.*, 2009**). Pollution severity and its variation along the sites were determined with the use of pollution load index. The PLI of the place is calculated by obtaining the n-root from the n-CFs that was obtained for all the metals using the given formula (**Table 3.4**).

Table 3.4 Classifications of Pollution indices namely Enrichment factor, Contamination Factor, Geo-accumulation Index and Pollution Load Index

No	Statistical Parameter	Reference	Classification
1	**Enrichment Factor** EF = (Y/X) sample / (Y/ X) reference	**Wedepohl, 1995; Magesh, *et al.*, 2011; Acevedo, *et al.*, 2006**	Deficiency to minimal enrichment if EF value is < 2 Moderate enrichment if EF value is 2 to 5 Significant enrichment if EF value is 5 to 20 Very high enrichment if EF value is 20 to 40 Extremely high enrichment if EF value is > 40
2	**Contamination Factor** $CF_{metal} = C_{metal\ concentration} / C_{background\ metal\ concentration}$	**Wedepohl, 1971**	Low contamination if CF value is ≤ 1 Moderate contamination if CF value is < 3 Considerably contaminated if CF value is < 6 Highly contaminated if CF value is >6
3	**Geo-accumulation Index** $$Igeo = \frac{Log2Cn}{1.5Bn}$$ C**n** is the concentration of the metal and B**n** is the average shale value (background value) of the metal	**Muller, 1981; Magesh, *et al.*, 2011; Loska *et al.*, 2004; Selvaraj *et al.*, 2004**	Practically uncontaminated if Igeo value is < 0 (class 0) Uncontaminated to moderately contaminated if Igeo value is <1(class 1) Moderately contaminated if Igeo value is < 2(class 2) Moderately to heavily contaminated if Igeo value is < 3(class 3) Heavily contaminated if Igeo value is < 4(class 4) Heavily to extremely contaminated if Igeo value is < 5(class 5) Extremely contaminated if Igeo value > 5(class 6)
4	**Pollution Load index** PLI= $n\sqrt{(CF_1 \times CF_2 \times \ldots\ldots CFn)}$ CF is the Contamination factor of metal n is the Number of metals analyzed	**Tomilson, *et al.*, 1980**	Unpolluted if PLI value is < 1 Polluted if PLI value is > 1

4.1 RIVERS

Five sediment cores were collected from Bicholim River (BR), Mandovi River (MR), Kushavati River (KR), Zuari River (ZR) and Terekhol River (TR) of Goa. The sediment components, down core variation, OC, TP and major elements and trace metals have been reported.

4.1.1 Bicholim River (BR)

4.1.1.1 Sediment components

The grain size distribution of core is important in understanding the depositional environment history of sediment (**Sunderarajan and Natesan, 2010).** The sand, silt and clay content (%) in the core varied from 1.67 to 40.07 (26.66); 51.9 to 87.02 (63.56) and 7.31 to 14.96 (9.79) respectively (**Table 4.1.1.a**). The down core variation of sand in BR core showed a decreasing trend from the bottom up to the 8 cm depth and thereafter it showed an increasing trend up to the surface of the core. At 8cm depth, it recorded highest silt content (82.07%), whereas, at the same depth, sand content was low (1.67 %) due to which sand showed a decreased and silt showed an increased peak at 8 cm depth in the core. Thus exhibiting sandy silt texture. The absence of fine silt and clay and dominance of medium to fine sand in this core can be attributed to tidal impacts and hydrodynamic sorting (**Ranjan *et al.* 2010; Gao *et al.* 2012; Jia *et al.* 2012 and Yang *et al.* 2015**). Distribution of silt and clay compensates the sand throughout the length of the core (**Fig. 4.1.1.a**).

Table 4.1.1.a Data on the sediment components, Organic Carbon (OC) and Total Phosphorus (TP) in sediment core of Bicholim River (BR), Goa-West coast of India

Depth (cm)	Sand	Silt	Clay (%)	OC	TP
0	35.66	55.95	8.40	0.27	0.010
2	31.77	60.92	7.31	0.31	0.013
4	40.07	51.90	8.03	0.22	0.012

6	26.24	58.80	14.96	0.07	0.012
8	1.67	87.02	11.31	0.13	0.010
10	23.61	64.61	11.78	0.04	0.012
12	26.39	64.84	8.77	0.03	0.014
14	27.84	64.41	7.74	0.04	0.013
Avg	**26.66**	**63.56**	**9.79**	**0.14**	**0.012**
Min	1.67	51.90	7.31	0.03	0.010
Max	40.07	87.02	14.96	0.31	0.014

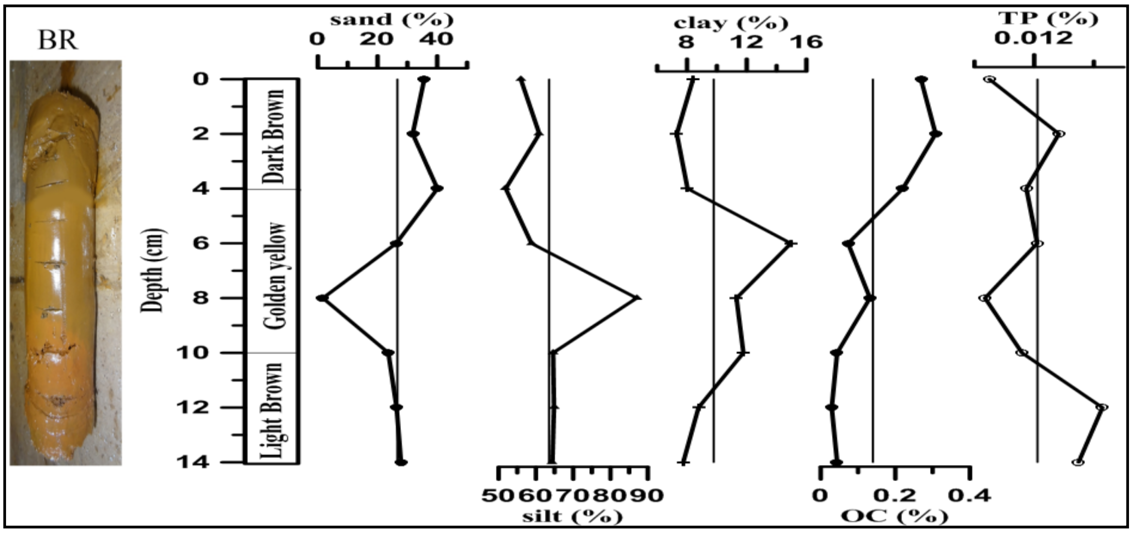


Fig. 4.1.1.a Down core variation of sand, silt, clay, organic carbon (OC) and total phosphorus (TP) in a sediment core of Bicholim River (BR), Goa-West coast of India

The sediment components are plotted on a triangular diagram proposed by **Pejrup, (1988**) to understand hydrodynamic conditions that prevailed during the deposition of sediments (**Fig. 4.1.1.b**). Sediment samples of BR core fell in section IVC indicating the deposition of finer sediments under very violent conditions

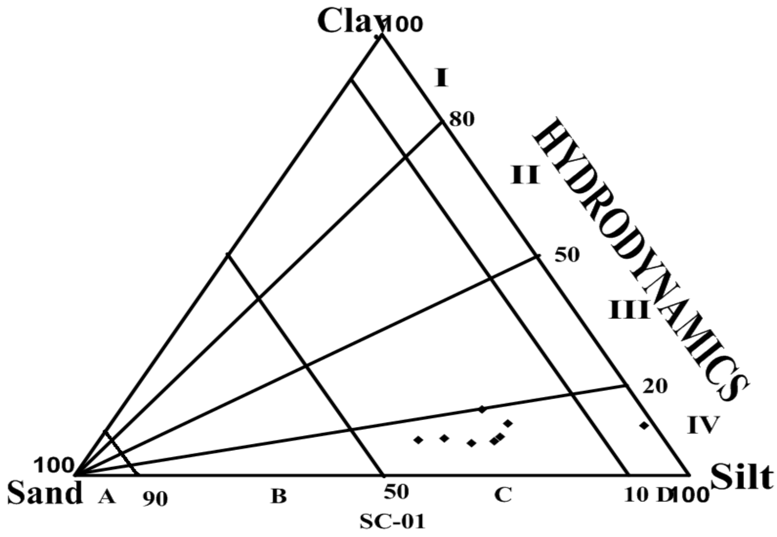


Figure 4.1.1.b Triangular diagram for the classification of the hydrodynamics of core collected from Bicholim River (BR), Goa-West coast of India (**Pejrup, 1988**)

4.1.1.2 Organic Carbon (OC)

Organic carbon (%) content in BR core varied from 0.03 to 0.31 with an average of 0.14 and showed a minimum at the bottom of the core, whereas at 2cm depth it exhibited maximum values (**Table 4.1.1.a**). The OC values recorded at 8cm depth up to the surface of the core are higher than those observed from the bottom of the core up to 8cm depth. This could be due to its direct discharge of wastes from the town. This may be responsible for higher OC in the upper few centimeters of the core (**Nazneen and Raju, 2017**). Down core variation of OC showed an increasing trend from the bottom up to the surface of the core (**Fig. 4.1.1.a**). The distribution pattern of OC is largely similar to that of silt and clay suggesting higher affinity for finer sediments towards organic carbon (**Kumar and Sheela, 2013**) due to the higher surface area/volume ratio of finer sediment grain (**Zhou *et al.*, 2007**) and similarity in settling velocity (**Raj *et al.*, 2013**). The increase in OC concentration in the top few centimeters in the core suggests that an increasing discharge of organic matter associated with industrial, agricultural, mining and domestic wastes into the estuaries is occurring in recent years (**Nasnodkar and Nayak, 2015**). The yellowish-brown color of the BR core (**Fig. 4.1.1.a**) indicates that the organic material has been oxidized and leached to some degree.

4.1.1.3 Total Phosphorus (TP)

The data on TP in BR core varied from 0.010-0.014 (0.012%). It showed high concentration at 12cm depth of the core unlike in OC (**Table 4.1.1.a**). The down core variation of TP showed a decreasing trend from the bottom up to 8cm depth and thereafter it showed an increasing trend up to 2cm and further, it showed a decreasing trend up to the surface of the core (**Fig. 4.1.1.a**). TP coincides with a trend exhibited by silt.

4.1.1.4 Major Elements (Fe, Mn, Al, and Mg)

The concentration and average values of major elements Fe, Mn, Al and Mg varied from 10.40-32.11 (25.98); 0.53-0.94 (0.81); 5.32-11.90 (10.16) and 0.14-0.33 (0.27) respectively (**Table 4.1.1.b)**. Fe showed higher concentration at 2cm, Mn at 6 cm and Al at the bottom of the sediment core. High content of Fe can be explained due to intense iron ore mining area comprises of five major mining leases (**Rane and Matta, 2019**). The values of Fe and Mn are in good agreement with those reported earlier by **Prajith *et al.*, (2015**) and **Veersingam *et al.*, (2014**) from Mandovi River. Fe, Mn and Al are higher when compared to Shale values (**Turekian and Wedehpohl, 1961**). Whereas, Mg (0.27) values are lower than that of Shale values. Fe and Mn recorded almost constant values from bottom up to 6 cm depth this may be due to several big open cast iron and manganese ore mines that operate in the drainage basins of the river. Fe and Mn ores brought from the mines are stored on the shore of the estuary, loaded on to barges at loading points, and transported through the river to the port (**Kessarkar *et al.*, 2013**). The ore and mine dump stored on the bank of the river is brought into the river basin as run-off during the monsoon (**Fig 4.1.1.c)**. Down core variation of Fe, Al, and Mg showed a decreasing trend from the bottom up to the surface of the core, whereas Mn, showed slightly increasing trend from the bottom up to 6cm depth and thereafter showed a decreasing trend up to the surface of the core (**Fig 4.1.1.d)**. In general, the distribution of major elements in sediment core followed the order (decreasing) Fe > Mn >Al> Mg.

Fig 4.1.1.c Photograph showing mining dumps that have been kept unprotected and unstabilized on the bank of Bicholim River (BR), Goa-West coast of India

Table 4.1.1.b Data on major elements and trace metals in a sediment core of Bicholim river (BR), Goa-West coast of India

Depth (cm)	Major Elements (%)				Trace metals (µg g^{-1})					
	Fe	**Mn**	**Al**	**Mg**	**Cu**	**Zn**	**Pb**	**Ni**	**Cr**	**Co**
0	14.36	0.78	5.32	0.14	72.66	90.24	78.67	80.33	397.00	24.33
2	32.11	0.78	10.66	0.28	87.99	97.90	60.00	106.00	378.00	43.67
4	10.40	0.83	9.91	0.33	74.33	100.24	90.67	83.33	382.00	40.00
6	28.11	0.94	11.10	0.33	59.99	123.57	71.33	65.33	413.00	74.00
8	30.63	0.88	9.68	0.29	76.99	115.57	76.00	67.00	357.66	30.67
10	30.87	0.89	11.34	0.29	84.66	94.57	92.00	71.00	380.33	45.00
12	30.73	0.86	11.38	0.22	84.99	109.57	86.33	101.33	420.33	65.67
14	30.67	0.53	11.90	0.30	86.33	102.57	83.00	102.00	349.33	62.67
Avg	**25.98**	**0.81**	**10.16**	**0.27**	**78.49**	**104.28**	**79.75**	**84.54**	**384.70**	**48.25**
Min	10.40	0.53	5.32	0.14	59.99	90.24	60.00	65.33	349.33	24.33
Max	32.11	0.94	11.90	0.33	87.99	123.57	92.00	106.00	420.33	74.00
Std Dev	8.54	0.12	2.10	0.06	9.47	11.21	10.69	16.59	24.71	17.55
Avg Shale	4.72	0.08	8.0	1.5	45	95	20	68	90	19

4.1.1.5 Trace metals (Cu, Zn, Pb, Ni, Cr, and Co)

Data on concentration and average values of trace metals Cu, Zn, Pb, Ni, Cr and Co (μgg^{-1}) in BR core varied from 59.99-87.99 (78.49); 90.24-123.57 (104.28); 60.00-92.00 (79.75); 65.33-106.00 (84.54); 349.33-420.33 (384.70) and 24.33-74.00 (48.25) respectively (**Table 4.1.1.b)**. Cu and Ni showed higher concentration at 2cm, Zn and Co showed at 6cm, Pb showed at 10cm and Cr showed at 12cm depth of the core. The values of Cu are in good agreement with those reported by **Singh *et al.*, (2014)** from Mandovi River, whereas Zn showed lower values than those reported by **Magesh *et al.*, (2011)** from Tamirparani River and **Shah *et al.*, (2013)** from Tapti River. However, the values of Pb are in broad agreement with those reported by **Dessai *et al.*, (2009)** from the Zuari River. All the trace metals recorded higher average concentrations, as compared to Shale values (**Turekian and Wedepohl, 1961**). Being reservoirs of the mining-related activities, as well as agricultural and domestic wastes, the input of Pb and Zn from automobile exhaust and domestic waste may be the major source of their enrichment in sediments. The input of Cu, Co and Zn might be associated with the presence of boatyard and small vessel building yards. Zn is derived from industries, liquid manure, composted materials and agrochemicals such as fertilizers and pesticides (**Krishna and Govil, 2004**). Down core variation of trace metals (**Fig. 4.1.1.d.)** Cu, Zn, and Co showed a decreasing trend from the bottom up to the surface of the core, whereas Pb and Ni showed a decreasing trend from the bottom up to 6cm depth and thereafter it showed an irregular trend up to the surface of the core. However, Cr showed an irregular trend. In general, the distribution of trace metals in sediment core followed the order (decreasing) Cr > Zn >Ni > Pb > Cu > Co.

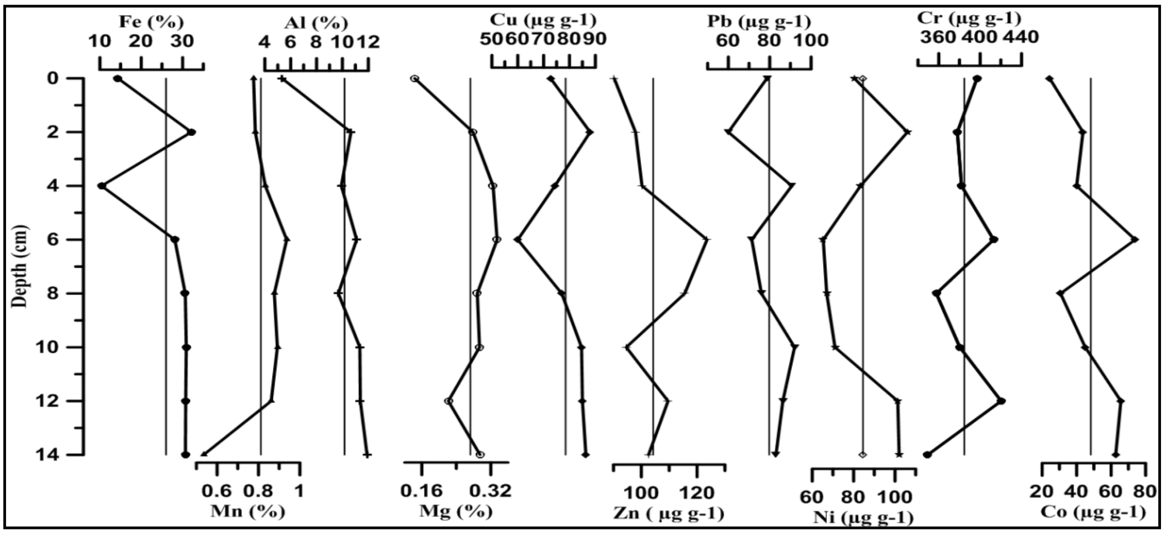


Fig. 4.1.1.d Down core variation of major elements (Fe, Mn, Al, and Mg) and trace metals (Cu, Zn, Pb, Ni, Cr, and Co) in sediment core of Bicholim River (BR), Goa-West coast of India

4.1.1.6 Pearson's Correlation Coefficient

To understand the influence of sediment components on metal distribution in the sediment, Pearson's correlation among the grain size, OC, TP, and metals were performed (**Table 4.1.1.c**). TP showed a positive correlation coefficient with Ni and Co, whereas Al showed good association with Mg; Co showed a good association with Ni indicating their common source. Similarly, Cu showed a good association with Ni.

Table 4.1.1.c Data on Pearson's correlation between different sediment components (sand, silt, clay), OC, TP, major elements (Fe, Mn, Al, and Mg) and trace metals (Cu, Zn, Pb, Ni, Cr, and Co) in sediment core of Bicholim River (BR), Goa-West coast of India (n=8)

Param.	**sand**	**silt**	**clay**	**OC**	**TP**	**Fe**	**Mn**	**Al**	**Mg**	**Cu**	**Zn**	**Pb**	**Ni**	**Cr**	**Co**
sand	1.00														
silt	**-0.97**	1.00													
clay	-0.46	0.24	1.00												
OC	0.40	-0.31	-0.47	1.00											
TP	0.28	-0.23	-0.30	-0.40	1.00										
Fe	-0.60	0.58	0.26	-0.50	0.43	1.00									
Mn	-0.24	0.10	0.65	-0.03	-0.33	-0.03	1.00								
Al	-0.21	0.17	0.19	-0.63	0.67	0.66	-0.05	1.00							
Mg	-0.17	0.09	0.40	-0.29	0.12	0.24	0.13	**0.73**	1.00						
Cu	-0.03	0.20	-0.66	-0.04	0.46	0.43	-0.47	0.33	-0.15	1.00					
Zn	-0.53	0.41	0.66	-0.47	0.13	0.37	0.38	0.43	0.50	-0.50	1.00				
Pb	0.11	-0.11	-0.04	-0.51	0.02	-0.33	-0.01	0.09	0.00	0.11	-0.24	1.00			
Ni	0.42	-0.25	**-0.81**	0.17	**0.76**	0.17	-0.63	0.23	-0.22	**0.71**	-0.35	-0.16	1.00		
Cr	0.34	-0.44	0.30	-0.08	0.23	-0.15	0.59	-0.13	-0.29	-0.41	0.21	0.01	-0.08	1.00	
Co	0.07	-0.16	0.34	-0.67	**0.76**	0.46	-0.03	**0.74**	0.43	-0.10	0.58	0.00	0.20	0.36	1.00

4.1.1.7 Pollution indices

a. Enrichment Factor (EF) It is evident from the figure (**Fig. 4.1.1.e**) that Fe and Mn showed significant enrichment (EF value 5 < 20), whereas Pb, Cr, and Co showed moderate enrichment. However, Mg, Cu, Zn, and Ni showed deficiency to minimal enrichment. The significant enrichment of Fe and Mn in BR core can be due to intense iron ore mining activities. The ore stored at different points on the shores of the river gets flushed into the river during heavy monsoon rains and also it indicates that they were sourced from ore material which accumulated at the core sites due to anthropogenic activity on the shores of the river (**Prajith *et al.*, 2016**).

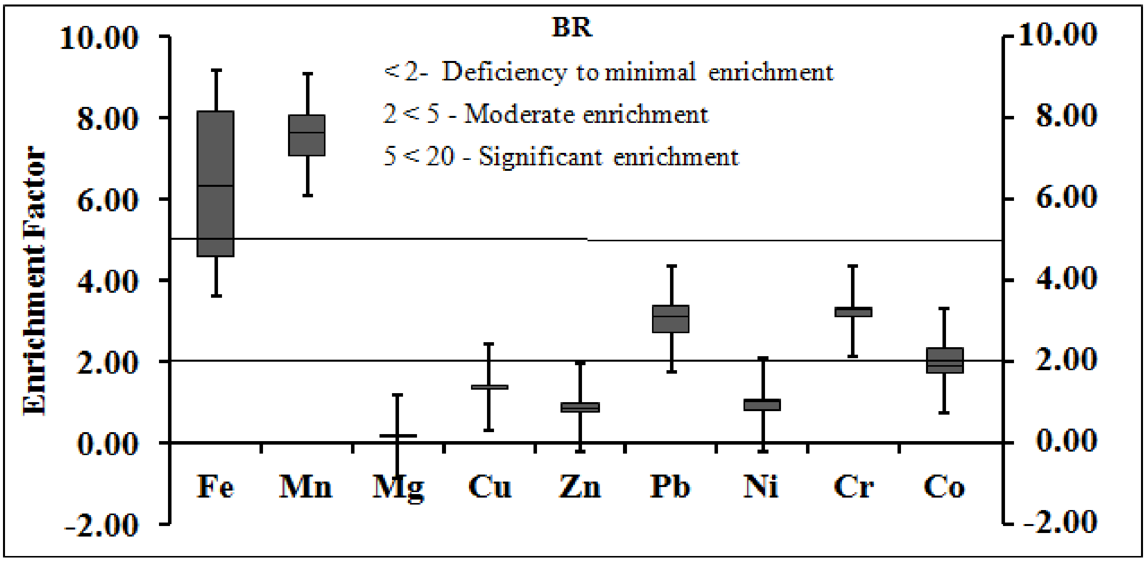


Fig. 4.1.1.e Enrichment factor for major elements and trace metals in core collected from Bicholim River (BR), Goa-West coast of India

b. Contamination Factor (CF)

Contamination factor for BR core showed high contamination for Fe and Mn, whereas Pb and Cr and Co showed considerable contamination and Al, Cu, Ni showed moderate contamination. However Mg and Zn showed low contamination (**Fig 4.1.1.f**). High contamination of Fe and Mn and considerable contamination for Pb and Cr in BR sediment core can be attributed to enormous mining activities and discharge of mining wastes in this region. Moderate contamination of Al may probably be due to use of aluminum salts in treating wastes from the mining pits (**Chaturvedi and Patra, 2016**).

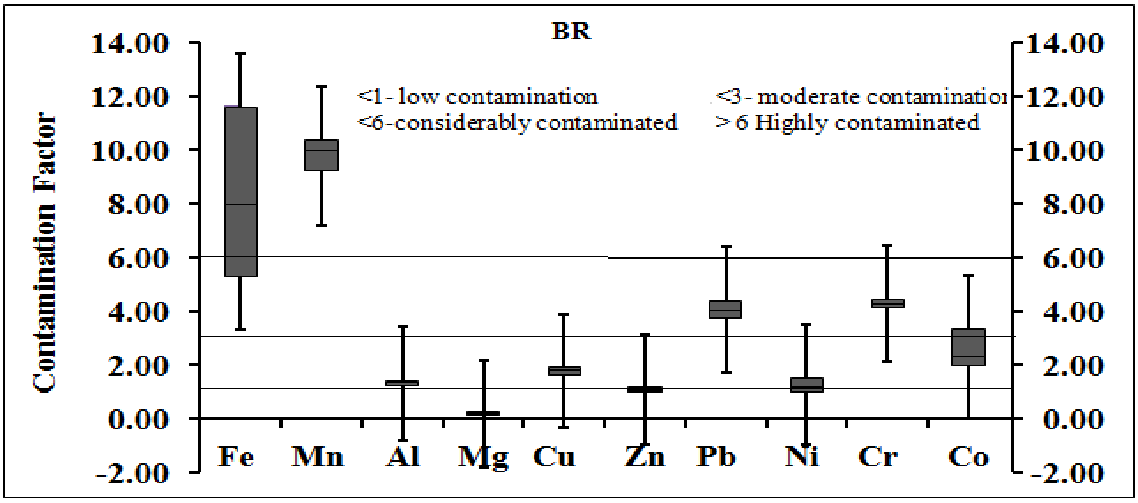


Fig. 4.1.1.f Contamination factor for major elements and trace metals in core collected from Bicholim River (BR), Goa-West coast of India

c. Geo-accumulation Index (Igeo)

Geo-accumulation index values in BR core (**Fig 4.1.1.g**) exhibited Moderately to Strongly Polluted (Igeo class 3) with Fe and Mn. Moderately Polluted (Igeo class 2) with Pb and Cr. Unpolluted to Moderately Polluted (Igeo class 1) with Cu and Co. Whereas Unpolluted (Igeo class 0) with Al, Mg, Zn and Ni. The Moderate Pollution of Fe and Mn in sediment cores is directly related to Fe-Mn ore deposits and human induced activity in handling and transportation of these ores.

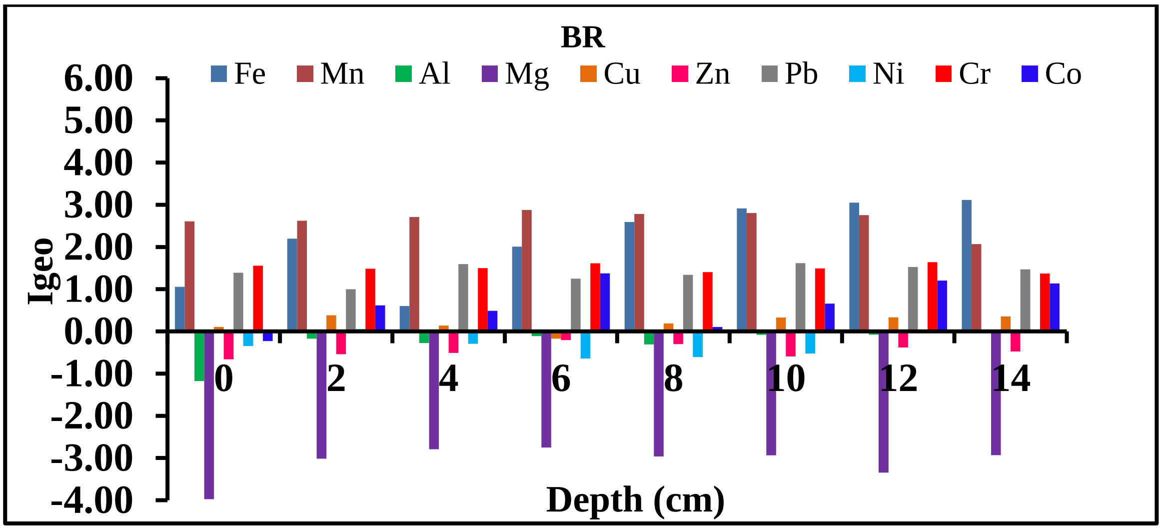


Fig. 4.1.1. g Geo-accumulation Index (Igeo) for major elements and trace metals in the sediment core from Bicholim River (BR), Goa-West coast of India

d. Pollution Load Index (PLI)

Pollution load index values in BR core varied from 1.54 to 2.39 (2.07) indicating that BR core is polluted (PLI > 1). The down core variation of PLI (**Fig. 4.1.1.h**) showed a decreasing trend from bottom (14cm) up to the surface of the sediment core with increased peak at 6cm and 2cm depth. This can be attributed to the directly related to Fe-Mn ore deposits and human induced activity in handling and transportation of these ores.

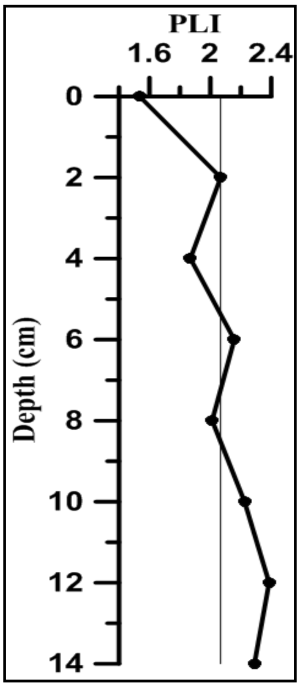


Fig. 4.1.1.h Down core variation of PLI in sediment core of Bicholim River (BR), Goa-West coast of India

4.1.1.8 Factor Analysis

Factor analysis is a statistical technique commonly used to reduce a large number of variables into few number of principal factors. It shows true correlation between variables and factors. Five factors were obtained for the sediment core with Eigen Values >1 is placed in table (**Table 4.1.1.d)**. In BR core, Factor 1 accounted for 30.80% of the total variance shows significant positive loadings for TP, Al and Co. Factor 2 showed 25.25% of total variance with strong positive loadings of Cu and Ni revealing anthropogenic sources which may be due to agrochemicals (pesticides and artificial fertilizers) from the nearby intensive agricultural fields, and deposition of wastes from the nearby towns (**Dirbaba *et al.*, 2018**). Factor 3 accounted for 17.91%

of the total variance and showed strong positive loading on silt and Fe suggests association of this metal with finer fractions. Factor 4 did not show any strong positive loading, whereas Factor 5 accounted for 8.20% of total variance with a good loading on Mg. Mn, Zn, Pb and Cr did not show high loading values in any component, indicating that these metals had different sources of pollution.

Table 4.1.1.d Factor analysis matrix after varimax rotation for sediment core of Bicholim River (BR), Goa-West coast of India

Parameters	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
sand	0.014	0.257	**-0.953**	0.011	-0.111
silt	-0.068	-0.055	**0.973**	0.005	0.096
clay	0.209	**-0.892**	0.258	-0.071	0.099
OC	-0.647	0.191	-0.362	0.602	-0.026
TP	**0.864**	0.442	-0.155	0.016	-0.151
Fe	0.591	0.123	**0.709**	0.196	-0.002
Mn	-0.029	**-0.781**	0.091	0.008	-0.271
Al	**0.842**	0.090	0.215	-0.116	0.402
Mg	0.425	-0.279	0.025	0.008	**0.818**
Cu	0.144	**0.875**	0.300	-0.119	-0.062
Zn	0.508	-0.630	0.328	0.206	0.161
Pb	-0.010	0.034	-0.136	**-0.980**	0.008
Ni	0.354	**0.850**	-0.201	0.241	-0.174
Cr	0.309	-0.476	-0.393	0.032	**-0.711**
Co	**0.958**	-0.162	-0.113	-0.015	0.045
Expl.Var	3.870	3.947	3.058	1.495	1.527
Prp.Totl	0.258	0.263	0.204	0.100	0.102
% Total variance	30.800	25.750	17.910	9.970	8.200

4.1.2 Mandovi River (MR)

4.1.2.1 Sediment components

The data on sand, silt, and clay is presented in the table (**Table 4.1.2.a).** MR sediment core exhibited higher average sand content (61.70%), it varied from 38.66 to 80.52%, whereas silt and clay content varied from 15.48 -50.32 (31.40%) and 4.00 -11.02 (6.90%) respectively. From bottom up to 30cm depth, it exhibited sandy type texture and from 30cm up to the surface of the core, it showed silty sand. Sand showed higher values and silt showed lower values at 6cm depth of the core. The down core variation of sand in MR core showed a fluctuating increasing trend from bottom to the surface of the core, whereas the distribution of silt and clay compensates the variation of sand throughout the length of the core (**Fig 4.1.2.a**). Higher sand content is due to higher fresh water discharge that occurs during the south-west monsoon which carries the finer sediments (**Kessarkar *et al.,* 2010**). The sediments are dominated by sand due to the influence of the sea (**Nazneen and Raju, 2017**).

Table 4.1.2.a Data on sediment components (sand, silt, clay). Organic Carbon (OC) and Total Phosphorus (TP) in sediment core of Mandovi River (MR), Goa-West coast of India

Depth (cm)	Sand	Silt	Clay (%)	OC	TP
0	69.80	26.01	4.19	0.95	0.012
2	78.58	17.32	4.10	1.13	0.012
4	80.52	15.48	4.00	1.19	0.010
6	76.76	19.11	4.13	1.34	0.016
8	74.76	20.69	4.54	1.34	0.014
10	78.34	17.61	4.05	1.43	0.011
12	61.82	30.87	7.31	1.49	0.012
14	62.22	30.24	7.54	1.49	0.015
16	65.05	28.59	6.37	1.64	0.011
18	53.32	37.11	9.57	2.54	0.035
20	57.01	35.85	7.14	2.69	0.013
22	53.70	38.56	7.74	2.93	0.011
24	63.65	30.24	6.11	2.99	0.013

26	65.70	27.43	6.86	3.14	0.012
28	52.55	39.44	8.02	3.29	0.013
30	47.77	42.80	9.42	3.32	0.016
32	56.68	35.07	8.26	3.29	0.010
34	56.29	36.48	7.23	2.69	0.010
36	38.66	50.32	11.02	2.54	0.017
38	50.47	40.65	8.88	2.54	0.013
40	52.07	39.51	8.42	2.39	0.011
Avg	**61.70**	**31.40**	**6.90**	**2.21**	**0.014**
Min	38.66	15.48	4.00	0.95	0.010
Max	80.52	50.32	11.02	3.32	0.035

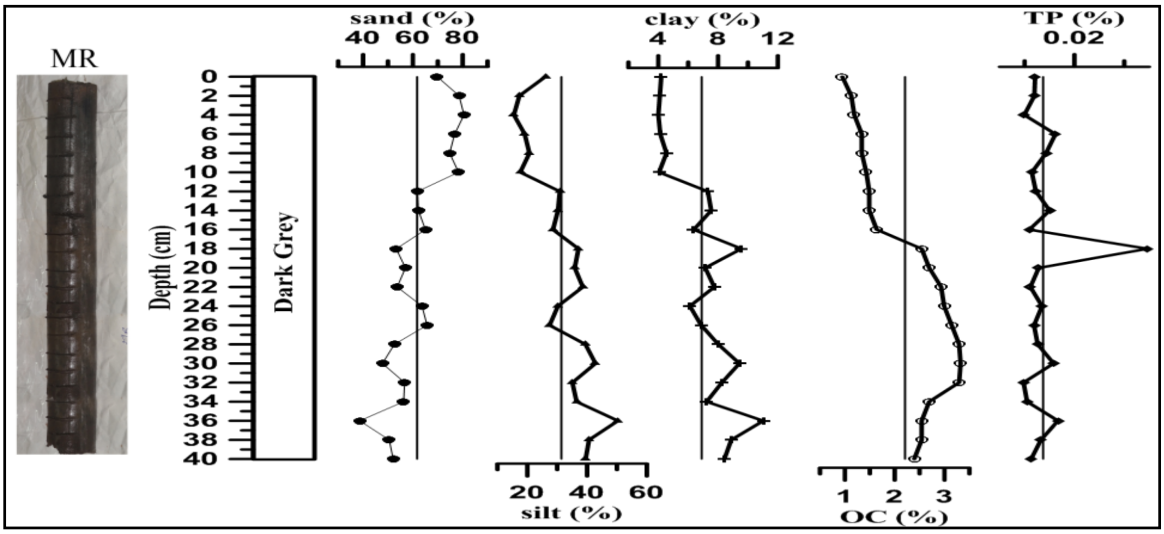


Fig. 4.1.2.a Down core variation of sand, silt, clay, Organic Carbon (OC) and Total Phosphorus (TP) in a sediment core of Mandovi River (MR), Goa-West coast of India

The hydrodynamic conditions in Mandovi River showed that the sediments fell in IV B and IVC indicating the deposition of finer to coarser sediment in very violent hydrodynamic conditions (**Fig. 4.1.2.b)**.

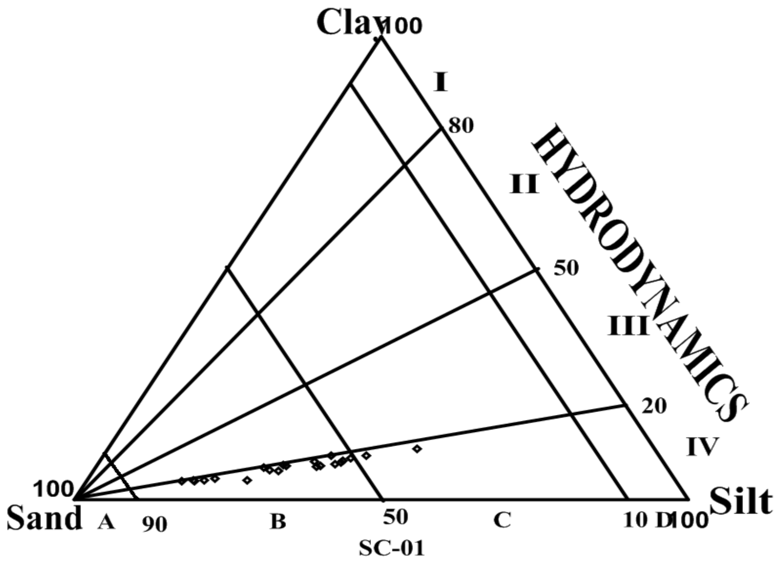


Fig. 4.1.2.b Triangular diagram for the classification of the hydrodynamics of core collected from Mandovi River (MR), Goa-West coast of India (**Pejrup, 1988**)

4.1.2.2 Organic carbon (OC)

Organic carbon (%) in MR core varied from 0.95 – 3.32 with an average of 2.21. OC showed lower concentration at the surface and higher concentration from 32cm up to 26cm depth of the core. Comparatively higher values in the bottom sediment indicates that primary production in the overlying water column influences the organic carbon content in the sediment core during their deposition period (**Devassy, 1983**). This is also supported by grey color with dark patches. The down core variation of organic carbon (**Fig 4.1.2.a**) showed a decreasing trend from the bottom up to the surface of the core. It is similar to finer fractions namely silt and clay. It is interesting to note that the average sand content is higher from 10cm up to the surface of the core as compared to the bottom sediments. Hence, lower average values of OC is seen in the core which may be due to more sand content in this core which holds less amount of nutrients since sediment texture plays a key role in controlling the OC content (**Hedges and Keil 1995 and Goni *et al.* 2003**). The decrease in OC with depth reflects the degradation of organic matter due to microbial activity (**Singh and Nayak, 2009**) and also due to dilution by the influx of coarse-grained sediments (**Pichaimani *et al.*, 2008**).

4.1.2.3 Total phosphorus (TP)

Total phosphorus in MR core is presented in table (**Table 4.1.2.a**). It varied from 0.010 – 0.035 (0.014%). The average value of 0.014 % for TP in the core is quite low. It showed higher concentration at 18cm depth of the core. The down core variation of total phosphorus showed an irregular trend with values almost similar to that of the average except at 18cm depth where it showed comparatively higher concentration of total phosphorus (**Fig 4.1.2.a)**. The increase in the concentration of phosphorus could be anthropogenic, as well as from calcium carbonate of the marine organisms since phosphorus binds Ca besides Fe and Al (**Sundareshwar and Morris, 1999 and Yang *et al.* 2015).**

4.1.2.4 Major elements (Fe, Mn, Al and Mg)

Data on major elements in MR sediment core is presented in table (**Table 4.1.2.b).** It is evident from the table that the concentration and average values of Fe, Mn, Al and Mg varied from 2.19-8.33 (6.26%); 0.03-0.46 (0.25); 3.00-9.41 (6.99) and 0.93-2.46 (1.96) respectively. Fe showed higher concentration at 22cm and 30cm, whereas Mn, Al and Mg showed at 36cm depth of the core. Fe and Mn values are in broad agreement with those reported from the same river by **Singh *et al.*, (2014) and Algarsamy, (2006)**. Fe and Mn values are higher as compared to Shale values, which may be attributed to high spillage (**Fig. 4.1.2.c**) during transportation of iron and ferromanganese ores down the Mandovi River (**Algarsamy, 2006**), Whereas Al (6.99%) recorded low average values. Mg recorded almost similar values to that of average Shale values (**Turekian and Wedehpohl, 1961**). Down core variation of Fe, Mn, Al, and Mg are presented in fig (**Fig 4.1.2.d).** Fe, Mn, Al, and Mg showed a decreasing trend from the bottom up to the surface of the core. It is interesting to note that at 36cm depth all four elements showed an increased peak which may be due to more spillage of ore during the transportation. In general, the distribution of major elements in sediment core followed the order (decreasing) Fe > Mn > Mg >Al.

4.1.2.5 Trace metals (Cu, Zn, Pb, Ni, Cr and Co)

The range and average values of trace metals Cu, Zn, Pb, Ni, Cr, and Co in MR core varied from 11.99-52.00 (34.23); 47.24-99.57 (79.57); 6.33-92.67 (53.76); 18.33-31.67 (26.60); 36.33-122.33 (85.25) and 13.33-42.00 (31.92) respectively **(Table 4.1.2.b).** Higher concentration was recorded by Cu at 18cm, Zn at 6cm, Pb at 14cm, Ni and Cr at 10cm, whereas Co at the bottom of the core. Cu and Zn concentrations are in good agreement with those reported by **Veersingam *et al.*, (2014)** from the same river, whereas the values of Pb are in good agreement with those reported by **Shah *et al.*, (2013)** from Tapti River. Pb and Co recorded higher average concentration, whereas Cu, Zn, Ni and Cr showed lower average concentration as compared to average Shale values (**Turekian and Wedepohl, 1961**). Increase of Pb flux from the bottom up to 4cm depth is probably due to increased vehicular traffic, and may be due to increased anthropogenic activities and industrial discharges into the coastal environment (**Siraswar and Nayak, 2011**). Down core variation of trace metals is Cu, Zn, Ni, and Cr showed an irregular trend from the bottom up to the surface of the core. Whereas Pb and Co showed a decreasing trend from the bottom up to the surface of the core (**Fig 4.1.2.d).** It agrees with the distribution trend of Fe and Mn. Trace metals may enter into riverine system due to spillage of Fe-Mn ore during transportation, and anthropogenic input (**Rao and Chakraborty, 2016**). In general, the distribution of Trace metals in sediment core followed the order (decreasing) Pb > Co > Cr > Zn > Ni > Cu.

Table 4.1.2.b Data on major elements and trace metals in a sediment core collected from Mandovi River (MR), Goa-West coast of India

	Major Elements (%)				Trace metals (µg g-1)					
Depth (cm)	**Fe**	**Mn**	**Al**	**Mg**	**Cu**	**Zn**	**Pb**	**Ni**	**Cr**	**Co**
0	5.29	0.23	6.80	2.02	30.33	78.90	6.33	24.33	81.00	13.33
2	2.83	0.13	6.23	1.86	33.99	62.24	16.33	29.67	119.67	19.67
4	3.54	0.03	3.00	0.93	11.99	47.24	15.67	29.33	86.67	16.33
6	5.93	0.15	4.57	1.40	39.99	95.57	25.00	30.00	100.00	25.33
8	6.62	0.09	5.92	1.78	36.66	95.24	34.00	24.67	77.67	36.33
10	7.62	0.10	6.93	1.99	35.33	92.90	73.67	31.67	122.33	18.67

12	7.27	0.13	5.67	1.64	35.33	83.90	82.67	30.00	89.33	22.67
14	6.63	0.18	6.94	1.97	32.66	90.90	92.67	27.67	95.33	39.00
16	7.17	0.12	6.58	1.88	33.66	74.24	73.67	24.00	68.33	33.67
18	8.27	0.25	8.05	2.24	52.00	84.57	54.67	31.33	86.67	38.67
20	6.86	0.29	8.32	2.24	36.33	77.90	52.00	23.00	117.00	39.33
22	8.33	0.33	7.17	1.98	32.00	67.24	57.00	31.33	73.67	30.33
24	6.96	0.05	7.96	2.29	37.66	85.57	56.00	22.33	115.67	34.67
26	6.93	0.44	7.70	2.16	32.66	71.24	48.67	18.33	83.67	39.67
28	8.00	0.46	8.25	2.17	36.33	75.24	52.67	22.33	74.67	38.33
30	8.33	0.45	8.42	2.15	40.66	90.57	19.33	26.33	77.67	38.00
32	6.24	0.33	6.61	1.91	31.33	74.57	69.00	29.00	36.33	34.00
34	5.70	0.26	6.24	1.78	24.99	99.57	82.00	22.00	78.33	31.67
36	7.82	0.46	9.41	2.46	46.66	87.90	65.67	23.33	89.00	37.67
38	2.95	0.31	7.78	2.09	28.99	68.24	64.33	30.00	63.00	41.00
40	2.19	0.39	8.28	2.18	29.33	67.24	87.67	28.00	54.33	42.00
Avg	**6.26**	**0.25**	**6.99**	**1.96**	**34.23**	**79.57**	**53.76**	**26.60**	**85.25**	**31.92**
Min	2.19	0.03	3.00	0.93	11.99	47.24	6.33	18.33	36.33	13.33
Max	8.33	0.46	9.41	2.46	52.00	99.57	92.67	31.67	122.33	42.00
Std dev	1.89	0.14	1.45	0.34	7.87	13.04	25.62	3.85	21.69	8.90
Avg shale	4.72	0.08	8.0	1.5	45	95	20	68	90	19

Fig. 4.1.2.c Photograph showing transportation of ore through barges in Mandovi River (MR), Goa-West coast of India

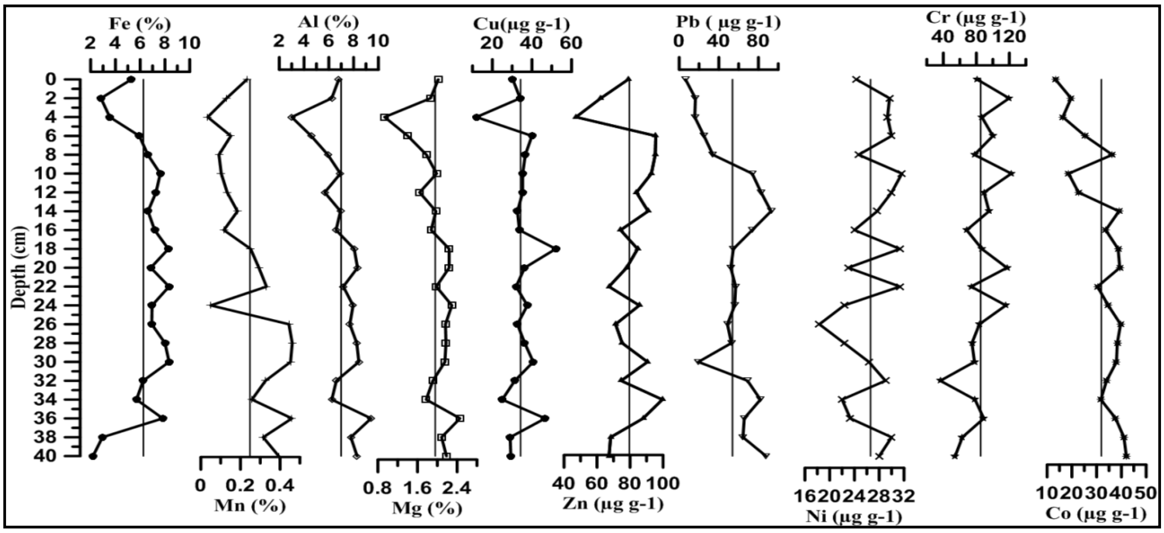


Fig. 4.1.2.d Down core major elements (Fe, Mn, Al, and Mg) and trace metals (Cu, Zn, Pb, Ni, Cr, and Co) in core collected from Mandovi River (MR), Goa-West coast of India

4.1.2.6 Pearson's Correlation Coefficient

The Correlation coefficient of metals in MR core (**Table 4.1.2.c**) showed a positive correlation between sand and Cr indicating its source as terrigenous. Whereas, silt, clay, and OC showed a positive correlation with Mn, Al, and Mg indicating that their association with finer sediments (**Abílio *et al.*, 2006**). Furthermore, the complexing nature of organic carbon plays an important role in the binding of metals (**Chatterjee *et al.*, 2007**). Iron showed a strong positive correlation with Cu and Zn indicating their common source of origin in sediments. Fe-Mn is known to scavenge metals from the water column (**Venkatramanan *et al.*, 2014**). Significant relation of Al with Mg and Co indicating their common source of origin in the sediment core.

Table 4.1.2.c Data on Pearson's Correlation between different sediment components (sand, silt, clay), OC, TP, major elements (Fe, Mn, Al, and Mg) and trace metals (Cu, Zn, Pb, Ni, Cr, and Co) in sediment core of Mandovi River (MR), Goa-West coast of India (n = 21)

Param	**sand**	**silt**	**clay**	**OC**	**TP**	**Fe**	**Mn**	**Al**	**Mg**	**Cu**	**Zn**	**Pb**	**Ni**	**Cr**	**Co**
sand	1.00														
silt	**-1.00**	1.00													
clay	**-0.96**	**0.95**	1.00												
OC	**-0.73**	**0.73**	**0.71**	1.00											
TP	-0.25	0.22	0.37	0.08	1.00										
Fe	-0.29	0.28	0.30	0.36	0.34	1.00									
Mn	**-0.78**	**0.78**	**0.74**	**0.72**	0.07	0.19	1.00								
Al	**-0.77**	**0.77**	**0.72**	**0.64**	0.28	0.33	**0.70**	1.00							
Mg	**-0.67**	**0.68**	**0.62**	**0.58**	0.29	0.34	**0.60**	**0.98**	1.00						
Cu	-0.38	0.36	0.42	0.23	**0.71**	**0.60**	0.26	**0.59**	**0.62**	1.00					
Zn	-0.12	0.12	0.09	0.02	0.29	**0.52**	-0.03	0.20	0.24	**0.55**	1.00				
Pb	-0.42	0.41	**0.47**	0.26	-0.05	0.14	0.12	0.31	0.30	0.06	0.23	1.00			
Ni	0.19	-0.20	-0.09	-0.35	0.22	-0.19	-0.31	-0.34	-0.36	-0.01	-0.16	0.02	1.00		
Cr	**0.44**	**-0.44**	**-0.44**	-0.35	0.12	0.14	**-0.45**	-0.06	0.00	0.22	0.22	-0.22	0.00	1.00	
Co	**-0.70**	**0.68**	**0.74**	**0.69**	0.28	0.20	**0.58**	**0.67**	**0.61**	0.37	0.17	**0.46**	-0.35	-0.35	1.00

4.1.2.7 Pollution Indices Techniques

a. Enrichment Factor (EF)

Enrichment factor for MR core is presented in fig (**Fig.4.1.2.e).** Mn and Pb exhibit moderate enrichment indicating that the sources are more likely to be of anthropogenic origin (EF > 1.5). Whereas Fe, Mg, Cu, Zn, Ni, Cr, and Co showed deficiency to minimal enrichment (EF < 1.5) indicating that they are of crustal origin (**Zang and Liu, 2000**).

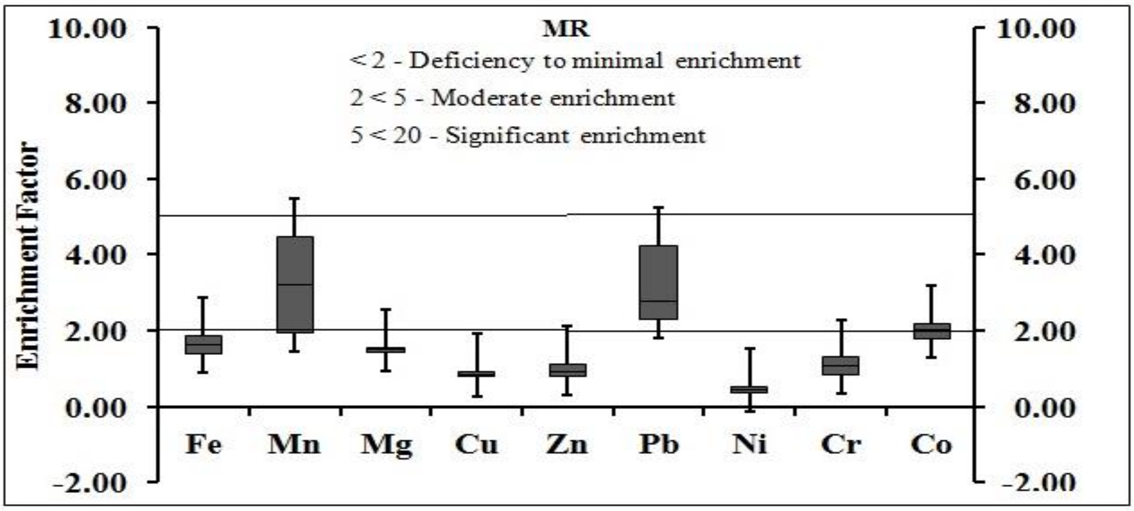


Fig. 4.1.2.e Enrichment factor for major elements and trace metals in core collected from Mandovi River (MR), Goa-West coast of India

b. Contamination Factor (CF)

Contamination factor of metals in MR core (**Fig 4.1.2.f**) revealed Moderate contamination for Mn and Pb; considerable contamination for Fe, Mg and Co, and Low contamination for Al, Cu, Zn, Ni, and Cr. Moderate contamination of Mn and Pb may probably be due to runoff from mining waste which includes trace elements and minerals often associated with iron deposits (**Chaturvedi and Patra, 2016**).

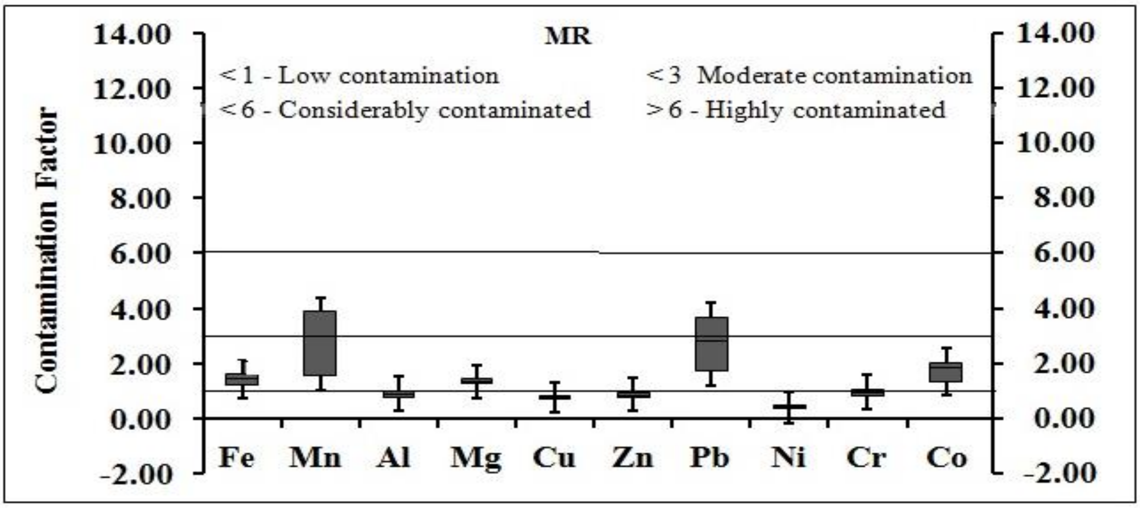


Fig.4.1.2.f Contamination Factor for major elements and trace metals in core collected from Mandovi River (MR), Goa-West coast of India

c. Geo-accumulation Index (Igeo)

Geo-accumulation Index for MR sediment core is presented in fig (**Fig 4.1.2.g)**. Igeo values showed Moderate Pollution for Mn and Pb (class 2), Unpolluted to Moderately Polluted by Fe and Co (class 1) and Unpolluted for Al, Mg, Cu, Zn, Ni and Cr (class 0). The Moderate Pollution of Mn in sediment core is directly related to Fe-Mn ore deposits and human-induced activity in handling and transportation of these ores through the river. **Shynu *et al.* (2012**) and **Alagarsamy, (2006)** also observed a high value of Fe and Mn in suspended matter and surface sediments in the Mandovi river, however pollution load of Pb is attributed to use of anti-fouling paints in boats which are anchored in this river during the monsoon season (**Shyanu *et al.*, 2012**).

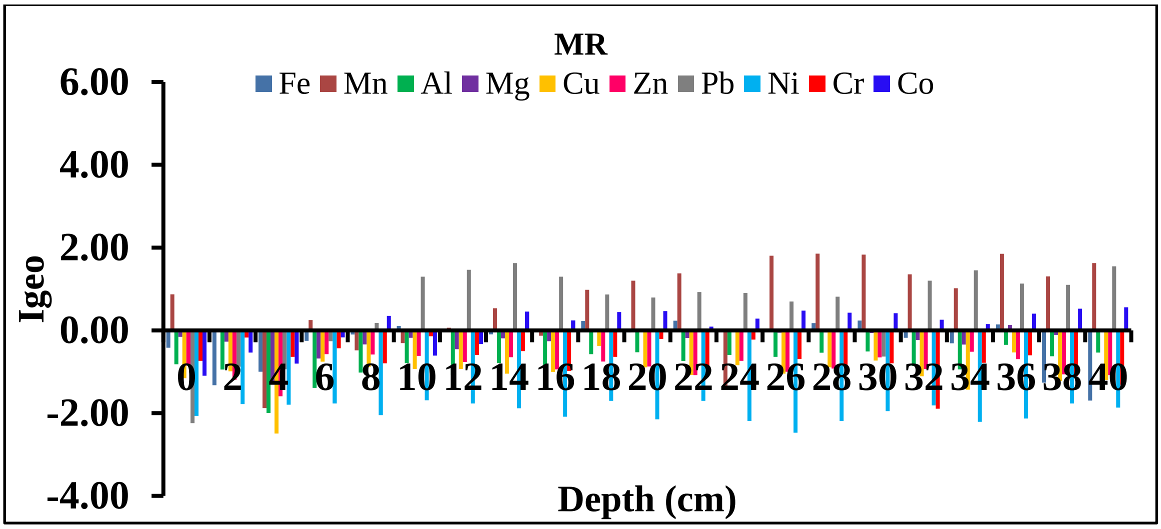


Fig. 4.1.2.g Geo-accumulation Index (Igeo) for major elements and trace metals in the core collected from Mandovi River (MR), Goa-West coast of India

d. Pollution Load Index (PLI)

PLI values are used to determine the possible risk levels of metals as one entity (**Kukrer, 2017**). PLI values in MR sediment core varied from 0.55 to 1.43 (1.12) indicating that MR is polluted with metals (as PLI values are greater than 1). The vertical profile of PLI showed a gradual decreasing trend from bottom of the core with increased peak at 36cm and decreased peak at 4cm depth of the sediment core (**Fig 4.1.2.h**).

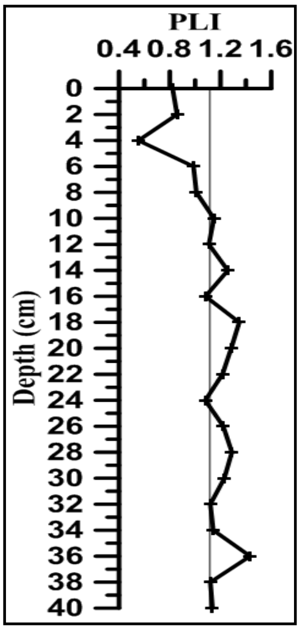


Fig. **4.1.2.h** Down core variation of PLI in sediment core of Mondovi River (MR), Goa-West coast of India

4.1.2.8 Factor Analysis

Correlations among a number of different variables in four factors obtained is placed in table (**Table 4.1.2.d)**. Factor 1 accounted for 47.11 % of the total variance. It shows significant positive loadings for silt, clay, OC, Mn, Al, Mg and Co which indicates the role of finer sediments and organic carbon in regulating the distribution of metals. Factor 2 showed 16.48 % of total variance with strong positive loading of Fe, Cu, and Zn, which indicates the role of Fe-oxide in adsorption of metals. Factor 3 showed 9.19 % of total variance with strong negative loading on Ni, whereas Factor 4 accounted for 7.47% of total variance with strong negative loading on Pb.

Table 4.1.2.d Factor analysis matrix after varimax rotation for sediment core of Mandovi River (MR), Goa-West coast of India

Parameters	Factor 1	Factor 2	Factor 3	Factor 4
sand	**-0.931**	-0.092	0.087	0.217
silt	**0.927**	0.086	-0.058	-0.208
clay	**0.907**	0.114	-0.218	-0.249
OC	**0.822**	0.044	0.207	-0.074
TP	0.235	0.568	-0.628	0.219
Fe	0.206	**0.710**	0.073	-0.115
Mn	**0.885**	-0.060	0.121	0.098
Al	**0.825**	0.392	0.153	0.058
Mg	**0.739**	0.461	0.184	0.075
Cu	0.358	**0.829**	-0.270	0.151
Zn	-0.056	**0.781**	0.096	-0.360
Pb	0.275	0.103	-0.007	**-0.870**
Ni	-0.279	-0.147	**-0.847**	-0.092
Cr	-0.483	0.539	0.148	0.320
Co	**0.765**	0.170	0.082	-0.260
Expl.Var	6.436	2.877	1.402	1.326
Prp.Totl	0.429	0.192	0.093	0.088
% Total variance	47.110	16.480	9.190	7.470

4.1.3 Kushavati River (KR)

4.1.3.1 Sediment components

Data on the distribution of sand, silt, clay, in KR sediment core are presented in table (**Table 4.1.3.a)**. It is evident from the table that the sediment core recorded the highest average sand content (59.46%). It varied from 35.15 to 84.09 followed by silt 14.05 to 55.76 (34.19%) and clay content 1.09 to 1.29 (1.22%). Sand showed maximum values, whereas silt and clay exhibited minimum values at 2cm depth of the sediment core. Thus exhibiting silty sand texture from the bottom up to 14cm depth and sandy silt texture of the sediment from 14cm up to the surface of the core. The grain size of sediment reflects prevailing hydrodynamic energy conditions (**Dolch and Hass, 2008**). The variation of sand percentage in the core indicates transition from a higher energy depositional environment to lower energy depositional environment (**Fox *et al.*, 1999**). The down core variation of sand showed an increasing trend from bottom to the surface of the core, whereas the distribution of silt compensates the variation of sand throughout the length of the core. Whereas clay showed an irregular increasing trend from the surface to the bottom of the core (**Fig 4.1.3.a**).

Table 4.1.3.a Data on sediment components (sand, silt, clay), Organic Carbon (OC) and Total Phosphorus (TP) in sediment core of Kushavati River (KR), Goa-West coast of India

Depth (cm)	sand	silt	clay	OC	TP
			(%)		
0	80.54	14.35	5.10	1.29	0.008
2	84.09	14.05	1.86	1.29	0.005
4	76.35	18.26	5.39	1.26	0.006
6	74.01	20.06	5.94	1.24	0.005
8	69.73	23.15	7.12	1.29	0.003
10	67.28	29.15	3.57	1.29	0.003
12	59.72	32.31	7.97	1.24	0.004
14	64.00	31.59	4.42	1.21	0.003
16	45.25	47.17	7.58	1.18	0.003
18	42.94	52.37	4.69	1.15	0.003

20	38.89	53.46	7.65	1.15	0.004
22	35.15	55.76	9.09	1.09	0.003
24	45.90	46.19	7.90	1.09	0.004
26	48.62	40.80	10.58	1.29	0.011
Avg	**59.46**	**34.19**	**6.35**	**1.22**	**0.005**
Min	35.15	14.05	1.86	1.09	0.003
Max	84.09	55.76	10.58	1.29	0.011

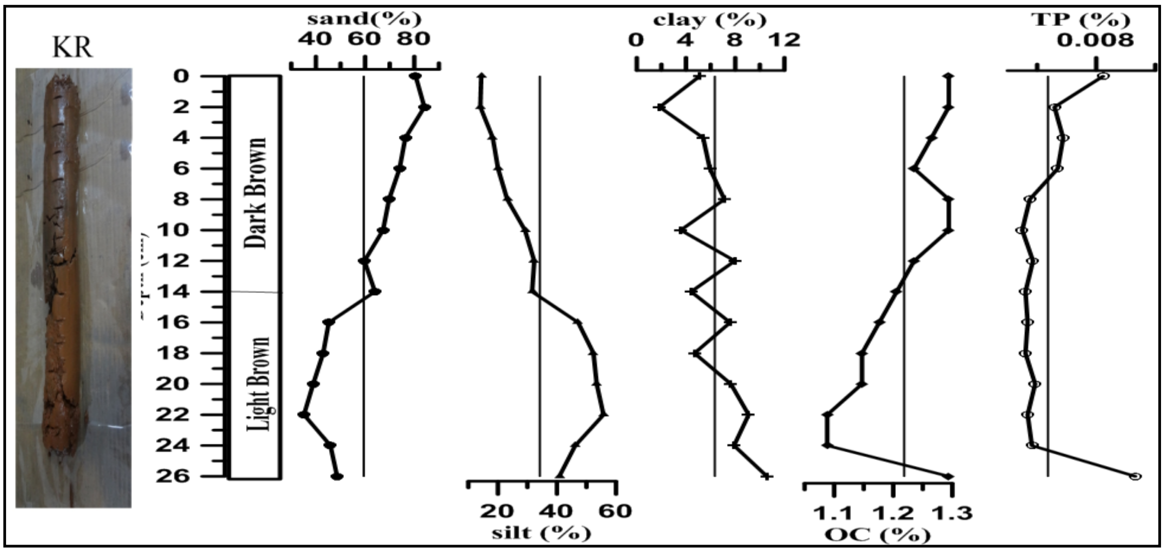


Fig.4.1.3. a Down core variation of sand, silt, clay, Organic Carbon (OC) and Total Phosphorus (TP) in a sediment core of Kushavati River (KR), Goa-West coast of India

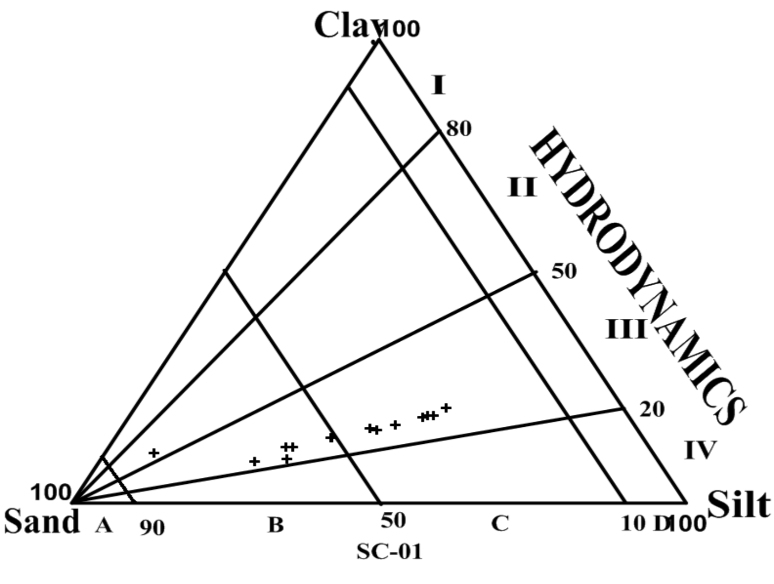


Fig. 4.1.3.b Triangular diagram for the classification of the hydrodynamics of core collected from Kushavati River (KR), Goa-West coast of India (**Pejrup, 1988**)

To understand the hydrodynamic conditions in which sediment deposition took place, the ternary diagram proposed by **Pejrup, (1988)** were employed (**Fig. 4.1.3.b**). Finer sediment samples of KR core falls largely in group (III) C indicating their deposition under relatively violent condition whereas, the coarser sediments fall largely in group (III) B, indicating deposition under relatively violent hydrodynamic conditions.

4.1.3 .2 Organic Carbon (OC)

Organic carbon content in the core is presented in table (**Table 4.1.3a)**. It varied from 1.09-1.29 (1.22%). OC showed almost similar concentration throughout the length of the core. The downcore variation of organic carbon in KR core showed an increasing trend from the bottom up to the surface of the core (**Fig 4.1.3.a**). It is interesting to note that organic carbon values increase with sand concentration. The concentration of OC in the core is supported by its brown color indicating that the sediments have been deposited in oxidizing environment and the organic material has been leached to some degree (**Daniels *et al.,* 2004**).

4.1.3 .3 Total Phosphorus (TP)

Total phosphorus values are presented in table (**Table 4.1.3.a)**. It varied from 0.003-0.011 (0.005%). TP registered almost similar values throughout the length of the core. The down core variation of TP did not show any variation from the bottom up to the surface of the core (**Fig. 4.1.3.a**).

4.1.3 .4 Major elements (Fe, Mn, Al and Mg)

Data on concentration ad average values of major elements Fe, Mn, Al and Mg in KR sediment core varied from 9.67-22.00 (14.23), 0.41-0.86 (0.66), 8.80-15.71 (12.72) and 0.07-0.42 (0.20) respectively (**Table 4.1.3.b).** Higher concentration of Fe, Mn and Al could be related to the release of material directly from iron-ore mining and mining associated activities (**Rane and Matta, 2019**). The values of Fe, Mn and Al are in broad agreement with those reported earlier by **Singh *et al.,* (2014)** from Mandovi River. Fe, Mn and Al registered higher values, whereas Mg registered lower values when compared to Shale values (**Turekian and Wedepohl, 1961**). A higher concentration of Fe and Mn can be related to the release of material directly from mining activities as it is highly influenced by mining and associated activities such as loading of ore, dumping of ore on the bank of the river (**Fig 4.1.3.c)**. The iron ore mining activity along the central portion of the state involves open cast mining largely for iron and manganese in the southern sector. This region is largely controlled by the southwest monsoon, it is expected that the large quantity of material flows from open cast mining of Fe and Mn ores to Zuari River is through tributaries such as the Kushavati River (**Dessai and Nayak, 2009**). Down core variation of Fe, Mn, Al, and Mg are presented in fig (**Fig 4.1.3.d).** Fe showed a decreasing trend from the bottom up to the surface of the core. Mn showed an irregular decreasing and an increasing trend. Whereas Al showed a decreasing trend from the bottom up to 6cm depth and thereafter it showed an increasing trend up to the surface of the core. However, Mg registered values almost similar to average values up to 6 cm depth and thereafter from 6cm depth; it showed a slight increase in values up to the surface of the core. In general, the distribution of major elements in sediment core followed the order (decreasing) Fe > Mn > Al > Mg.

Table 4.1.3.b Data on major elements and trace metals in a sediment core collected from Kushavati River (KR), Goa-West coast of India

Depth	Major Elements (%)				Trace metals (µg g-1)					
(cm)	Fe	Mn	Al	Mg	Cu	Zn	Pb	Ni	Cr	Co
0	22.00	0.75	13.41	0.37	91.66	42.24	36.33	252.00	571.66	24.33
2	14.87	0.74	11.79	0.42	85.33	44.57	43.00	320.00	476.00	8.00
4	18.28	0.47	9.86	0.30	95.99	50.24	38.00	222.66	372.66	25.33
6	14.18	0.59	8.80	0.18	86.66	52.57	18.67	198.00	411.66	8.33
8	11.43	0.52	11.36	0.20	101.33	51.57	33.67	267.66	338.33	18.00
10	11.54	0.84	12.51	0.18	105.00	68.90	45.67	274.00	334.00	9.00
12	16.87	0.85	13.94	0.20	126.66	73.57	15.67	204.00	316.33	12.33
14	15.66	0.86	11.80	0.07	88.33	70.90	48.67	186.00	279.66	19.00

16	13.22	0.52	15.30	0.12	88.66	72.24	8.33	136.33	231.66	10.00
18	10.49	0.41	12.02	0.07	101.33	59.24	52.33	210.33	214.33	10.33
20	16.82	0.48	13.85	0.12	144.66	61.90	57.00	231.33	210.66	26.33
22	9.67	0.56	15.71	0.14	101.33	59.24	44.00	197.66	185.00	10.67
24	11.50	0.85	13.56	0.12	106.33	72.57	57.67	114.33	153.67	21.33
26	12.75	0.86	14.12	0.26	107.33	71.24	17.67	113.67	163.33	7.67
Avg	**14.23**	**0.66**	**12.72**	**0.20**	**102.19**	**60.78**	**36.90**	**209.14**	**304.21**	**15.05**
Min	9.67	0.41	8.80	0.07	85.33	42.24	8.33	113.67	153.67	7.67
Max	22.00	0.86	15.71	0.42	144.66	73.57	57.67	320.00	571.66	26.33
Std dev	3.44	0.17	1.94	0.11	16.42	11.05	16.07	59.91	123.69	7.03
Avg shale	4.72	0.08	8.0	1.5	45	95	20	68	90	19

Fig 4.1.3.c. Photograph showing the mining-related activities on the bank of Kushavati River (KR), Goa-West coast of India

4.1.3 .5 Trace metals (Cu, Zn, Pb, Ni, Cr and Co)

The range and average concentration of trace metals Cu, Zn, Pb, Ni, Cr and Co in KR core varied from 85.33-144.66 (102.19); 42.24-73.57 (60.78); 8.33-57.67 (36.90); 113.67-320.00 (209.14); 153.67-571.66 (304.21) and 7.67-26.33 (15.05) respectively (**Table 4.1.3.b).** Cu and Co showed higher concentration at 20cm depth, Zn at 12cm, Pb at 24cm, Ni at 2cm and Cr at the surface of the core. The values of Cu, Pb and Co are in broad agrrement with those reported earlier by **Shah *et al.*, (2013)** from Tapti River. However the values of Zn are in good agreement with those reported by **Cuong and Obbard, (2006**) from Tropical Kranji estuary, Singapore. It is evident from the table that Cr, Ni, Cu and Pb recorded higher average concentration, whereas Zn and Co showed low values as compared to Shale values (**Turekian Wedepohl, 1961**). The down core variation of Cu and Zn (**Fig 4.1.3.d**) showed a decreasing trend, whereas Ni and Cr showed an increasing trend from the bottom up to the surface of the core. However, Pb and Co showed an irregular trend from the bottom up to the surface of the core. The distribution of Cr in sediment core largely follows the trend of Fe. Association of Cr with Fe ores has been reported (**Bukhari, 1994**) within the catchment area of Mandovi River. In addition to loading jetties on the bank of this river, it is also expected to release a considerable amount of Fe, Mn, and Cr. Higher concentration of Cu can be directly related to the material input from the catchment area brought by other tributaries (**Dessai *et al.*, 2009**). In general, the distribution of trace metals in sediment core followed the order (decreasing) Cr > Ni > Cu > Pb > Zn > Co.

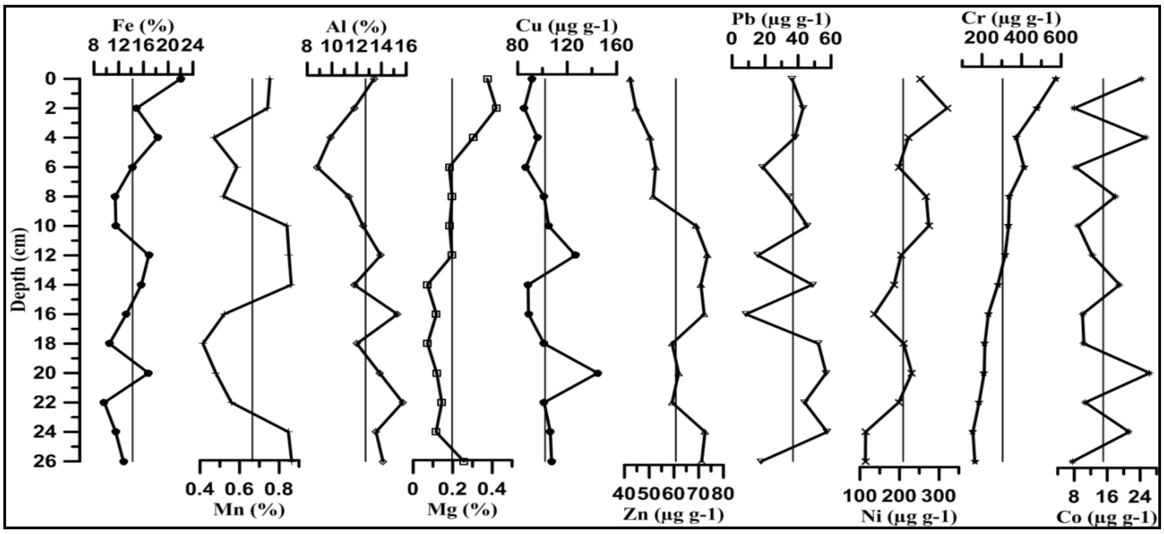


Fig. 4.1.3.d Down core variation of major elements (Fe, Mn, Al, and Mg) and trace metals (Cu, Zn, Pb, Ni, Cr, and Co) in sediment core collected from Kushavati River (KR), Goa-West coast of India

4.1.3 .6 Pearson's Correlation Coefficient

The Correlation coefficient matrix (**Table 4.1.3.c**) exhibited a significant positive correlation between sand, organic carbon Mg, Ni, and Cr, whereas silt showed a positive correlation with Al and Zn. However, clay showed a positive correlation with Al. TP showed a positive correlation with Mg, Cr showed good association with Fe, Co, Mg, and Ni indicating their common source of origin.

Table 4.1.3.c Data on Pearson's Correlation between different sediment components(sand, silt, clay), OC, TP, major elements (Fe, Mn, Al, and Mg) and trace metals (Cu, Zn, Pb, Ni, Cr, and Co) in sediment core of Kushavati River (KR), Goa-West coast of India (n = 14)

Param	**sand**	**silt**	**clay**	**OC**	**TP**	**Fe**	**Mn**	**Al**	**Mg**	**Cu**	**Zn**	**Pb**	**Ni**	**Cr**	**Co**
sand	1.00														
silt	**-0.99**	1.00													
clay	**-0.66**	**0.57**	1.00												
OC	**0.80**	**-0.82**	-0.36	1.00											
TP	0.27	-0.33	0.24	0.51	1.00										
Fe	0.53	**-0.55**	-0.23	0.41	0.42	1.00									
Mn	0.22	-0.24	-0.02	0.27	0.27	0.12	1.00								
Al	**-0.67**	**0.65**	**0.54**	-0.43	-0.02	-0.18	0.18	1.00							
Mg	**0.73**	**-0.75**	-0.32	**0.70**	**0.62**	0.53	0.19	-0.21	1.00						
Cu	-0.50	0.48	0.45	-0.26	-0.13	0.05	-0.03	0.37	-0.28	1.00					
Zn	**-0.62**	**0.61**	0.47	-0.38	-0.27	-0.38	0.40	0.48	**-0.67**	0.37	1.00				
Pb	-0.15	0.22	-0.34	-0.39	-0.35	-0.12	-0.06	-0.05	-0.19	0.21	-0.13	1.00			
Ni	**0.61**	**-0.56**	**-0.72**	0.49	-0.17	0.24	-0.16	-0.37	0.51	-0.07	**-0.68**	0.27	1.00		
Cr	**0.91**	**-0.89**	**-0.64**	**0.68**	0.26	**0.65**	0.07	-0.49	**0.75**	-0.43	**-0.75**	-0.15	**0.69**	1.00	
Co	0.08	-0.09	0.01	-0.12	0.01	**0.58**	-0.16	-0.08	0.03	0.31	-0.21	0.45	0.06	0.12	1.00

4.1.3.8 Pollution Indices

a. Enrichment Factor (EF)

Enrichment factor for Mn in KR core (**Fig. 4.1.3.e**) showed moderate to significant enrichment; Fe, Ni, and Cr exhibited moderate enrichment. Whereas, Cu, Zn, Pb and Co showed deficiency to minimal enrichment in KR core. Moderate to significant enrichment (EF values over 2.0) of Fe, Ni and Cr can be attributed to anthropogenic inputs (**Qi *et al.*, 2010**). According to **Zang and Liu, (2000)**, if EF values are between the range of 0.05 and 1.5 then it indicates that the metal is entire of the crustal origin or is due to natural processes. Whereas if EF values obtained are higher than 1.5, it suggests that the sources are more likely to be due to anthropogenic influence. The main source of Mn is the run-off from the mine wastes dumped on the bank of this river. The main anthropogenic sources of Cr and Ni is pesticides and herbicides. And it is also used in alloys with lead and copper, oxidizing agents, Cr-plating, corrosion inhibitors, ceramics, glass (**Hall *et al.*, 2014**).

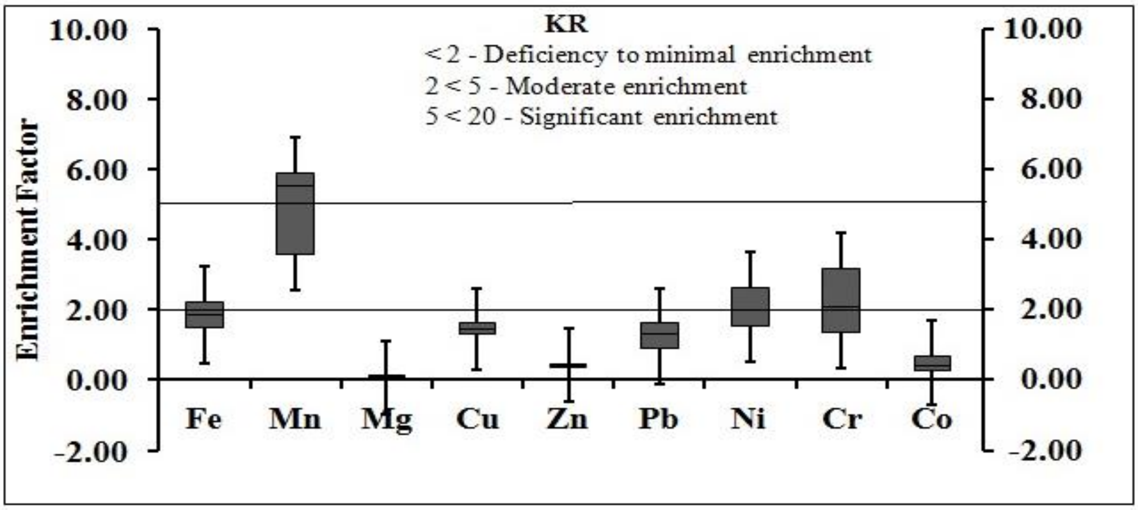


Fig.4.1.3.e Enrichment factor for major elements and trace metals in core collected from Kushavati River (KR), Goa-West coast of India

b. Contamination Factor (CF)

Contamination Factors for KR core (**Fig. 4.1.3.f**) revealed that it is very highly contaminated with Mn; considerably contaminated with Fe, Ni, and Cr; moderately contaminated with Al, Cu, and Pb, while low contamination is shown by Mg, Zn and

Co. High contamination for Mn and considerable contamination for Fe and Cr in KR sediment core can be attributed to exhaustive iron-ore mining activities and discharge of mining wastes in this region. Moderate contamination of Al in the core may probably be due to the use of aluminium salts in the treatment of wastes from the mining pits.

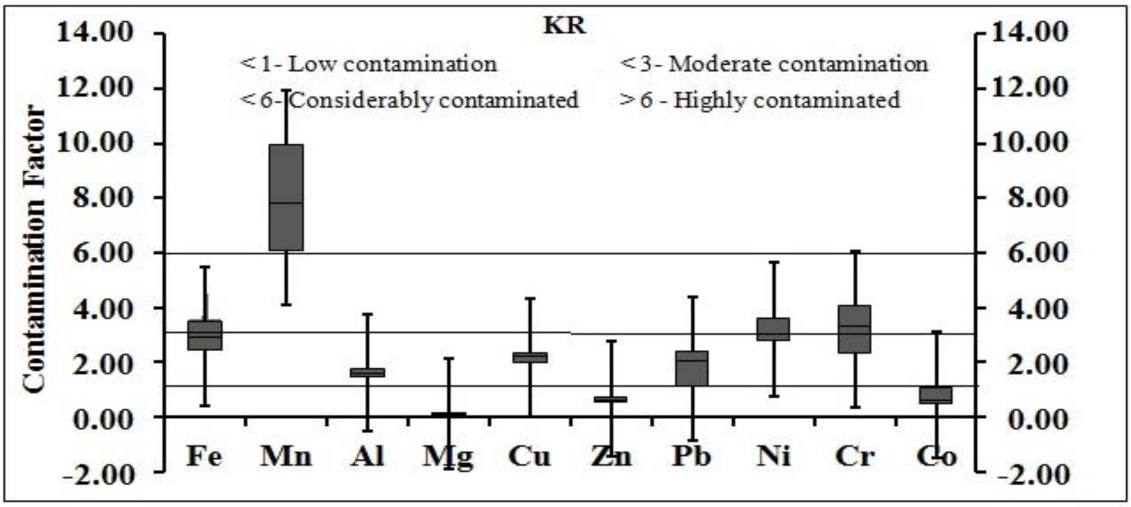


Fig. 4.1.3.f Contamination factor for major elements and trace metals in core collected from Kushavati River (KR), Goa-West coast of India

c. Geo-accumulation Index (Igeo)

Geo-accumulation Index values in KR core indicated that the sediments are moderately to strongly polluted with Mn (class 3); moderately polluted with Fe and Cr (class 2) ; whereas unpolluted to moderately polluted with Cu and Pb (class 1) and however unpolluted (class 0) with Al, Mg, Cu, Zn and Co (**Fig. 4.1.3.g**). Moderate pollution of Fe, Mn and Cr is attributed to mining related activities in the vicinity of the river.

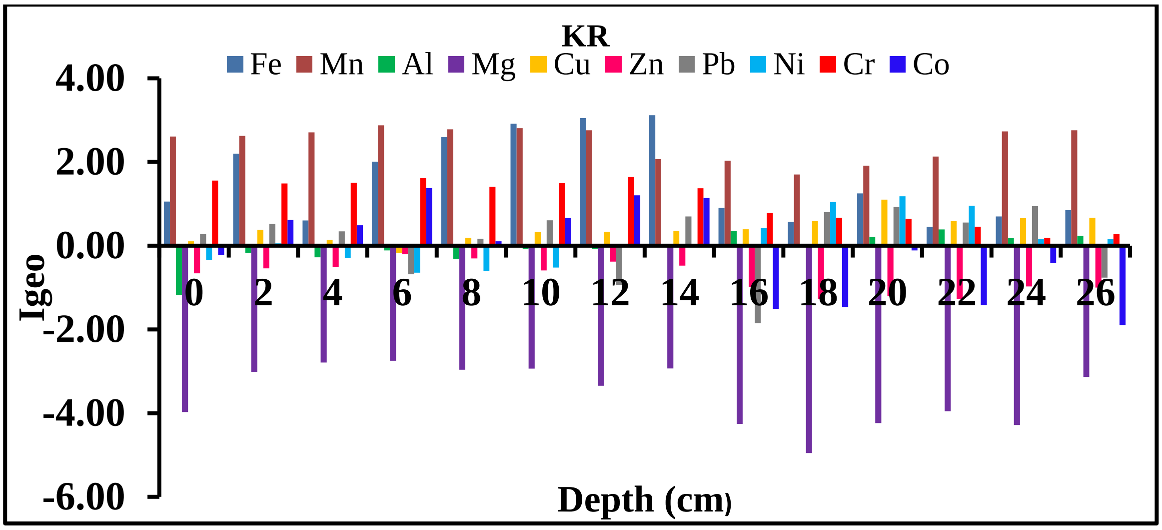


Fig. 4.1.3.g Geo-accumulation index (Igeo) for major elements and trace metals in sediment core collected from Kushavati River (KR), Goa-West coast of India

d. Pollution Load Index (PLI)

Pollution Load index values in KR sediment core (**Fig. 4.1.3.h)** showed an average value of 1.52 that varied from 1.16 to 1.96 indicating that KR core is polluted with metals (as PLI values are greater than 1). The vertical profile of PLI showed almost an increasing trend from bottom up to 20cm depth and from 20cm up to 16 cm it showed a decreasing trend and from 16cm up to the surface of the core it showed an increasing trend.

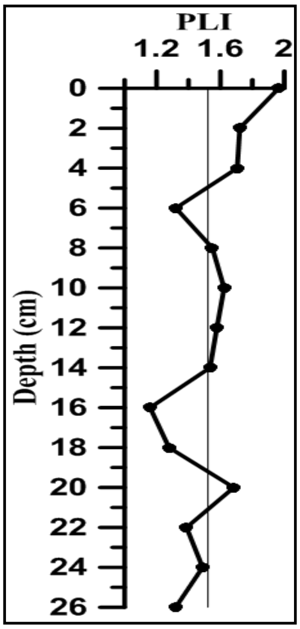


Fig. 4.1.3.h Down core variation of PLI in sediment core of Kushavati River (KR), Goa-West coast of India

4.1.3.8 Factor Analysis

The loadings between the different parameters in four factors is given in table (**Table 4.1.3.d)**. Factor 1 accounted for 44.38% of the total variance. It shows significant positive loadings for sand, Ni and Cr. Suggesting that these metals are derived from an anthropogenic source. Factor 2 with 16.08% of total variance showed a positive loading on TP. Factor 3 with 12.25% of the total variance shows significant positive loadings for Fe and Co. It represents a mixture of dust and pollutants. Factor 4 with 9.4% of the total variance shows significant positive loadings for Mn representing dust dominance.

Table 4.1.3.d Factor analysis matrix after varimax rotation for sediment core of Kushavati River (KR), Goa-West coast of India

Parameters	Factor 1	Factor 2	Factor 3	Factor 4
sand	**0.919**	0.315	0.004	0.149
silt	**-0.872**	-0.401	-0.009	-0.150
clay	**-0.866**	0.358	0.030	-0.084
OC	0.646	0.548	-0.099	0.242
TP	0.030	**0.868**	0.096	0.080
Fe	0.387	0.488	0.641	0.091
Mn	0.029	0.168	-0.025	**0.956**
Al	-0.695	0.034	0.102	0.198
Mg	0.617	0.617	0.136	0.045
Cu	-0.503	-0.133	0.566	0.087
Zn	**-0.718**	-0.227	-0.186	0.542
Pb	0.116	**-0.709**	0.492	-0.010
Ni	**0.804**	-0.180	0.170	-0.123

Cr	**0.878**	0.342	0.130	-0.013
Co	0.051	-0.037	**0.894**	-0.138
Expl.Var	5.989	2.812	1.903	1.415
Prp.Totl	0.399	0.187	0.127	0.094
% Total variance	44.380	16.080	12.250	8.060

4.1.4 Zuari River (ZR)

4.1.4.1 Sediment components

Data on the distribution of sand, silt, and clay, in ZR sediment core, is presented in table (**Table 4.1.4.a).** It is evident from the table that the sediment core recorded the highest average silt content (66.25%). It varied from 54.01 to 84.67 followed by clay 9.42 to 32.99 (19.63%) and sand content 1.71 to 28.44 (14.12 %), thus exhibiting sandy silt from the bottom up to 8cm depth and clayey silt texture of the sediment from 8cm up to the surface of the core this may be due to high-energy conditions in the study region that carried the finer sediments in suspension and got deposited in places in calm hydrodynamic conditions (**Noronha-D'Mello and Nayak, 2015**). Silt showed maximum values and sand showed minimum values at 4cm depth of the core. A higher concentration of silt and clay may be due to the settling of these particles in lower energy conditions. The flocculation process during estuarine mixing helps in faster settling of fine colloidal aggregates in this region (**Dessai and Nayak, 2007**). The down core variation of sand showed an irregular decreasing trend from the bottom of the core with an increased peak at 18cm, 14cm and 10cm depth up to the surface of the sediment core, whereas the distribution of silt compensates the variation of sand throughout the length of the core. Whereas clay showed an irregular increasing trend from the surface to the bottom of the core (**Fig 4.1.4.a**).

Table 4.1.4.a Data on sediment components (sand, silt, clay), Organic Carbon (OC) and Total Phosphorus (TP), in sediment core of Zuari River (ZR), Goa-West coast of India

Depth (cm)	**sand**	**silt**	**clay (%)**	**OC**	**TP**
0	9.38	69.26	21.36	3.08	0.018
2	3.07	77.33	19.60	3.08	0.018
4	1.71	84.67	13.62	3.17	0.019
6	1.74	72.24	26.02	2.99	0.022
8	2.44	64.56	32.99	2.99	0.018
10	23.60	57.69	18.70	2.54	0.014
12	15.28	68.40	16.32	2.39	0.016
14	28.44	54.01	17.55	1.94	0.015
16	12.60	71.08	16.32	1.85	0.017
18	20.07	63.24	16.69	1.85	0.016
20	10.27	63.98	25.74	2.57	0.015
22	14.60	62.31	23.09	2.63	0.017
24	13.96	62.43	23.62	1.91	0.018
26	12.39	64.98	22.62	1.67	0.015
28	8.78	66.50	24.72	1.61	0.015
30	23.33	64.24	12.43	1.37	0.016
32	24.46	66.12	9.42	1.31	0.015
34	28.00	59.39	12.61	1.31	0.018
Avg	**14.12**	**66.25**	**19.63**	**2.24**	**0.017**
Min	1.71	54.01	9.42	1.31	0.014
Max	28.44	84.67	32.99	3.17	0.022

The ternary diagram (**Fig. 4.1.4.b**) of ZR core fell in section IIIC, indicating that grain size varies from finer to coarser and deposited in violent hydrodynamic condition, and IVC indicating the deposition of finer sediments under very violent condition.

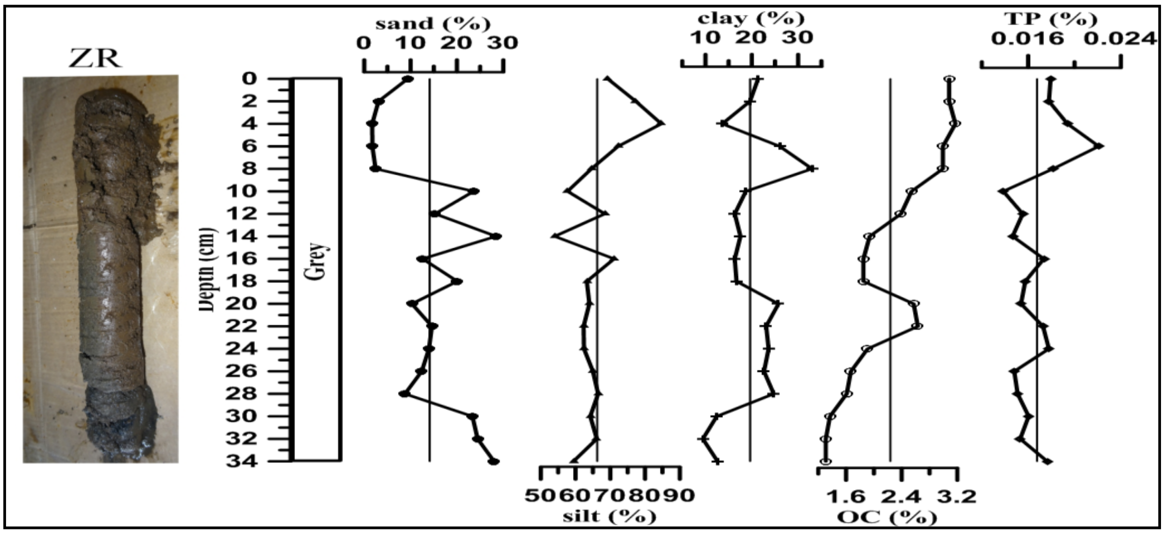


Fig.4.1.4.a Down core variation of sand, silt, clay, Organic Carbon (OC) and Total Phosphorus (TP) in a sediment core of Zuari River (ZR), Goa-West coast of India

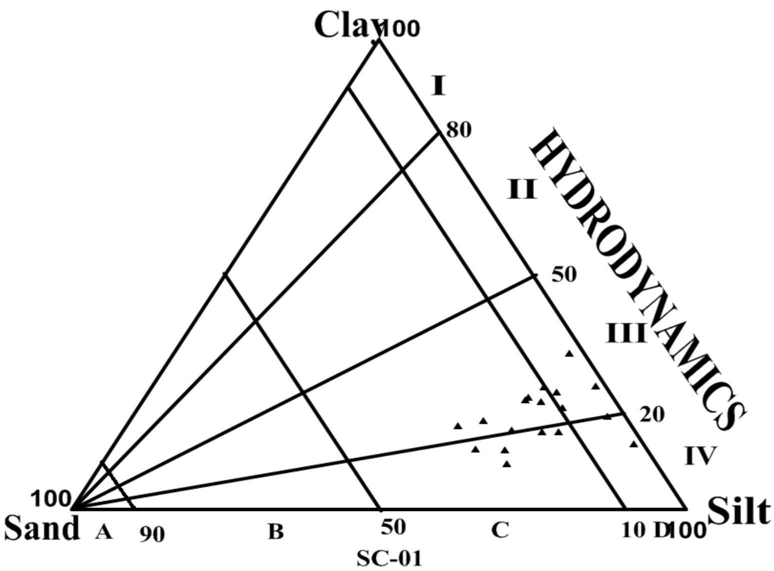


Fig. 4.1.4.b Triangular diagram for the classification of hydrodynamics of core collected from Zuari River (ZR), Goa-West coast of India (**Pejrup, 1988**)

4.1.4.2 Organic carbon (OC)

Organic carbon content (%) in ZR core varied from 1.31–3.17 with an average value of 2.24. OC recorded highest concentration at first 4cm of the sediment core (**Table 4.1.4.a**). Higher values of OC are observed wherever silt content is high and sand is low. It is well established that organic carbon is generally associated with the finer sediments as compared to the coarser sediments. Which is mainly due to the surface area/volume ratio of the sediment grain (**Muzuka and Shaghude, 2000**). Relative higher values of organic carbon in a few centimeters of the surface core could be due to primary production in the overlying water column of the sediment during their deposition period. It is also supported by grey color with dark patches of the cores indicating lack of oxidation and leaching of the materials (**Fig. 4.1.4.a**).

4.1.4.3 Total phosphorus

Total phosphorus content (%) in ZR core varied from 0.014–0.022 with an average of 0.017. TP registered highest concentration at first 6cms of the sediment core (**Table 4.1.4.a**) this coincides with OC distribution pattern. The down core variation of total phosphorus showed an irregular trend up to 10cm depth and thereafter it showed an increasing trend up to the surface of the core (**Fig. 4.1.4.a**).

4.1.4.4 Major elements (Fe, Mn, Al and Mg)

The concentration and average values of Fe, Mn, Al and Mg in ZR core varied from 2.6-1.3 (7.0), 0.0-0.6 (0.3), 4.9-10.9 (8.3) and 1.5-3.0 (2.2) respectively (**Table 4.1.4.b).** Fe showed higher concentration at 20cm**,** Mn showed at 6cm, Al showed at 24cm and Mg showed at 8cm depth of the sediment core. The values of Fe, Mn and Al are in broad agreement with those reported by **Noronha-D'Mello and Nayak, (2015)** from the same river. It is evident from the table that the average values of Fe and Mn are higher, whereas Mg recorded slightly higher values and Al recorded almost similar values when compared with the Shale values (**Turekian and Wedepohl, 1961**). A higher concentration of Fe and Mn in the ZR core could be related to the release of material directly from mining activities as it is highly influenced by mining and associated activities. The iron ore mining activity along the central portion of the state involves open cast mining largely for iron and manganese in the southern sector and this region is largely controlled by the southwest monsoon. It is expected that the large quantity of material flow from open cast mining to Zuari River is through tributaries such as the Kushavati River (**Dessai and Nayak, 2009**). It is also attributed to high spillage during transportation of iron and ferromanganese ores down the Mandovi River. (**Algarsamy, 2006**). Down core variation of Fe, Mn, Al and Mg are presented in fig **(Fig. 4.1.4.c**) Fe showed a decreasing trend from the bottom up to the surface of the core, Mn showed an irregular decreasing and an increasing trend, whereas Al showed a decreasing trend from the bottom up to 6cm depth and thereafter it showed increasing trend up to the surface of the core. However, Mg registered values almost similar to average values up to 6 cm depth and thereafter from 6cm depth; it showed a slight increase in values up to the surface of the core. In general, the distribution of major elements in sediment core followed the order (decreasing) Fe > Mn > Mg > Al.

Table 4.1.4.c Data on major elements and trace metals in a sediment core of Zuari River (ZR), Goa-West coast of India

Depth (cm)	Major Elements (%)				Trace metals (µg g-1)					
	Fe	Mn	Al	Mg	Cu	Zn	Pb	Ni	Cr	Co
0	3.8	0.4	4.9	1.5	44.7	116.9	34.7	60.3	130.7	29.7
2	6.4	0.5	10.1	2.7	39.7	106.2	57.3	74.7	140.7	42.0
4	7.0	0.5	10.0	2.7	44.3	111.9	42.3	102.7	126.7	43.7
6	6.5	0.6	8.0	2.8	53.3	128.9	47.0	122.0	204.3	49.7
8	7.2	0.4	9.9	3.0	25.0	110.6	52.0	108.0	155.3	25.7
10	7.9	0.2	6.8	1.6	41.7	73.2	77.3	89.3	190.7	39.7
12	7.2	0.4	8.0	2.2	37.7	93.6	64.3	80.7	204.3	26.7
14	9.7	0.2	7.4	1.9	38.7	84.6	69.3	70.3	220.7	32.0
16	8.0	0.2	9.4	2.4	40.0	127.9	66.0	69.7	237.3	35.7

18	8.0	0.2	7.7	1.9	42.3	90.6	53.7	69.3	230.3	30.7
20	11.3	0.2	9.2	2.2	56.7	71.6	43.0	68.7	227.3	38.7
22	7.1	0.4	9.3	2.2	45.3	73.2	20.3	68.0	219.0	47.7
24	6.3	0.3	10.9	2.5	44.3	72.6	53.0	66.3	212.7	42.3
26	6.7	0.3	7.8	2.1	18.7	76.2	58.7	45.0	170.0	39.3
28	7.7	0.2	8.1	2.1	26.3	76.9	55.3	40.3	190.3	27.7
30	6.3	0.3	5.8	1.8	25.0	68.6	23.3	54.3	229.0	39.3
32	6.0	0.0	7.6	2.1	15.0	53.2	19.3	69.7	200.3	27.3
34	2.6	0.1	8.5	2.6	30.7	76.9	17.7	71.3	238.7	31.7
Avg	**7.0**	**0.3**	**8.3**	**2.2**	**37.2**	**89.6**	**47.5**	**73.9**	**196.0**	**36.1**
Min	2.6	0.0	4.9	1.5	15.0	53.2	17.7	40.3	126.7	25.7
Max	11.3	0.6	10.9	3.0	56.7	128.9	77.3	122.0	238.7	49.7
Std Dev	1.9	0.2	1.5	0.4	11.4	22.3	18.1	20.7	36.7	7.4
Avg Shale	4.72	0.08	8.0	1.5	45	95	20	68	90	19

4.1.4.5 Trace metals (Fe, Mn, Al and Mg)

Data on concentration and average (µg g-1) of trace metals Cu, Zn, Pb, Ni, Cr and Co in ZR sediment core varied from 15,0-56.7 (37.2), 53.2-128.9 (89.6), 17.7-77.3 (47.5), 40.3-122.0 (73.9), 126.7-238.7 (196.0) and 25.7-49.7 (36.1) respectively (**Table 4.1.4.c).** It is evident from the table that the average values of Pb, Ni, Cr and Co showed higher values when compared with Shale values (**Turekian and Wedepohl, 1961)**. Cu showed higher concentration at 20cm, Zn, Ni and Co showed at 6cm, Pb showed at 10cm and Cr showed at the bottom of the sediment core. The values of Zn and Pb are in broad agreement with those reported by **Amor *et al.*, (2019)** from Gulf of Tunis, Tunisi, whereas the values of Ni are in good agreement with those reported by **Li *et al.*, (2013)** from Pearl river, China. However, Cu and Zn did not show much variation. The down core variation of Cu, Zn, Pb, and Ni showed an increasing trend from the bottom up to the surface of the core, whereas Cr showed a gradual decreasing trend from bottom to the surface of the sediment core. However, Co showed an irregular trend (**Fig 4.1.4.c**). The higher concentration of these metals may be attributed to anthropogenic input (**Fig 4.1.3.d**) such as the contribution of leaded fuel in the past from automobiles and car batteries and extensive use of the antifouling paints by shipping activities and industrial effluents (**Khan *et al.,* 2017**). In general, the distribution of trace metals in sediment core followed the order (decreasing) Cr > Ni > Pb > Co > Zn > Cu.

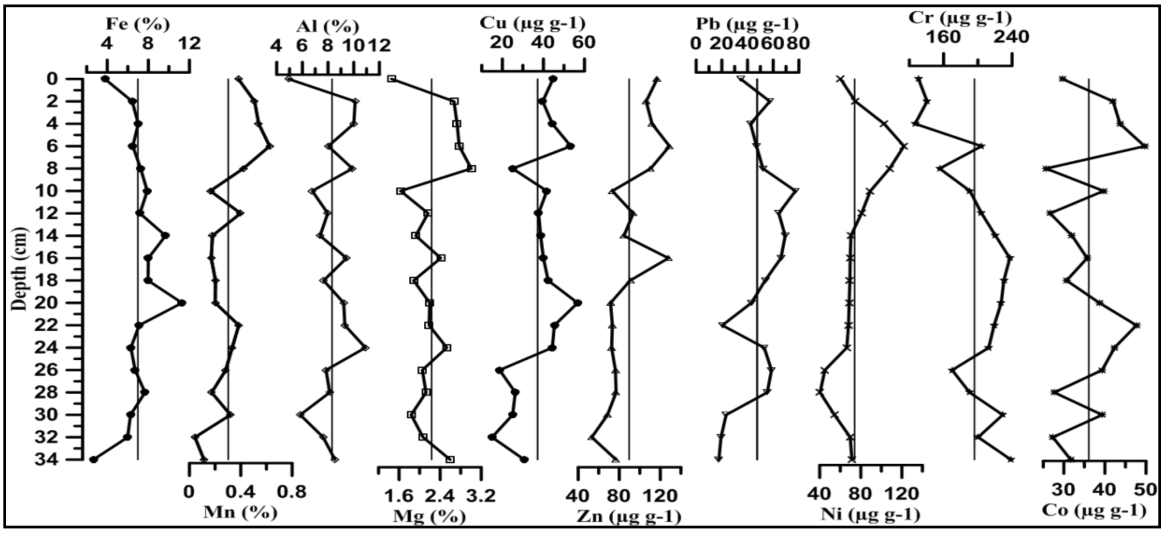


Fig. 4.1.4.c Down core major elements (Fe, Mn, Al, and Mg) and trace metals (Cu, Zn, Pb, Ni, Cr, and Co) in core collected from Zuari River (ZR), Goa-West coast of India

Fig 4.1.3.d. Photograph showing the anthropogenic activities on the bank Zuari River (ZR), Goa-West coast of India

4.1.4.6 Pearson's Correlation Coefficient

The Correlation coefficient matrix in ZR core exhibited a significant positive correlation between organic carbon and Mn, Cu, Zn, and Ni, indicating that these are derived from the finer fractions of sediments (**Table 4.1.4.c**). It is a well-established fact that organic carbon content, as well as finer sediments are one of the important controlling factors in the abundance of trace metals in the sediment core (**Rubio *et al.*, 2000**). Taking into account its high specific surface area, organic matter can form complexes with metals and consequently influence their distribution (**Loomb, 2001**). It is interesting to note that Fe showed a significant positive correlation with Pb. Since Fe-oxyhydroxide phase is a good scavenger of Pb, it is one of the major controlling factors for its distribution in the sediment core.

Table 4.1.4.c Data on Pearson's correlation between different sediment components (sand, silt, clay), OC, TP, major elements (Fe, Mn, Al, and Mg) and trace metals (Cu, Zn, Pb, Ni, Cr, and Co) in sediment core of Zuari River (ZR), Goa-West coast of India (n=18)

param	sand	silt	clay	OC	TP	Fe	Mn	Al	Mg	Cu	Zn	Pb	Ni	Cr	Co
sand	1.00														
silt	**-0.75**	1.00													
clay	**-0.61**	-0.07	1.00												
OC	**-0.73**	**0.51**	**0.48**	1.00											
TP	**-0.62**	**0.58**	0.24	**0.52**	1.00										
Fe	-0.07	-0.14	0.28	0.11	-0.38	1.00									
Mn	**-0.76**	**0.64**	0.38	**0.76**	**0.74**	-0.12	1.00								
Al	-0.44	0.30	0.30	0.21	0.33	0.22	0.24	1.00							
Mg	**-0.55**	0.43	0.31	0.28	**0.66**	-0.06	0.47	**0.81**	1.00						
Cu	-0.31	0.17	0.26	**0.60**	0.39	0.32	0.40	0.19	0.07	1.00					
Zn	**-0.65**	**0.59**	0.27	**0.63**	**0.69**	-0.09	**0.62**	0.13	0.39	0.40	1.00				
Pb	-0.14	-0.05	0.27	0.20	-0.27	**0.52**	0.03	0.11	-0.05	0.18	0.30	1.00			
Ni	-0.39	0.32	0.20	**0.63**	**0.63**	0.03	**0.56**	0.28	**0.57**	0.38	**0.54**	0.12	1.00		
Cr	**0.63**	**-0.60**	-0.23	**-0.65**	-0.26	0.24	**-0.54**	-0.02	-0.13	0.07	-0.39	-0.11	-0.22	1.00	
Co	-0.29	0.27	0.12	0.34	0.45	0.08	**0.52**	0.29	0.23	**0.52**	0.12	-0.07	0.26	0.00	1.00

4.1.4.7 Pollution Indices Techniques

a. Enrichment Factor (EF)

Enrichment factor for ZR core showed moderate enrichment for Mn, Pb and Cr (values 2<5) whereas, Fe, Cu, Zn, and Co exhibited deficiency to minimal enrichment (**Fig. 4.1.4.e**). Moderate enrichment of Mn, Pb, and Cr can be attributed to anthropogenic input. An overall higher EF value for Pb shows atmospheric deposition of Pb from fly ash and other industries and also from the constant movement of fishing boats and barges (**Stephen-Pichaimani *et al.*, 2008**). The loading jetties along the bank of Zuari River may release a considerable amount of Fe, Mn, and Cr. Loading and Unloading of mining ores and shipping activities at the harbor may release Cr in the form of leachates (**Noronha-D'Mello and Nayak, 2015**).

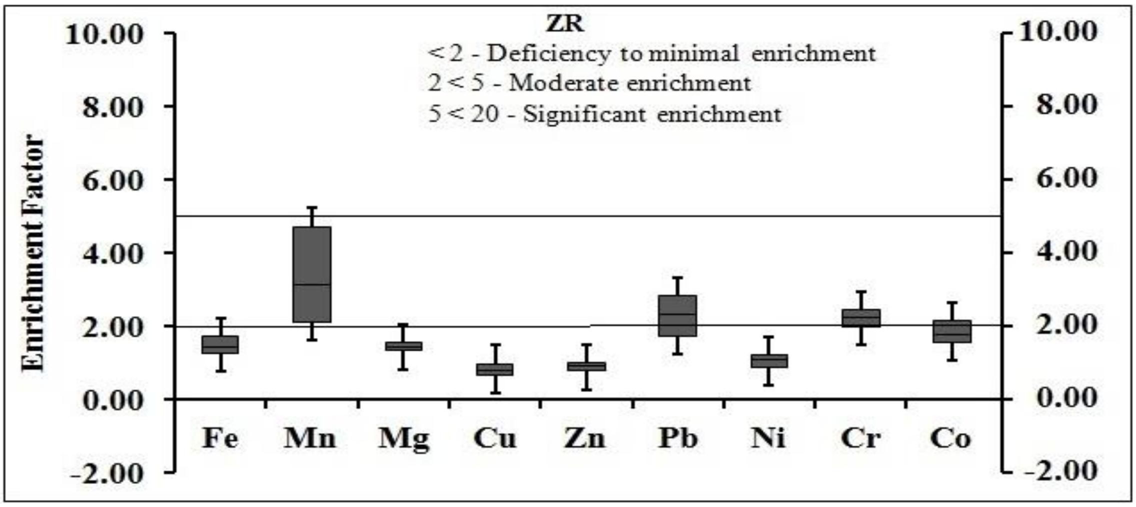


Fig. 4.1.4.e Enrichment Factor for major elements and trace metals in core collected from Zuari River (ZR), Goa-West coast of India

b. **Contamination Factor (CF)**

Contamination factors of metals in ZR core revealed considerable contamination for Mn; moderate contamination for Fe, Al, Mg, Pb, Cr and Co; and low contamination for Cu and Zn (**Fig. 4.1.4.f**). Considerable contamination of Mn may probably be due to run-off from mining waste dumps which include trace elements and minerals which are often associated with iron deposits and dumps piled along the shore (**Chaturvedi and Patra, 2016**). It is important to note that a substantial amount of material from the Mandovi River is added to Zuari River through Cumbharjua canal (**Noronha-**

D'Mello and Nayak, 2015). It is also directly related to the Fe–Mn ore deposits and human-induced activity in handling and transportation of these ores through the river and ore transportation by barges. The increased accumulation of Mn can considerably trap trace metals that can cause damage to sediment quality (**Singh *et al.*, 2013**).

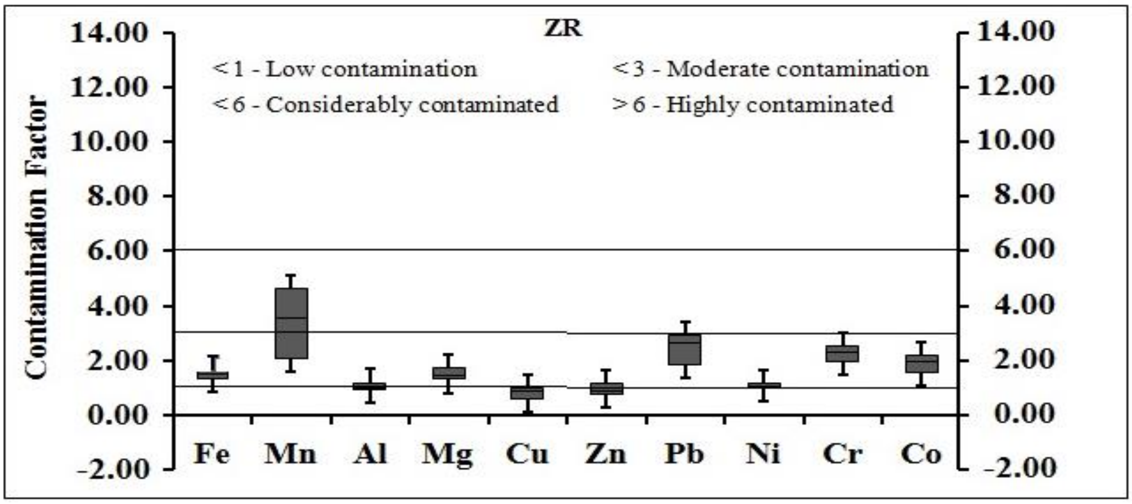


Fig. 4.1.4.f Contamination factor for major elements and trace metals in core collected from Zuari River (ZR), Goa-West coast of India.

c. **Geo-accumulation Index (Igeo)**

The Igeo values for ZR sediment core showed (**Fig. 4.1.4.g**) Moderate Pollution for Mn; Unpolluted to Moderately Polluted by Fe, Pb, Cr and Co, and Unpolluted for Cu and Zn. The Moderate pollution (class 2) of Fe and Mn is directly related to Fe-Mn ore deposits on the banks of the river, and loading and transportation of it through the riverine system of Goa (S**hynu *et al.*, 2012**). The Zuari River receives a large input of mining material from Mandovi River via Cumbharjua canal. Part of this material must have settled within the canal leading to the enrichment of Fe, Mn, Pb and Cr in the sediments (**Noronha-D'Mello and Nayak, 2015**). I-geo values >1 in the present study suggests that the metals are mainly derived from mining-related anthropogenic activities. While values < 1 indicates that they could have been derived from natural weathering processes. Ore processing units operating all along the bank of this river and the industries also release associated elements to the waters of the river. In addition, the loading jetties in the upstream of Zuari River is also expected to release a considerable amount of Fe, Mn, and Cr. Chromium may have been released as leachates from loading of mining ores and shipping activities at the Mormugao harbor located nearby in addition to effluents from treated domestic sewage and industrial discharges and corrosion of uncoated steels from ships in the harbor at the mouth and shipbuilding industries located along the river.

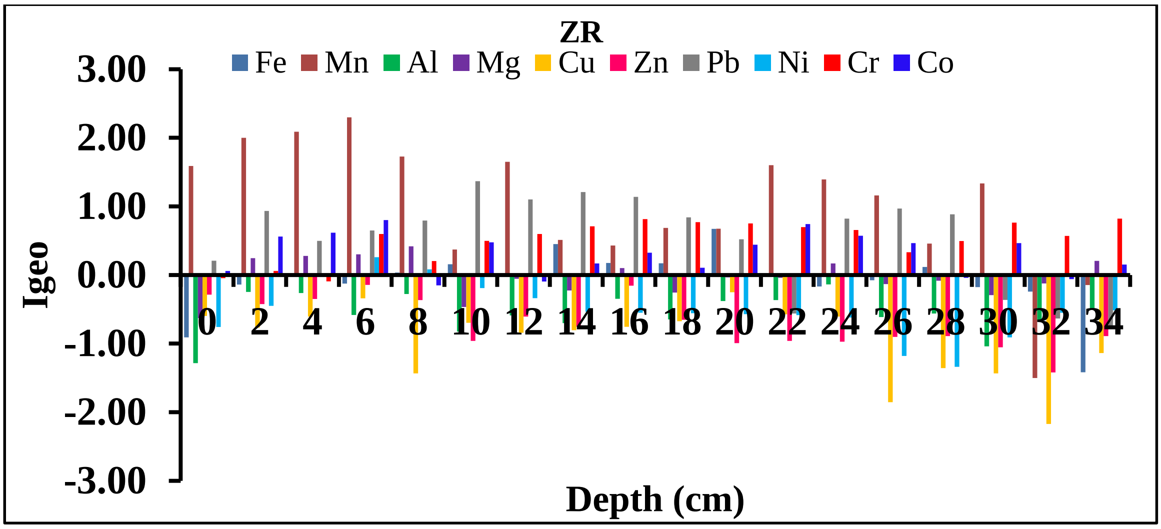


Fig. 4.1.4.g Geo-accumulation Index (Igeo) for major elements and trace metals in the sediment core collected from Zuari River (ZR), Goa-West coast of India

d. Pollution load Index (PLI)

This empirical index provides a simple, comparative means for assessing the level of metal pollution. PLI values in ZR sediment core varied from 0.93 to 1.94 (1.47) indicating higher pollution that can be attributed to the enrichment of pollutants due to exhaustive iron-ore mining activities along the shores of Zuari River. The down core variation of PLI values (**Fig.4.1.3.h**) showed an increasing trend up to the 6 cm depth of the core and thereafter it showed a decreasing trend from 6 cm up to the surface of the core. Higher PLI values in sediments demonstrated substantial anthropogenic impacts on the sediment quality, whereas lower PLI values pointed to no considerable anthropogenic activities.

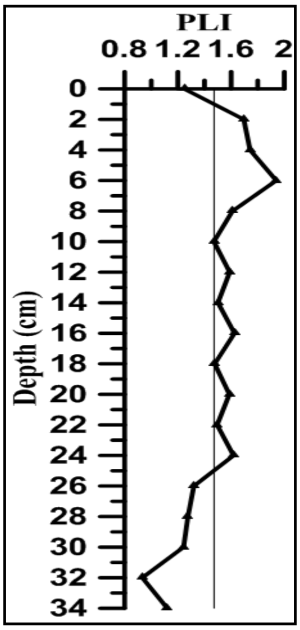


Fig. 4.1.4.h Down core variation of PLI in sediment core of Zuari River (ZR), Goa-West coast of India

4.1.4.8 Factor Analysis

The loadings between different parameters in five factors are given in table (**Table 4.1.4.d).** Factor 1 accounted for 41.28 % of the total variance and showed significant positive loadings for silt, organic carbon, Mn and Zn suggesting these is mostly derived from finer fractions of sediment. Factor 2 exhibited 14.28% of the total variance and showed significant positive loading for Fe and Pb indicating that these are derived from a mixture of dust dominated and anthropogenic input. Factor 3 accounted for 11.21% of the total variance and shows a significant loading on Al and Mg indicating its terrestrial origin. Factor 4 exhibited 9.39% of the total variance and shows a significant loading for Cu and Co representing that these are derived from industrial discharge.

Table 4.1.4.d Factor analysis matrix after varimax rotation for sediment core of Zuari River (ZR), Goa-West coast of India

Parameters	Factor 1	Factor 2	Factor 3	Factor 4
sand	**-0.81**	-0.22	-0.39	-0.14
silt	**0.75**	-0.20	0.24	0.10
clay	0.32	0.57	0.30	0.09
OC	**0.77**	0.29	0.03	0.43
TP	0.58	-0.37	0.42	0.50
Fe	-0.25	**0.82**	0.07	0.17
Mn	**0.76**	-0.04	0.21	0.44
Al	0.04	0.19	**0.90**	0.11
Mg	0.29	-0.07	**0.92**	0.11
Cu	0.16	0.30	-0.05	**0.85**
Zn	**0.74**	0.10	0.11	0.28
Pb	0.13	**0.81**	-0.07	-0.06
Ni	0.44	0.04	0.33	0.47
Cr	**-0.87**	-0.02	0.08	0.25
Co	0.08	-0.07	0.18	**0.77**
Expl.Var	4.54	2.11	2.36	2.41
Prp.Totl	0.30	0.14	0.16	0.16
% Total variance	41.28	14.28	11.21	9.39

4.1.5 Terekhol River (TR)

4.1.5.1 Sediment components

Data on concentration and average values (%) of sand, silt and clay in Terekhol River (TR) sediment core varied from sand 24.07-64.95 (49.60); silt 25.19-68.23 (41.55) and clay 3.28-15.92 (8.85%) respectively (**Table 4.1.5.a**). Sand showed higher values and silt showed lower values at 8cm depth of the core. Higher sand content may be due to higher hydrodynamic conditions prevailing owing to high energy waves that prevent the accumulation of finer sediments (**Noronha-D'Mello and Nayak, 2015**). Based on the sand, silt and clay composition, the texture of the sediment was assessed as sandy silt. The down core variation of sand showed an increasing trend from the bottom up to the 16 cm depth, showed a decreased value at 14 cm and thereafter it showed an increasing trend up to the 8 cm depth. Further, it showed decreasing trend up to the surface of the core (**Fig. 4.1.5.a**). Distribution of silt compensates the variation of sand throughout the length of the core. Clay showed an irregular decreasing trend from bottom up to the surface of the core.

Table 4.1.5.a Data on sediment components (sand, silt, clay), Organic Carbon (OC) and Total Phosphorus (TP) in sediment core of Terekhol River (TR), Goa-West coast of India

Depth (cm)	**sand**	**silt**	**clay (%)**	**OC**	**TP**
0	44.57	49.03	6.40	0.24	0.008
2	41.45	55.16	3.39	0.28	0.009
4	37.46	55.79	6.75	0.31	0.009
6	45.21	46.17	8.62	0.34	0.010
8	64.95	25.19	9.86	0.34	0.009
10	54.15	38.48	7.38	0.37	0.010
12	46.49	37.60	15.92	0.40	0.010
14	24.07	68.23	7.70	0.40	0.011
16	57.10	36.65	6.26	0.37	0.010
18	62.23	34.49	3.28	0.37	0.010
20	61.57	27.47	10.96	0.40	0.010
22	57.69	33.88	8.43	0.46	0.011
24	56.14	34.84	9.02	0.49	0.010
26	49.37	36.94	13.70	0.49	0.011
28	54.00	39.05	6.94	0.43	0.011
30	50.86	39.13	10.02	0.49	0.011
32	49.64	40.66	9.70	0.49	0.008
34	41.94	44.94	13.12	0.52	0.010
36	43.56	45.82	10.62	0.49	0.010
Avg	**49.60**	**41.55**	**8.85**	**0.40**	**0.010**
Min	24.07	25.19	3.28	0.24	0.008
Max	64.95	68.23	15.92	0.52	0.011
Std Dev	9.89	10.30	3.23	0.08	0.001

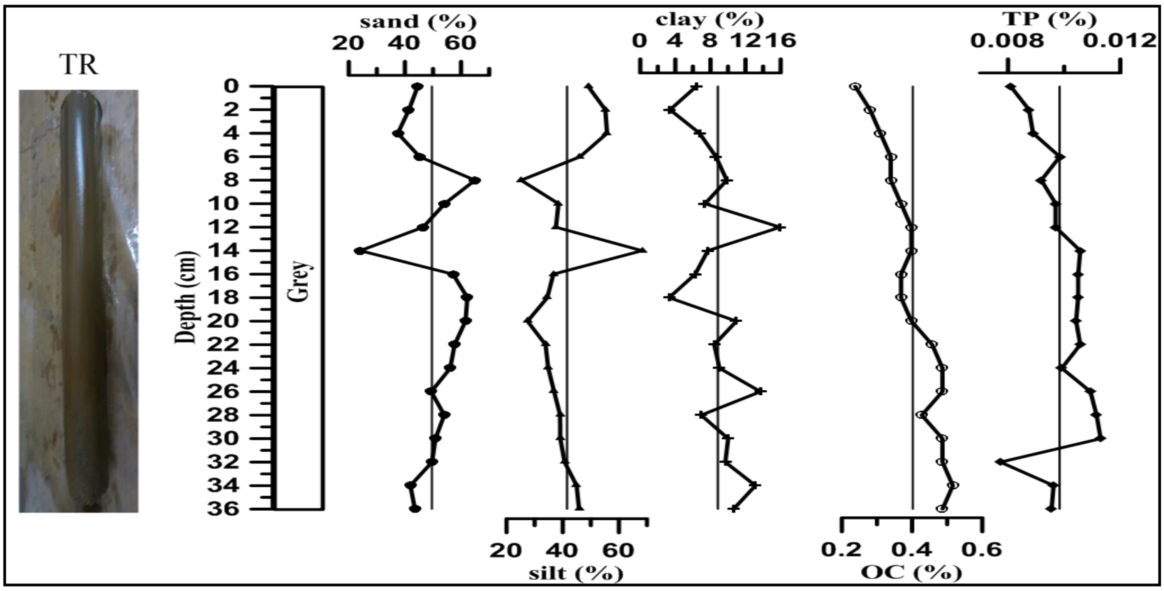


Fig.4.1.5.a Down core variation of sand, silt, clay, Organic Carbon (OC) and Total Phosphorus (TP) in a sediment core of Terekhol River (TR), Goa-West coast of India

The ternary diagram (**Fig. 4.1.5.b**) of TR core showed that the sediments fell in section IIIB, IIIC, IVB and IVC indicating that grain size varies from finer to coarser deposited in violent hydrodynamic condition.

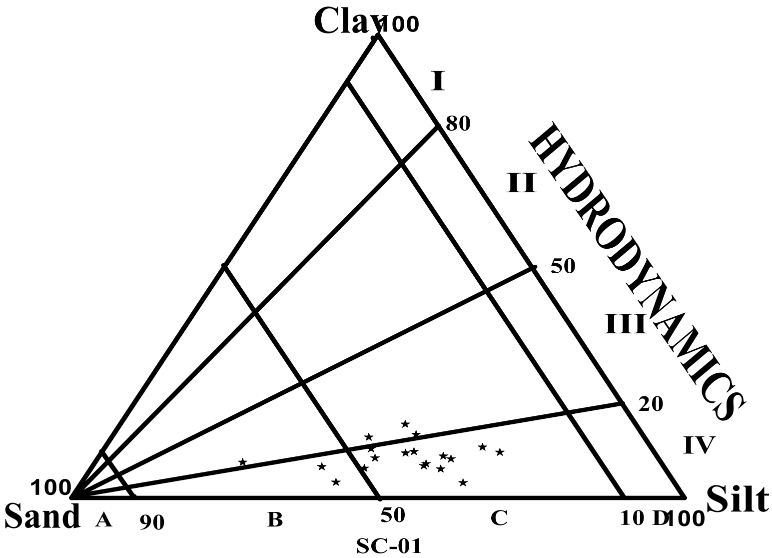


Fig. 4.1.5.b Triangular diagram for the classification of the hydrodynamics of core collected from Terekhol River (TR), Goa-West coast of India (**Pejrup, 1988**)

4.1.5.2 Organic Carbon (OC)

Organic carbon (%) content varied from 0.24-0.52 (0.40) in TR core (**Table 4.1.5.a**). OC showed higher values from bottom up to the surface of the core. The down core variation of OC in TR sediment core showed a sharp decreasing trend from bottom to the surface of the core (**Fig. 4.1.5.a**). Relatively lower values of OC in the top few centimeters of the core is due to oxidation process and comparatively higher values at the bottom are due to lack of oxygen for the decomposition of organic matter (**Sundararajan and Natesan, 2010**). Lower OC values indicate that the sediments are collected from reducing environments. This was also supported by the grey color of the TR core (**Fig. 4.1.5.a**).

4.1.5.3Total Phosphorus (TP)

Total phosphorus content (%) in TR core varied from 0.008–0.011 (0.001) (**Table 4.1.5.a**). It is interesting to note that unlike OC it showed higher concentration from 30cm up to 10cm depth of the sediment core. The down core variation of total phosphorus showed a decreasing trend from the bottom up to the surface of the core (**Fig. 4.1.5.a**).

4.1.5.4 Major Elements (Fe, Mn, Aland Mg)

Data on concentration and average values (%) of major elements Fe, Mn, Al and Mg in TR sediment core varied from 0.11-0.28 (0.19); 0.04-0.12 (0.08); 6.74-10.71 (8.90) and 0.54-2.49 (1.83) respectively (**Table 4.1.5.b).** Fe showed higher concentration at 30cm, Mn showed at 12cm and 36cm, Al showed at the surface, whereas Mg showed at 28cm depth of the sediment core. The values of Mn and Al are in broad agreement with those reported by **Fernandes *et al.*, (2019)** from the same area. It is evident from the table that Fe exhibited much lower average values than that of Shale (**Turekian and Wedepohl, 1961**). Whereas Mn, Al and Mg recorded values almost similar to average Shale values. Hence, the lower value of Fe in TR core cannot be explained except dilution by other minerals containing Mg. In general, the down core variation of Fe showed a decreasing trend from the bottom up to the surface of the core, whereas Mn and Al showed an irregular trend from bottom to the surface of the core. However, Mg exhibited an irregular trend from the bottom up to 26cm depth and thereafter the values are almost similar to that of the average values (**Fig. 4.1.5.c**). In general, the distribution of major elements in sediment core followed the order (decreasing) Al > Mg > Mn > Fe.

Table 4.1.5.b Data on major elements and trace metals in core of Terekhol River (TR), Goa-West coast of India

Depth	Major Elements (%)				Trace metals (μg g-1)					
(cm)	Fe	Mn	Al	Mg	Cu	Zn	Pb	Ni	Cr	Co
0	0.12	0.11	10.71	2.01	118.33	103.47	56.33	98.00	244.00	64.67
2	0.18	0.09	9.60	1.97	116.99	68.57	63.67	112.00	211.00	60.67
4	0.17	0.09	8.31	2.05	116.66	88.57	31.00	96.00	204.66	57.00
6	0.18	0.10	8.81	1.84	138.66	108.24	35.33	97.00	210.66	59.67
8	0.19	0.04	6.74	1.97	132.99	90.24	23.33	117.33	201.33	61.00
10	0.19	0.08	10.05	2.03	120.66	101.90	36.67	115.33	248.00	60.67
12	0.21	0.12	10.02	1.92	113.66	106.24	34.00	125.33	206.00	57.33
14	0.22	0.10	9.43	1.76	117.33	95.24	23.67	122.00	269.33	61.33
16	0.20	0.05	9.42	2.11	120.00	97.57	16.00	118.00	270.00	67.00
18	0.22	0.10	7.44	2.03	120.33	88.90	7.33	96.00	250.00	66.67
20	0.26	0.08	7.42	1.87	121.33	105.24	7.00	112.67	219.00	55.67
22	0.22	0.05	8.66	2.15	126.33	118.90	10.33	97.67	237.00	70.33
24	0.18	0.05	10.29	2.08	116.33	100.47	46.00	96.00	224.33	72.33
26	0.15	0.09	8.38	1.72	95.66	107.24	28.33	101.33	196.00	35.00
28	0.23	0.11	8.92	2.49	96.66	111.81	10.33	99.33	292.66	62.00
30	0.28	0.06	7.46	0.54	14.66	73.81	18.33	71.33	273.33	56.00
32	0.11	0.06	8.55	1.52	77.33	65.47	18.67	62.33	156.00	51.00
34	0.23	0.07	8.80	0.61	14.99	81.90	10.33	96.00	271.00	49.67

36	0.12	0.12	10.13	2.16	22.99	106.47	28.33	49.33	192.33	68.67
Avg	**0.19**	**0.08**	**8.90**	**1.83**	**100.10**	**95.80**	**26.58**	**99.10**	**230.35**	**59.82**
Min	0.11	0.04	6.74	0.54	14.66	65.47	7.00	49.33	156.00	35.00
Max	0.28	0.12	10.71	2.49	138.66	118.90	63.67	125.33	292.66	72.33
Std Dev	0.05	0.05	0.03	0.80	0.49	39.16	14.87	16.17	19.95	8.56
Avg Shale	4.72	0.08	8.0	1.5	45	95	20	68	90	19

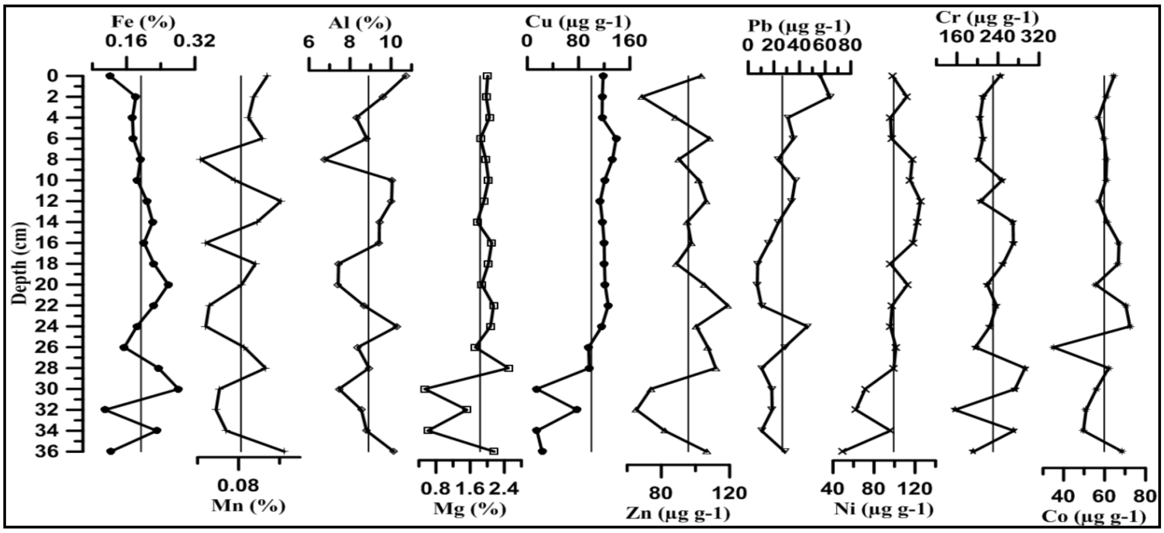


Fig. 4.1.5.c Down core variation of major elements (Fe, Mn, Al, and Mg) and trace metals (Cu, Zn, Pb, Ni, Cr, and Co) in core of Zuari River (ZR) Goa, West coast of India

4.1.5.5 Trace Metals (Cu, Zn, Pb, Ni, Cr and Co)

Data on concentration and average of trace metals (µg g-1) Cu, Z, Pb, Ni, Cr and Co in TR sediment core varied from 14.66-138.66 (100.10), 65.47-118.90 (95.80), 7.00-63.67 (26.58), 49.33-125.33 (99.10), 156.00-292.66 (230.35) and 35.00-72.33 (59.82) respectively (**Table 4.1.5.b).** Cu showed higher concentration at 6cm, Zn showed at 22cm, Pb showed at 2cm, Ni showed at 12cm, Cr showed at 28cm and Co showed at 24cm depth of the sediment core. The values of Cu, Ni and Cr are in broad agreement with those reported by **Fernandes *et al.*, (2019)** from the same area, whereas the values of Zn are in good agreement with those reported by **Noronha-D'Mello and Nayak, (2015**) from Zuari River. It is evident from the table that metals Cu, Pb, Ni, Cr and Co exhibited high concentrations in TR core except Zn compared to Shale values (**Turekian and Wedepohl, 1961**). The down core variation of Cu, Pb, and Ni showed an increasing trend from the bottom up to the surface of the core, whereas Zn showed an irregular trend from the bottom up to the surface of the core. However, Cr and Co showed an irregular trend from the bottom up to 26cm depth of the core, and thereafter the values are the same as that of the average value (**Fig. 4.1.5.c**). In the case of Pb, there is an additional atmospheric input apart from land as it is used in petrol as an additive. But in recent years this has been reduced to a great extent by the use of unleaded gasoline. Lead aerosols are carried to rivers and seas in rain and snow and are greatly scattered. The relatively high concentration of Cu can be attributed to the dumping of ship wastes, sewage, bulge water, and solid wastes at Redi Port (**EIA/EMP, 2012**). Ni is released into the environment from a variety of natural and anthropogenic sources (**Fig. 4.1.5.d**). Among industrial sources, a considerable amount of environmental Ni is derived from the combustion of coal, oil, and other fossil fuels. Other industrial sources that contribute to nickel emissions are mining incineration of municipal wastes (**Ensink *et al.*, 2007**). Wastewater from municipal sewage treatment plants also contributes to environmental metal accumulation (**Van der Hoek *et al.*, 2002**)Chromium may also reach waterways via road dust; cement-producing plants; the wearing down of asbestos brake linings from automobiles or similar asbestos sources; municipal refuse and sewage sludge incineration (**Nair and Sujatha, 2013**). In general, the distribution of trace metals in sediment core followed the order (decreasing) Cr > Cu > Ni > Co > Pb > Zn.

Fig. 4.1.5.d Photograph showing dumping of wastes near Terekhol River (TR), Goa-West coast of India

4.1.5.6 Pearson's Correlation Coefficient

The correlation coefficient matrix in TR core (**Table 4.1.5.c**) exhibited a significant positive correlation between clay and organic carbon. Indicating that these are derived from the finer fractions of sediments. Total phosphorus showed a positive correlation between Fe, and Cr. A good correlation was noticed between Fe and Cr at $P < 0.01$. Mg showed good association with Cu, Zn and Co suggesting some common sources of elements in the Terekhol River. However Cu showed good association with Ni. In addition to industrial effluents and urban wastewater, possibly urban runoffs and atmospheric deposition were also contributing to the element pollution of the river.

Table 4.1.5.c Data on Pearson's Correlation between different sediment components (sand, silt, clay) OC, TP, major elements (Fe, Mn, Al, and Mg) and trace metals (Cu, Zn, Pb, Ni, Cr and Co) in sediment core of Terekhol River (TR) (n = 19)

Param	**sand**	**silt**	**clay**	**OC**	**TP**	**Fe**	**Mn**	**Al**	**Mg**	**Cu**	**Zn**	**Pb**	**Ni**	**Cr**	**Co**
sand	1.00														
silt	**-0.95**	1.00													
clay	-0.03	-0.28	1.00												
OC	0.09	-0.27	**0.58**	1.00											
TP	0.21	-0.24	0.12	0.41	1.00										
Fe	0.22	-0.23	0.04	0.19	**0.73**	1.00									
Mn	**-0.48**	0.45	0.02	-0.28	-0.05	-0.21	1.00								
Al	-0.43	0.43	-0.04	-0.12	-0.29	**-0.47**	0.37	1.00							
Mg	0.20	-0.07	-0.39	-0.43	-0.07	-0.32	0.27	0.30	1.00						
Cu	0.21	-0.09	-0.38	**-0.65**	-0.09	-0.08	-0.03	0.03	**0.68**	1.00					
Zn	0.18	-0.24	0.21	0.01	0.41	0.03	0.28	0.26	**0.56**	0.35	1.00				
Pb	-0.36	0.41	-0.20	**-0.52**	**-0.53**	**-0.53**	0.26	**0.62**	0.20	0.24	-0.11	1.00			
Ni	0.04	-0.02	-0.06	**-0.48**	0.17	0.35	-0.05	0.03	0.26	**0.68**	0.24	0.12	1.00		
Cr	-0.02	0.11	-0.28	0.01	**0.59**	**0.66**	-0.05	0.05	-0.15	-0.12	0.15	-0.29	0.29	1.00	
Co	0.19	-0.02	**-0.53**	-0.25	-0.02	0.05	-0.03	0.33	**0.49**	0.26	0.25	0.12	0.00	0.26	1.00

4.1.5.7 Pollution Indices

a. Enrichment Factor (EF)

Enrichment factor in TR core recorded moderate enrichment for Cu, Cr and Co, whereas Fe, Mn, Ca, Mg, Zn, Pb, and Ni showed deficiency to minimal enrichment (**Fig. 4.1.5.e**). Moderate enrichment of Cu, Cr and Co can be attributed to anthropogenic inputs. While other elements may be of crustal origin.

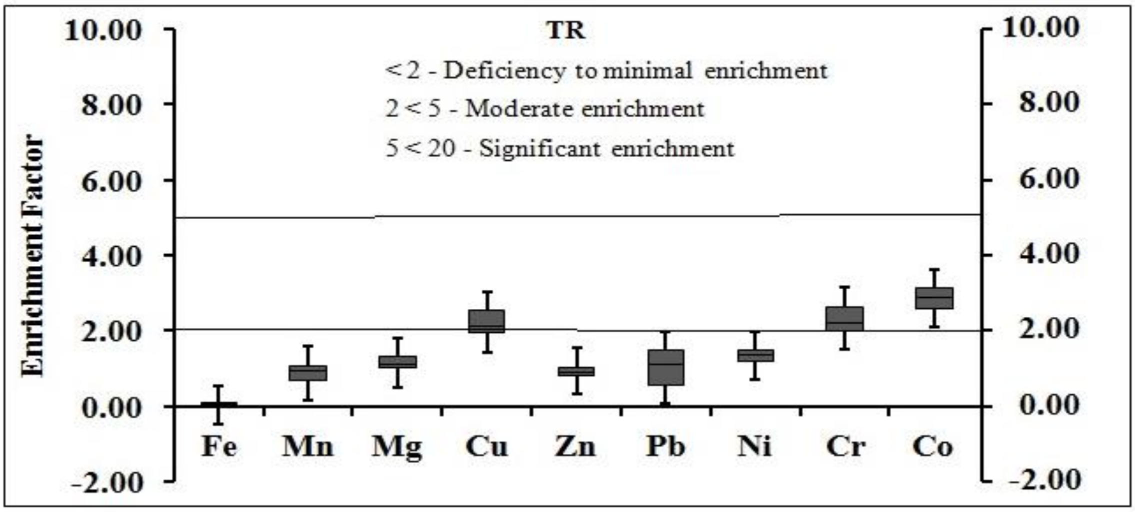


Fig. 4.1.5.e Enrichment factor for major elements and trace metals in core collected from Terekhol River (TR), Goa-West coast of India

b. Contamination Factor (CF)

Contamination Factor for TR core indicated moderate contamination for Mg, Cu, Pb, Ni and Cr; and low contamination of Fe, Mn, Al and Zn (**Fig. 4.1.5.f**). Low contamination of Fe and Mn in TR core reveal that this area is not affected by mining activities (**Kessarkar *et al*., 2015**). High contamination of Cu in TR core could be due to the operation phase of cargo vessels and domestic wastes. Anthropogenic sources of emission of Cr in the surface water are from municipal wastes, chemical industries, paints, leather, road runoff due to tyre wear, corrosion of bushings, brake wires and radiators (**Dixit and Tiwari, 2008**).

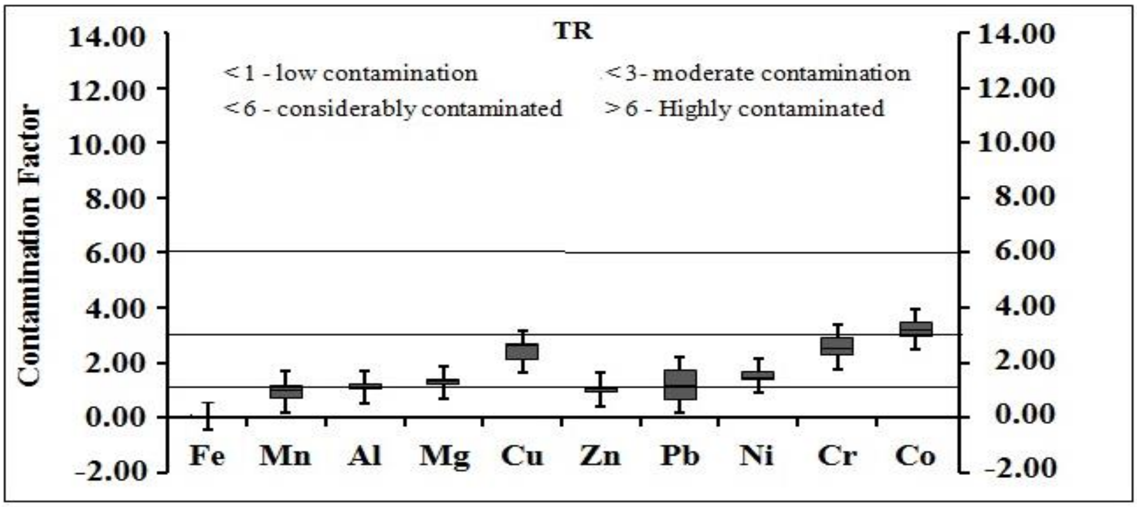


Fig. 4.1.5.f Contamination factor for major elements and trace metals in core collected from Terekhol River (TR), Goa-West coast of India

c. Geo-accumulation Index (Igeo)

Igeo values for TR sediment core showed unpolluted to moderately polluted by Cu and Cr. Upper few centimeters of sediment core showed unpolluted to moderately polluted with Pb and Ni. The core was moderately polluted with Co. However Fe, Mn, Al, Mg, Zn, did not show any pollution (**Fig. 4.1.5.g**). The moderate contamination of Cu and Cr might be associated with the presence of boatyard and small vessel building yards at the Redi port (**EIA/EMP, 2012**). The increase of Pb in sediments is caused by the use of anti-fouling paints, combustion of petroleum and diesel in the boat, ferry and other traffic activities (**Veerasingam *et al*., 2014**). Igeo values greater than 1 suggest that the metals (Fe, Mn, Pb, and Cr) are derived from anthropogenic activities, while values less than 1 indicates that metals (Cu) are entirely derived from natural weathering processes.

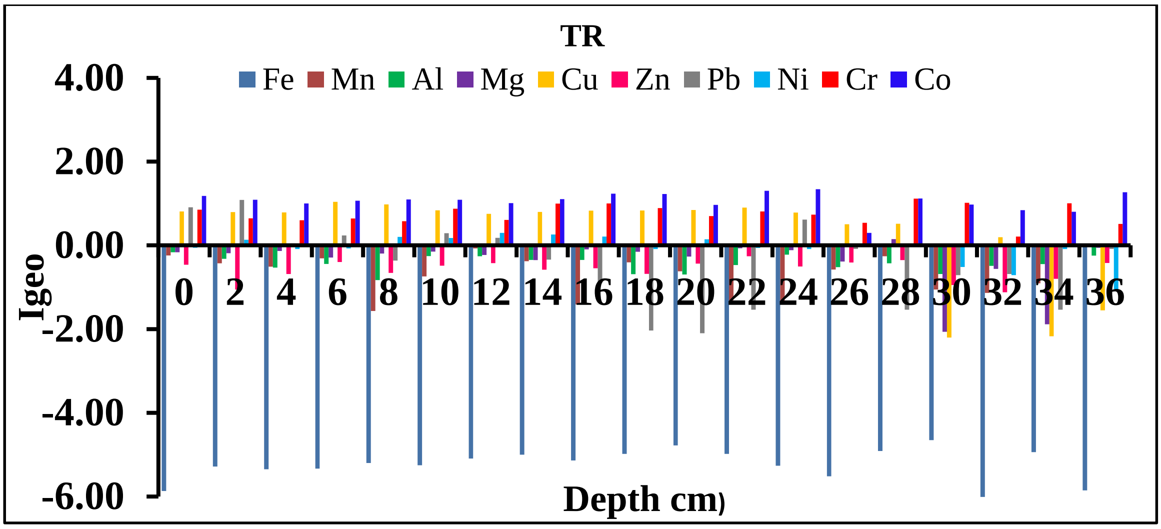


Fig. 4.1.5.g Geo-accumulation Index (Igeo) for major elements and trace metals in the sediment core from Terekhol River (TR), Goa-West coast of India

d. Pollution Load Index (PLI)

PLI values in TR sediment core varied from 0.70 to 1.20 (1.02). Indicating that it is getting polluted. The down core variation of Pollution load index showed a decreasing trend from the bottom up to 30cm depth and thereafter it showed an increasing trend up to the surface of the core **(Fig. 4.1.5.h)**.

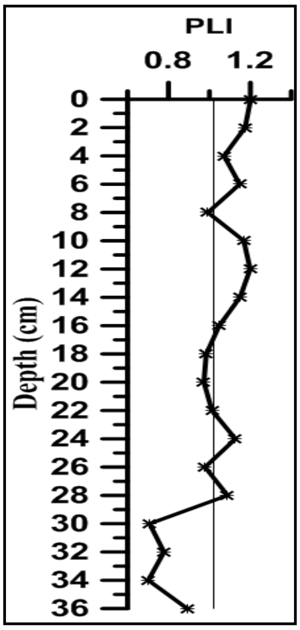


Fig. 4.1.5.h Down core variation of PLI in sediment core of Terekhol River (TR), Goa-West coast of India

4.1.5.8 Factor Analysis

The loadings between five principal factors and metals of TR sediment core are given in table (**Table 4.1.5.d).** Factor 1 accounted for 26.81% of the total variance and showed positive loading on the sand. Factor 2 showed for 21.11% of the total variance with good loading of Cu and Ni. Factor 3 accounted for 14.44 % of the total variance and showed strong positive loading of TP, Fe, and Cr. Factor 4 showed for 11.63% of the total variance with strong loading on Zn. Whereas Factor 5 showed for 9.45% of the total variance with good loading of clay.

Table 4.1.5.d Factor analysis matrix after varimax rotation for sediment core of Terekhol River (TR), Goa-West coast of India

Parameters	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
sand	**0.93**	0.05	0.05	0.17	-0.14
silt	**-0.91**	0.05	-0.04	-0.24	-0.13
clay	0.07	-0.30	-0.01	0.23	**0.85**
OC	0.23	**-0.77**	0.24	0.07	0.37
TP	0.17	-0.09	**0.85**	0.27	0.12
Fe	0.22	0.10	**0.90**	-0.16	0.05
Mn	-0.65	0.04	-0.08	0.39	0.09
Al	-0.62	-0.08	-0.27	0.44	-0.25
Mg	0.06	0.41	-0.25	0.67	-0.42
Cu	0.17	**0.86**	-0.15	0.28	-0.20
Zn	0.04	0.13	0.21	**0.92**	0.05
Pb	-0.49	0.29	-0.56	0.01	-0.18
Ni	-0.02	**0.86**	0.31	0.11	0.12
Cr	-0.17	0.02	**0.85**	-0.02	-0.32
Co	0.05	-0.01	0.06	0.32	**-0.85**

Expl.Var	2.95	2.48	2.94	2.08	2.08
Prp.Totl	0.20	0.17	0.20	0.14	0.14
% Total variance	26.81	21.11	14.44	11.63	9.45

Based on the above observations, it is evident from the color of the cores that BR and KR core are collected from the oxidizing environment, whereas MR, ZR and TR core are collected from reducing environment. BR and KR core exhibited the sandy silt texture with relatively lower organic carbon content. On the other hand, MR, ZR and TR cores showed silty sand texture with relatively high organic carbon content support the view that these are derived from reducing environments. Of the 5 rivers, Bicholim River is more enriched with respect to Fe and Mn, which was attributed to large-scale extraction of minerals from Fe-Mn ore mines and dumping of their mine wastes. BR and KR core showed comparatively higher values of Al. Enrichment of Mg in MR and ZR core may be due to larger marine input in addition to the diagenetic precipitation. Zn, Pb, and Cr showed comparatively higher values in BR core. Whereas, KR core showed enrichment with Cu and Ni, and TR core showed higher values of Cu and Co. However, MR and ZR cores registered comparatively lower values of major elements except for Mg and trace metals. Significant moderate enrichment of Fe and Mn in BR and KR sediment core is due to high levels of manganese in the surrounding ore-bearing landmass as the rivers flowing through the ore-bearing (iron and manganese) terrain might be picking up the element. Whereas, moderate enrichment of Mn, Pb, and Cr can be attributed to anthropogenic inputs while other elements (Mg, Zn, Ni and Co) may be of crustal origin. On the other hand, enrichment of Cu and Ni in TR core may be due to anthropogenic input. Contamination factors revealed that Bicholim and Kushavati river areas are highly contaminated with Fe and Mn due to the run-off from mining-related activities. Moderate contamination of Mn, Pb, and Cr is observed in MR and ZR cores. The increase of Pb in sediments is caused by the use of anti-fouling paints, combustion of petroleum and diesel in the boat, ferry and other traffic activities. High contamination of Mn is due to Fe–Mn ore deposits and human-induced activity in handling and transportation of these ores through the river and ore transportation by barges.

The distribution of major elements and trace metals in different rivers follows the trend (decreasing)

Riverine stations	Major elements	Trace metals
Bicholim River (BR)	Fe > Mn > Al > Mg	Cr > Zn > Ni > Pb > Cu > Co
Mandovi River (MR)	Fe > Mn > Mg > Al	Pb > Co > Cr > Zn > Ni > Cu
Kushavati River (KR)	Fe > Mn > Al > Mg	Cr > Ni > Cu > Pb > Zn > Co
Zuari River (ZR)	Fe > Mn > Mg > Al	Cr > Ni > Pb > Co > Zn > Cu
Terekhol River (TR)	Al > Mn > Mg > Fe	Cr > Cu > Ni > Co > Pb > Zn

It is interesting to note that BR, MR, KR and ZR rivers exhibited highest concentration of Fe and Mn indicating that these rivers are influenced by mining activities. On the other hand, Terekhol River recorded highest concentration of Al and Mn. It is further noted that BR and KR followed the similar trend of major elements similarly MR and ZR also showed the similar trend. However, no similar trends were observed in rivers with respect to concentration of trace metals. All the rivers except the Mandovi River exhibited the highest concentration of chromium. Variations in concentration of different metals in rivers is attributed to difference in physiography, hydrographic regimes, amount of industrial effluent added and iron ore mining activities.

Geo accumulation index (Igeo) of metals indicated that BR and KR core is moderately polluted by Fe and Mn and it is believed to be due to anthropogenic input; MR and ZR core is moderately polluted by Mn and Pb. The ore deposits brought from the mines are stored and loaded onto barges at several shore stations in the upper/middle part of the river and transported through the river to the port for export and also due to natural weathering process. And TR core is moderately polluted by Co.

Pollution load index indicated that the Bicholim River is the most polluted river (PLI value 2.07), whereas the Terekhol River is least polluted (PLI value 1.02). The pollution load index of five rivers varied in the order of (decreasing) BR > KR > ZR >

MR > TR Hence, our study showed that past mining has an adverse impact on the sediment quality of Bicholim and Kushavati rivers of Goa.

Factor loading revealed that the texture of the sediment and intensity of mining activities and anthropogenic input are major factors responsible for trace elements accumulation in both the rivers. However, the difference in the accumulation of pollutants in both rivers can be related to the difference in the mining activities and the anthropogenic input of metal. It is therefore concluded that exhaustive iron-ore mining in the past had a considerable impact on the sediment quality of BR and KR cores.

4.2 WATER RESERVOIRS / DAM

4.2.1 Mayem Lake (ML)

4.2.1.1 Sediment Components:

Data on sand, silt and clay (%) in ML sediment core is presented in table (**Table 4.2.1.a.).** The ML sediment core recorded highest average silt content (59.87) that ranged from 49.71-66.97; moderate content of clay (24.59) it varied from 17.68-34.75 and comparatively lower sand content (15.54) which ranged from 10.15-17.91. Higher values of silt and lower values of clay was recoreded at 18cm depth of the sediment core. Higher percentage of silt may be due to relatively larger supply of material dominant in silt and clay fraction along the eastern portion of the lake. This is also supported by relatively less and near uniformity in sand fraction. From this mixture of silt and clay, relatively finer fractions (clay) remains entrapped within the eastern shallower portion of the lake due to the presence of macrophytes (**Girap, 1997**), thus exhibiting clayey silt type texture (**Fig. 4.2.1.a)**. The down core variation of sand and clay showed an increasing trend from bottom up to the surface of the core. However, the distribution of silt compensated with clay throughout the length of the core (**Fig.4.2.1.b**). This was attributed to anthropogenic activities like dumping of iron ore mining wastes; input of substances rich in inorganic detritus. **Girap, (1997)** while studying Mayem Lake reported high concentrations of silt and was related to inorganic detritus.

Table**. 4.2.1.a** Data on the sediment components (sand, silt, clay), Organic Carbon (OC) and Total Phosphorus (TP) in sediment core of Mayem Lake (ML), Goa-West-coast of India

Depth (cm)	**Sand**	**Silt**	**Clay (%)**	**OC**	**TP**
0	15.87	57.27	26.86	0.24	0.009
2	15.20	58.85	25.95	0.30	0.008
4	16.78	56.03	27.18	0.65	0.008
6	15.53	49.71	34.75	0.65	0.009
8	15.66	57.62	26.72	0.65	0.009
10	15.02	62.31	22.67	0.71	0.012
12	14.75	60.16	25.09	0.68	0.014
14	15.15	64.05	20.80	0.48	0.014
16	14.67	62.53	22.80	1.54	0.014
18	15.35	66.97	17.68	1.72	0.018
20	10.15	66.18	23.66	2.97	0.017
22	17.57	59.08	23.34	2.79	0.018
24	17.90	58.72	23.38	2.76	0.019
26	17.91	58.68	23.41	2.61	0.016
Avg	**15.54**	**59 .87**	**24.59**	**1.34**	**0.013**
Min	10.15	49.71	17.68	0.24	0.008
Max	17.91	66.97	34.75	2.97	0.019
Std Dev	1.92	4.43	3.88	1.03	0.004

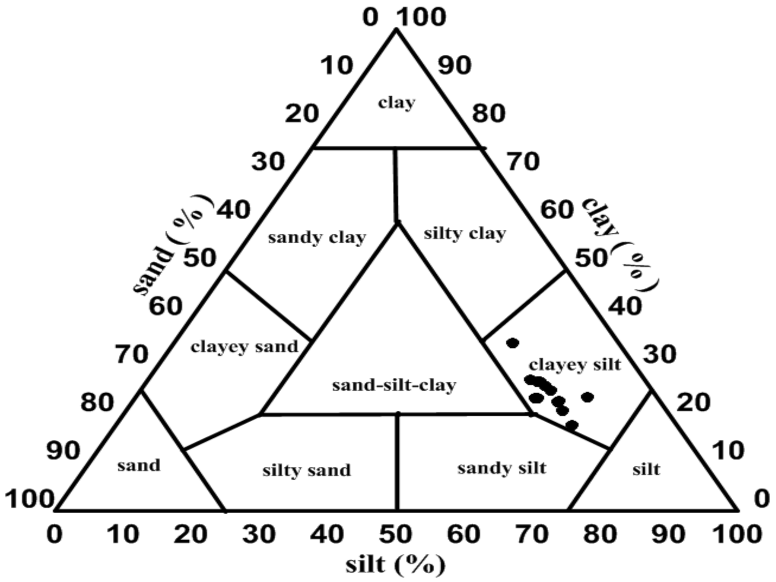


Fig. 4.2.1.a. Ternary diagram for sediment texture classification of core for Mayem Lake (ML), Goa-West coast of India (**Pejrup, 1988**)

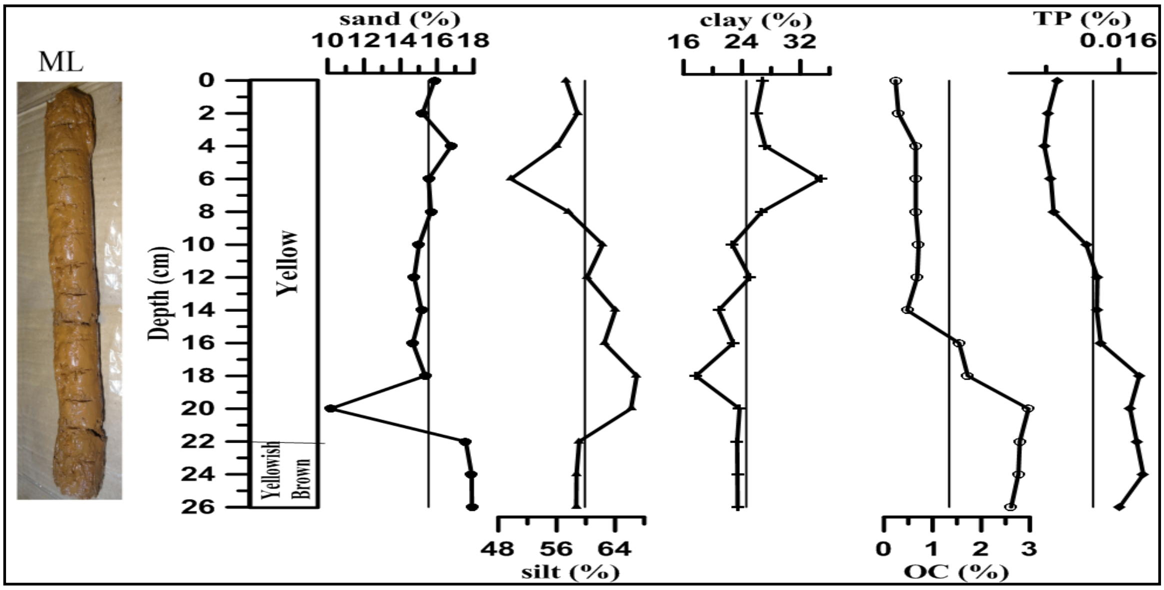


Fig. **4.2.1.b.** Down core variation of sand, silt, clay, Organic Carbon (OC) and Total Phosphorus (TP) in sediment core of Mayem Lake (ML) Goa-West coast of India

4.2.1.2 Organic Carbon (OC)

The range and average values of OC (%) in ML core are presented in table (**Table 4.2.1.a**.). OC content varied from 0.24-2.97(1.34). It recorded higher concentrations from bottom upto 20cm depth of the core. The values obtained for organic carbon content in the sediment were lower than those reported by **Girap, (1997**) from the same area. This is also supported by yellow to brown color of the core which indicates that the organic material has been oxidized and leached to some degree (**Daniels *et al.*, 2004**). Anthropogenic interference like dumping of mine wastes in recent years within this part of the catchment area, increased rate of siltation and dilution of organic carbon content. The down core variation of OC showed a decreasing trend throughout the length of the core (**Fig.4.2.1.b**) and showed almost similar values coinciding with silt. This may probably due to oxic conditions at the surface. It is interesting to note that lower organic carbon values in upper few centimeters receives may be due to sediment material which is relatively barren with little or no soil cover and wherein mine rejects are being dumped, whereas comparatively higher concentration in the bottom sediments can be related to organic detritus input during earlier years (**Girap, 1997**).

4.2.1.3 Total Phosphorus (TP)

The range and average values of TP (%) in ML core are presented in table (**Table 4.2.1.a.)**. The TP content in sediment core varied from 0.01-0.02 (0.01) which is lower than those reported by **Girap, (1997**) from the same area. The vertical profile of TP revealed a decreasing trend from bottom up to the surface of the sediment core (**Fig. 4.2.1.b**).

4.2.1.4 Major elements (Fe, Mn, Al and Mg)

Data on concentration and average of major elements (%) Fe, Mn, Al and Mg in ML sediment core varied from 5.23-13.70 (11.40), 0.09-0.21 (0.11), 4.03-10.89 (8.61) and 0.63-1.02 (0.74) respectively (**Table 4.2.2.b**). It showed higher concentration of Fe and Mg at 6cm, Mn showed at 12cm and Al showed at 22cm depth of the sediment core. The values of Mn and Al are in good agreement with those reported by **Selvam *et al.*, (2012)** from Vembanad Lake, southwest coast of India. The observed average values in the present study for Fe, Mn, Al, are slightly higher as compared to those reported by **Girap, (1997**) in the same area and was ascribed to mining dumps in the vicinity of Mayem Lake and discharge of industrial and domestic sewage, whereas Mg registered lower average value than the shale (**Turekian and Wedepohl, 1961**). The down core variation of Fe and Al showed a gradual decreasing trend from the bottom of the core up to the surface. Whereas, Al showed a decreasing trend from bottom up to 8cm depth interval and thereafter it showed increasing trend towards surface of the core. However, Mg showed an irregular trend throughout the length of the core (**Fig. 4.2.1.c)**. The higher concentration of Fe and Mn could be due to intense iron ore mining activities and also due to release of material from old and new mine dumps in the vicinity of lake area in the recent past and the ore dump stored at different points may gets flushed into the lake during heavy monsoon rains (**Girap, 1997**). In general, the distribution of major elements in sediment core followed the order (decreasing) Fe > Al >Mn> Mg.

Table 4.2.1.b Data on major elements and trace metals in a sediment core of Mayem Lake (ML), Goa-West coast of India

Depth	Major Elements (%)				Trace metals (µg g^{-1})					
(cm)	Fe	Mn	Al	Mg	Cu	Zn	Pb	Ni	Cr	Co
0	5.23	0.09	9.41	0.75	115.00	96.24	26.67	102.00	125.00	48.33
2	5.63	0.09	5.06	0.67	108.66	72.57	49.33	78.67	102.33	52.67
4	12.35	0.09	8.70	0.70	108.00	87.57	30.67	96.67	119.00	37.00
6	13.70	0.09	7.69	1.02	77.33	96.90	55.33	74.00	116.00	20.33
8	13.24	0.10	4.03	0.90	50.66	100.57	57.00	69.33	133.67	23.33
10	13.02	0.18	6.87	0.76	75.66	91.57	63.67	90.67	113.33	47.67
12	10.48	0.21	9.17	0.66	76.33	116.90	64.00	84.67	119.00	49.67
14	10.54	0.09	9.61	0.75	61.66	120.57	65.33	88.67	109.67	52.33
16	11.49	0.09	8.95	0.66	55.66	133.24	89.00	89.33	127.67	49.00
18	12.35	0.10	10.16	0.72	49.00	151.90	81.67	74.00	122.67	47.00
20	12.73	0.10	9.05	0.63	39.66	198.57	47.67	69.33	118.33	51.00
22	12.78	0.11	10.89	0.72	32.00	175.90	50.67	84.00	126.67	37.33
24	13.16	0.13	10.44	0.71	23.33	132.90	72.67	78.33	113.67	47.33
26	12.89	0.11	10.44	0.76	24.11	142.80	72.85	83.42	115.56	51.67

Avg	**11.40**	**0.11**	**8.61**	**0.74**	**64.08**	**122.73**	**59.04**	**83.08**	**118.75**	**43.90**
Min	5.23	0.09	4.03	0.63	23.33	72.57	26.67	69.33	102.33	20.33
Max	13.70	0.21	10.89	1.02	115.00	198.57	89.00	102.00	133.67	52.67
Std Dev	2.70	0.04	2.04	0.10	30.80	35.81	17.62	9.84	8.06	10.53
Avg Shale	4.72	0.08	8.0	1.5	45	95	20	68	90	19

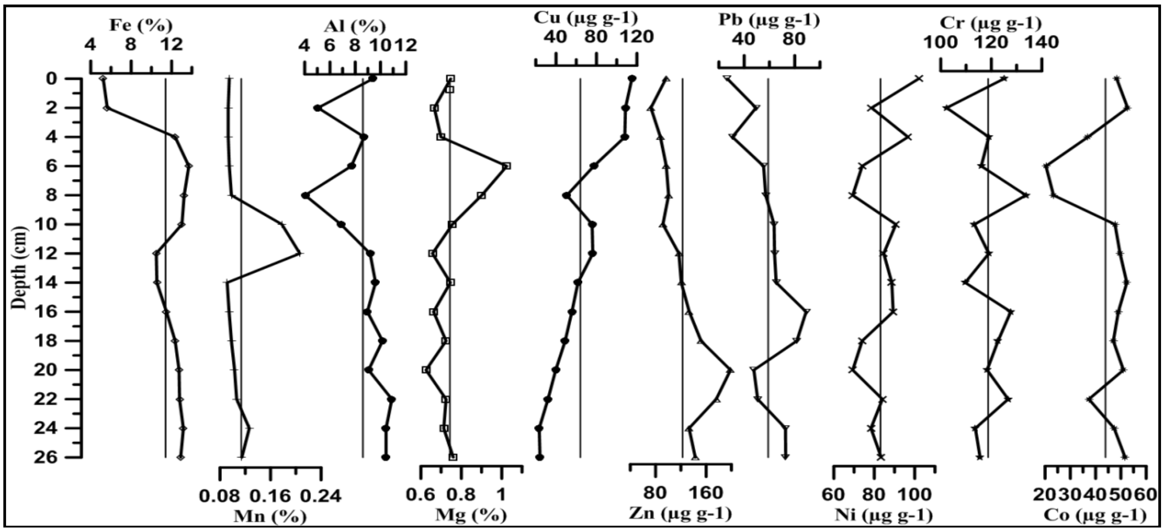


Fig. 4.2.1.c Down core variation of major elements (Fe, Mn, , and Mg) and trace metals (Cu, Zn, Pb, Ni, Cr, and Co) in sediment core of Mayem Lake (ML), Goa-West coast of India

4.2.1.5 Trace metals (Cu, Zn, Pb, Ni, Cr and Co)

Data on trace metals (μgg^{-1}) in ML core is presented in table (**Table 4.2.1.c.**). It is evident from the table that the concentration of Cu ranged from 23.33-115.00(64.08); Zn varied from 72.57-198.57 (122.73); Pb varied from 26.67-89.00 (59.04); Ni varied from 69.33-102.00 (83.08); Cr varied from 102.33-133.67 (118.05) and Co varied from 20.33-52.67 (43.90). Cu and Ni recorded higher concentration at the surface, Zn at 20cm, Pb at 16cm, Cr at 8cm and Co at 14cm depth of the sediment core. The values of Pb and Cr are in good agreement with those reported by **Yin *et al.*, (2011**) from Tihu Lake in China. All metals recorded higher average concentrations, as compared to shale values (**Turekian and Wedepohl, 1961**). Cu and Co exhibited slightly higher values, whereas lower values for Zn, Ni and Cr as compared to those reported by **Girap,** (**1997**) from the same area and was ascribed to mining dumps in the vicinity of Mayem Lake and discharge of industrial and domestic sewage. The concentrations of Cu, Zn, and , Pb, are often elevated above crustal (background) levels in sediments that have been affected by human activities (**Icela *et al.*, 2012**) particularly from mining waste sites (**Ana *et al.*, 2011**). The down core variation of trace metals is presented in fig (**Fig. 4.2.1.c)**. Zn, and Pb showed a sharp decreasing trend from bottom up to the surface of the sediment core, while Cu showed a reverse trend. However, Ni, Cr and Co showed an irregular trend. Zn showed almost similar pattern of distribution of Fe and Mn indicating that the role of Fe-Mn oxide in the concentration of these metals in the core (**Siraswar and Nayak, 2011**). Higher concentrations of Cu in the core was attributed to operational boats for recreational purpose in recent years. It may also be associated with activities such as industrial and municipal activities (**Krishna and Govil, 2004**). Copper is widely used in electrical wiring, roofing and production of alloys, pigments, cooking utensils, and piping. Further, input of pesticides enhances copper from urban and agricultural areas (**Pandey and Singh, 2017**). The iron ore mining and processing constitute potential source of trace metals and may contribute to metal pollution in the nearby water resources (**Satapathy *et al.*, 2009**). Iron and manganese oxides have been well recognized for their abilities to absorb and enrich other metallic elements such as Cr, Cu, and Ni and also play an important role to the extent that their deposition occurred in the bed sediments (**Gharibreza *et al.*, 2013**). In general, the distribution of trace metals in sediment core followed the order (decreasing) Zn > Cr > Ni > Cu >Pb > Co.

4.2.1.6 Pearson's correlation Coefficient

Pearson's correlation coefficient matrix of metals in ML core (**Table 4.1.1.c)** showed a significant positive correlation of clay with silt, Mg, Zn and Co indicating that their strong association with finer sediments (clay+silt). On the other hand OC showed a significant positive correlation withTP, Zn and Al indicating the influence of organic carbon and TP in the process of trapping of Zn and Al in the sediments (**Loomb, 2001**).

Table 4.2.1.c Data on Pearson's correlation between different sediment components (sand, silt, clay), OC, TP and major elements (Fe, Mn, Al, and Mg) and trace metals (Cu, Zn, Pb, Ni, Cr, and Co) in sediment core of Mayem Lake (ML), Goa-West coast of India (n=14)

Par	**sand**	**silt**	**clay**	**OC**	**TP**	**Fe**	**Mn**	**Al**	**Mg**	**Cu**	**Zn**	**Pb**	**Ni**	**Cr**	**Co**
sand	1.00														
silt	-0.48	1.00													
clay	0.06	**-0.90**	1.00												
OC	0.02	0.32	-0.37	1.00											
TP	-0.01	**0.61**	**-0.69**	**0.85**	1.00										
Fe	0.07	0.01	-0.04	0.51	0.41	1.00									
Mn	-0.04	0.11	-0.11	-0.04	0.18	0.13	1.00								
Al	0.22	0.25	-0.40	**0.59**	0.71	0.17	0.04	1.00							
Mg	0.26	**-0.67**	**0.63**	-0.29	-0.41	0.32	-0.20	-0.34	1.00						
Cu	-0.10	-0.33	0.43	**-0.84**	**-0.82**	**-0.68**	-0.04	-0.41	0.01	1.00					
Zn	-0.29	**0.54**	-0.47	**0.87**	**0.85**	0.42	-0.07	**0.62**	-0.34	**-0.76**	1.00				
Pb	0.06	0.42	-0.51	0.33	**0.56**	0.41	0.19	0.20	-0.06	**-0.62**	0.29	1.00			
Ni	0.31	-0.11	-0.03	-0.38	-0.28	-0.44	0.10	0.28	-0.26	0.53	-0.37	-0.33	1.00		
Cr	0.03	-0.01	0.00	0.14	0.07	0.27	-0.12	0.05	0.18	-0.22	0.28	0.02	-0.02	1.00	
Co	-0.20	**0.68**	**-0.67**	0.19	0.43	-0.44	0.23	0.39	**-0.83**	-0.03	0.23	0.23	0.31	-0.45	1.00

4.2.2 Selaulim Dam/Reservoir (SL)

4.2.2.1 Sediment Components

The data on concentration and average values (%) of sand, silt and clay is presented in table (**Table 4.2.2.a).** SL sediment core exhibited higher average silt content (57.73), it varied from 43.65 to 75.57, whereas sand and clay content varied from 19.71 - 47.15 (34.00) and 3.47 – 10.59 (8.27) respectively. Higher silt content and lower sand and clay content was recorded at 18cm depth of the sediment core. Higher values of silt may be due to the finest sediments that have been transported by fluvial inputs (**Amor *et al.,* 2019**), thus exhibiting sandy silt texture (**Fig. 4.2.2.a**). The down core variation of sand and clay showed an increasing trend from bottom up to the surface of the core. However, the distribution of silt compensated with sand throughout the length of the core (**Fig.4.2.2.b**).

Table 4.2.2.a Data on the sediment components, Organic Carbon (OC) and Total Phosphorus (TP) in sediment core of Selaulim Dam (SL), Goa-West coast of India

Depth (cm)	Sand	Silt	Clay (%)	OC	TP
0	39.33	50.75	9.92	0.37	0.005
2	46.40	45.70	7.90	0.46	0.003
4	47.15	43.65	9.20	0.83	0.006
6	41.18	50.15	8.67	0.92	0.006
8	21.02	69.11	9.87	0.98	0.008
10	36.76	59.77	3.47	1.85	0.008
12	35.58	54.43	9.98	2.00	0.006
14	27.64	63.61	8.75	1.75	0.006
16	33.19	58.91	7.90	1.57	0.007
18	19.71	75.57	4.72	1.57	0.007
20	26.07	63.33	10.59	1.51	0.007
Avg	**34.00**	**57.73**	**8.27**	**1.26**	**0.006**
Min	19.71	43.65	3.47	0.37	0.003
Max	47.15	75.57	10.59	2.00	0.008

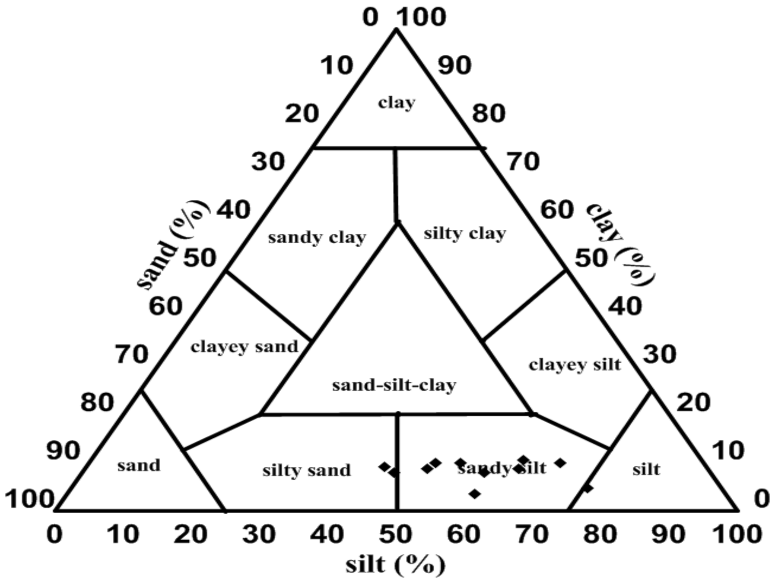


Fig. 4.2.2.a. Ternary diagram for sediment texture classification of core for Selaulim Dam (SL), Goa-West coast of India (**Pejrup, 1988**)

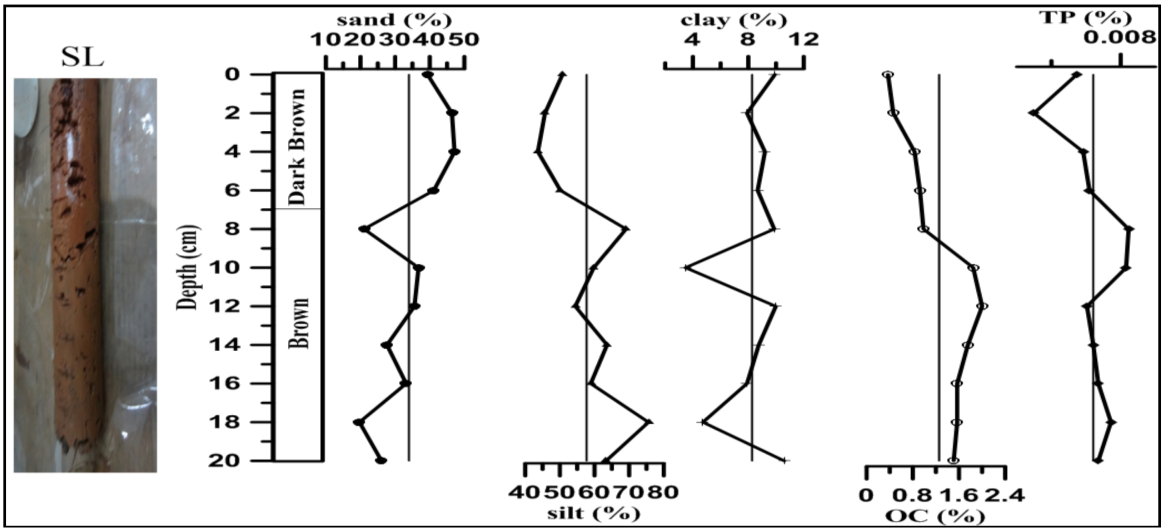


Fig. 4.2.2.b. Down core variation of sand, silt, clay, Organic Carbon (OC) and Total Phosphorus (TP) in sediment core of Selaulim Dam (SL), Goa-West coast of India

4.2.2.2 Organic Carbon (OC)

The data on OC in SL core are presented in table (**Table 4.2.2.a.).** OC content varied from 0.24-2.97 (1.34). Higher OC values are recorded from bottom up to 10cm depth of the sediment core. A good amount of organic matter is supplied by river run off and considerable volume of organic debris is retained in the overlying water column.

Relatively rapid rate of accumulation of fine grained organic matter, and low oxygen content of the water immediately above the bottom sediments would favor high organic matter in the bottom sediments. The enrichment of organic matter in deeper layers suggests deposition under calm conditions prevailed during the slow accumulation of finer sediment (**Anitha and Kumar, 2014**). The down core variation of OC showed a decreasing trend throughout the length of the core (**Fig. 4.2.2.b.**). It is interesting to note that from bottom up to 8cm depth, OC concentrations were comparatively higher with higher percentage of silt and from 8cm up to the surface of the core, OC values were comparatively less (below 1%) this is also supported by Dark brown color of the core indicating that that the organic material has been oxidized and leached to some degree (**Daniels *et al.,* 2004**). Concentration of organic matter in the fine grained fraction of the sediment often higher than that in the sand sized fractions (**Seshan *et al.,* 2010**).

4.2.2.2 Total phosphorus (TP)

The data on TP (%) in SL core are presented in table (**Table 4.2.2.a).** TP content in sediment core varied from 0.003-0.008 (0.006). Higher concentration of TP was recorded at 8cm and 10cm depth of the sediment core. The down core variation of Total Phosphorus (TP) showed a gradual decreasing trend from bottom up to the surface of the sediment core and it coincides with the trend of OC (**Fig.4.2.2.b**).

4.2.2.3 Major elements (Fe, Mn, Al and Mg)

The data on major elements (%) in SL sediment core is presented in table (**Table 4.2.2.b**). It is evident from the table that the concentration of Fe varied from 8.45-10.29 (9.44); Mn varied from 0.094-0.43 (0.23); Al varied from 8.02-11.97 (10.36); and Mg varied from 0.21-0.58 (0.38). Fe and Al showed higher concentration at the bottom of the sediment core, Mn showed at 6cm and Mg showed at12cm depth of the sediment core. Concentration of Fe and Mn are in good agreement with those reported by **Dessai *et al.,* (2009)** from Zuari River. The increase in OC content with decrease in Fe and Mn towards few centimeters in upper part of the core was due to decrease in deposition of ore material (**Prajith *et al.,* 2015**). The down core variation of Fe, Mn and Mg showed a fluctuating decreasing trend from bottom up to the surface of the sediment core. Whereas, Al showed a decreasing trend from bottom up to 6cm depth and thereafter it showed an increasing trend up to the surface of the core (**Fig. 4.2.2.c).** It is interesting to note that at 6cm depth Mn showed an increased peak (0.43%), whereas Al showed a decreased peak (8.02%). Relative high concentration of Al in SL core sediments may probably due to local human activities. Generally Al is present in solution at pH between 6-8 and its concentration in sediment increases in acidic conditions. Variation of Al concentrations between SL core may probably be due to difference in pH of the waters in that region (**Balaintova *et al.*, 2009**). In general, the distribution of major elements in sediment core followed the (decreasing) order Al > Fe > Mn > Mg.

Table 4.2.2.b Data on major elements and trace metals in sediment core of Selaulim Dam (SL), Goa-West coast of India

Depth (cm)	Major Elements (%)				Trace metals (µg g-1)					
	Fe	**Mn**	**Al**	**Mg**	**Cu**	**Zn**	**Pb**	**Ni**	**Cr**	**Co**
0	9.11	0.04	11.92	0.24	102.66	70.57	60.33	29.67	190.33	39.67
2	9.72	0.09	10.46	0.21	50.33	41.57	79.33	21.67	230.33	25.00
4	8.49	0.22	9.90	0.35	90.33	97.24	66.33	41.67	171.00	61.33
6	9.77	0.43	8.02	0.29	101.33	102.57	71.33	21.00	190.66	62.33
8	8.76	0.25	10.95	0.47	91.33	125.90	69.67	18.00	195.33	60.00
10	8.45	0.16	8.95	0.47	87.00	135.57	63.33	48.33	212.00	51.67
12	9.08	0.25	11.58	0.58	80.66	122.24	71.67	19.33	222.66	30.00
14	9.82	0.31	9.16	0.41	82.66	153.90	89.33	17.00	197.00	40.00
16	10.06	0.24	10.35	0.40	95.66	126.90	89.67	48.67	203.66	57.67
18	10.29	0.31	10.75	0.35	88.00	193.23	76.67	63.67	216.66	39.67
20	10.28	0.25	11.97	0.43	93.66	127.90	77.33	51.33	214.00	66.67
Avg	**9.44**	**0.23**	**10.36**	**0.38**	**87.60**	**117.96**	**74.09**	**34.58**	**203.97**	**48.54**
Min	8.45	0.04	8.02	0.21	50.33	41.57	60.33	17.00	171.00	25.00
Max	10.29	0.43	11.97	0.58	102.66	193.23	89.67	63.67	230.33	66.67
Std Dev	0.69	0.11	1.27	0.11	14.14	40.34	9.58	16.60	17.16	14.27
Avg Shale	4.72	0.08	8.0	1.5	45	95	20	68	90	19

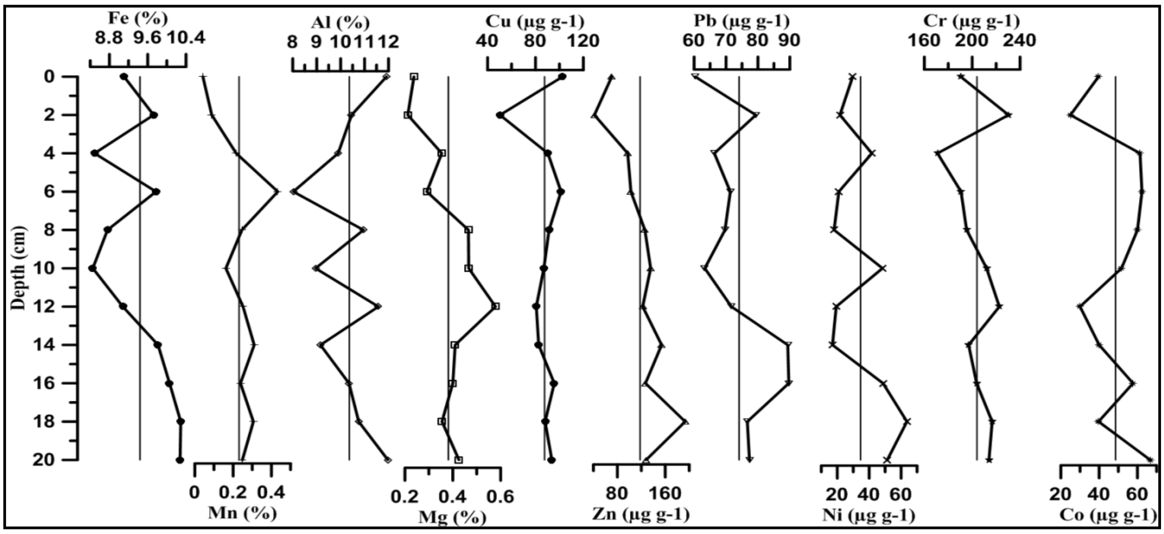


Fig. 4.2.2.c. Down core variation of major elements (Fe, Mn, Al, and Mg) and trace metals (Cu, Zn, Pb, Ni, Cr, and Co) in sediment core of Selaulim Dam (SL), Goa-West coast of India

4.2.2.4 Trace metals (Cu, Zn, Pb, Ni, Cr and Co)

The data on trace metals (µg g-1) is presented in table (**Table 4.2.2.b).** It is evident from the table that SL core exhibited higher average concentration of Cu, Zn, Pb, Cr and Co. The values ranged for Cu from 50.33-102.66 (87.60); Zn 41.57-193.23 (117.96); Pb 60.33-89.67 (74.09); Cr 171.00-230.33 (203.97) and Co 25.00-66.67 (48.54). However Ni registered lower average values 34.58 with a range of 17.00-63.67 as compared to average Shale values (**Turekian and Wedepohl, 1961**). Copper registered higher values at the surface, Zn and Ni at 18cm, Pb at 16cm, Cr at 2cm and Co at the bottom of the sediment core. The values of Cr are in good agreement with those reported **by Ra *et al.,* (2011);** Zn is in broad agreement with those reported by **Kaidao *et al.,* (2012)** from Mekong river and **Siddique *et al.,* (2012)** from Bakhadi Esuary, Bangladesh; Pb by **Spencer, (2002**) from Medway estuary, UK. The observed higher values of metals in SL core might be due to input from mining in the past. Iron ores are naturally contaminated with a large number of toxic metals such as Mn, Cu, Co, Ni, Zn, Pb etc. (**Gupta *et al.,* 2014**). The main anthropogenic sources of Zn are related to the non-ferric metal industry and agricultural practice (**Yaylali-Abanuz, 2011 and Kabata, 2000**). Zinc is a very readily mobile element. The down core variation of Cu showed values almost similar to those of average from bottom up to 8cm depth and thereafter it showed a decreasing trend up to 2cm depth, from 2cm up to the surface of the core it showed increased values, whereas Zn, Pb and Cr showed a decreasing trend from the bottom up to the surface of the core. However Ni and Co showed an irregular trend from bottom up to the surface of the core (**Fig. 4.2.2.c.).** In general, the distribution of trace metals in SL reservoirs follows the trend (decreasing) Cr > Zn > Cu > Pb > Co > Ni.

4.2.2.5 Pearson's Correlation Coefficient

Pearson's correlation coefficient matrix of metals showed a significant positive correlation (**Table 4.2.2.c**) of silt with OC , TP and Zn indicating that Zn had the strongest affinity for finer sediment and organic matter (**Rosales *et al.,* 2000**). Fe showed good association with Pb, whereas Cu showed good association with Co indicating that they have a common source of origin.

Table 4.2.2.c Data on Pearson's correlation between different sediment components (sand, silt, clay), OC,TP, major elements (Fe, Mn, Al, and Mg) and trace metals (Cu, Zn, Pb, Ni, Cr, and Co) in sediment core of Selaulim Dam (SL), Goa-West coast of India (n=11)

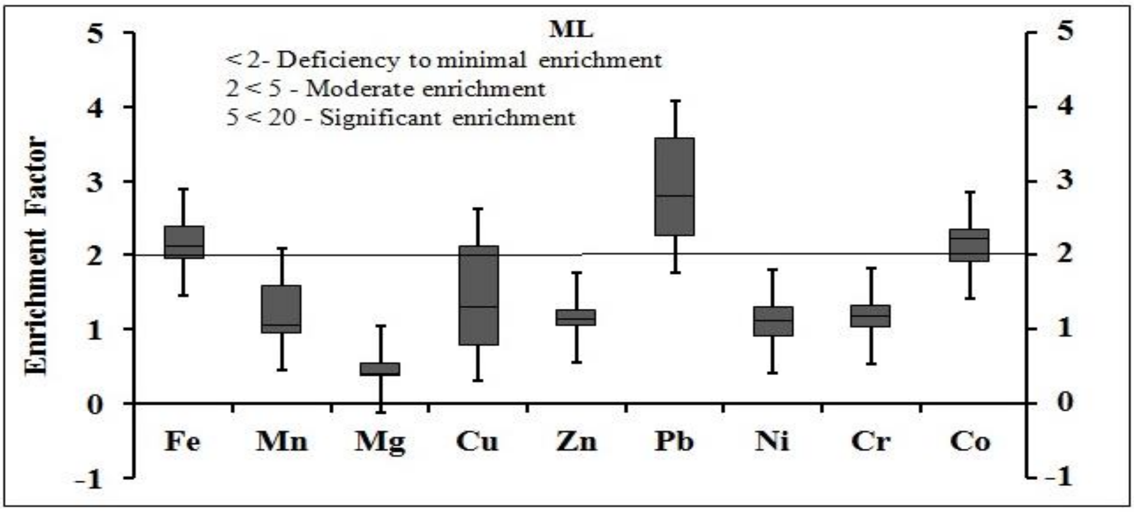
Parm	**sand**	**silt**	**clay**	**OC**	**TP**	**Fe**	**Mn**	**Al**	**Mg**	**Cu**	**Zn**	**Pb**	**Ni**	**Cr**	**Co**
sand	1.00														
silt	-0.97	1.00													
clay	0.08	-0.31	1.00												
OC	-0.49	0.54	-0.32	1.00											
TP	-0.68	0.72	-0.31	0.55	1.00										
Fe	-0.38	0.35	0.03	0.14	-0.20	1.00									
Mn	-0.35	0.34	0.00	0.43	0.38	0.36	1.00								
Al	-0.28	0.17	0.44	-0.09	-0.11	0.11	-0.50	1.00							
Mg	-0.45	0.43	0.01	**0.83**	0.63	-0.24	0.30	0.13	1.00						
Cu	-0.25	0.20	0.16	0.07	0.58	-0.05	0.33	-0.02	0.13	1.00					
Zn	-0.79	**0.85**	-0.41	**0.77**	**0.75**	0.27	0.57	-0.09	0.56	0.32	1.00				
Pb	-0.31	0.29	0.03	0.36	-0.14	**0.72**	0.35	-0.11	0.06	-0.28	0.29	1.00			
Ni	-0.26	0.37	-0.53	0.28	0.34	0.27	-0.02	0.15	0.02	0.25	0.47	0.02	1.00		
Cr	-0.20	0.26	-0.29	0.35	-0.19	0.39	-0.17	0.29	0.17	-0.63	0.07	0.29	0.10	1.00	
Co	-0.16	0.11	0.15	0.02	0.54	-0.06	0.41	-0.21	0.14	**0.67**	0.19	-0.10	0.30	-0.57	1.00

4.2.3 Pollution Evaluation Indices

a. Enrichment Factor (EF)

Enrichment factors in ML core showed moderate enrichment for Fe, Pb and Co; Deficiency to minimal enrichment for Mn, Mg, Cu, Zn, Ni, Cr and Co (**Fig. 4.2.3. a)**. On the other hand, SL core showed moderate enrichment for Mn and Pb; and deficiency to minimal enrichment for Fe, Cu, Zn, Ni and Cr (**Fig. 4.2.3. a**). If EF values are between 0.05 - 1.5 it indicates that the metal is entirely from crustal materials and if EF values are higher than 1.5 it suggests that the sources may be anthropogenic origin (**Zang and Liu, 2000**). Higher EF values of Fe and Mn can be attributed to run-off from the mining activities in the past. Whereas, enrichment of Pb was attributed to use of in anti-fouling paints for boats, combustion of diesel in boat and other traffic activities (**Veerasingam *et al.*, 2014**). Higher EF values for Cu, Zn, Ni and Cr was attributed to anthropogenic input of these metals into the river.

a.



b.

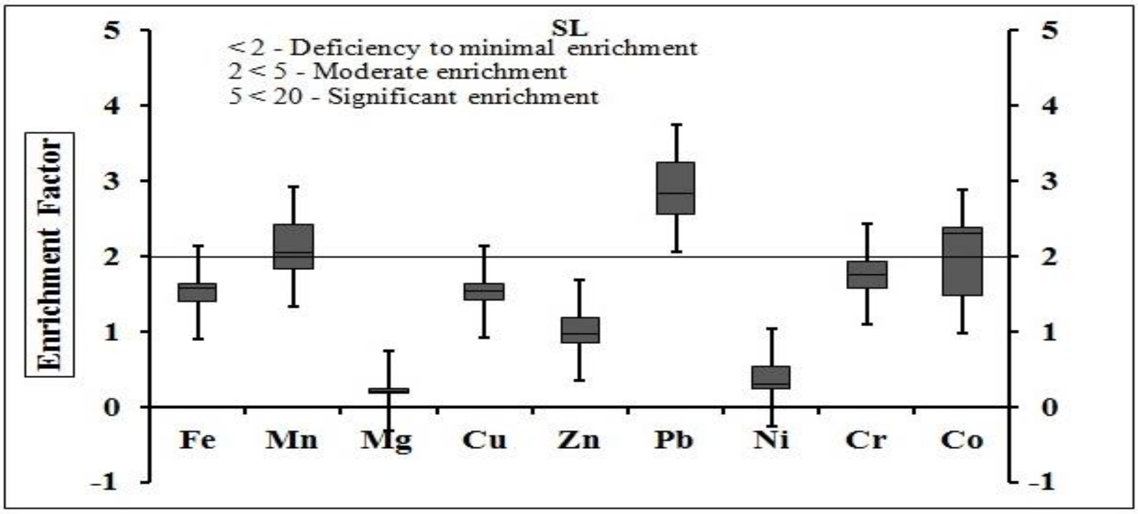
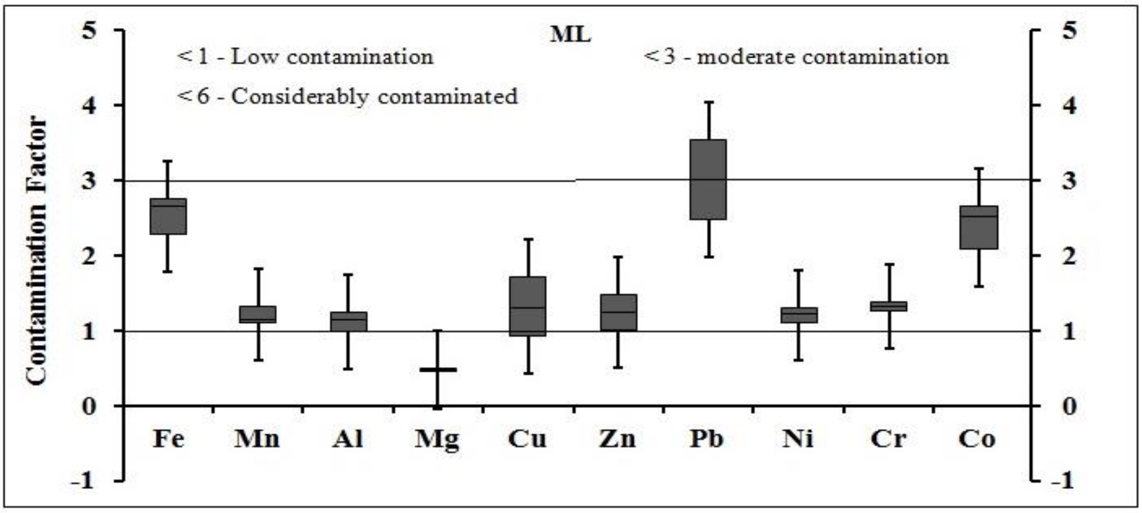


Fig. 4.2.3. a Enrichment factor for major elements and trace metals in core collected from a. Mayem lake (ML) and b. Selaulim Dam (SL), Goa-West coast of India

b. Contamination Factors (CF)

Contamination factors for ML core indicated that sediment core is considerably contaminated with Pb, whereas moderately contaminated with Fe, Mn, Al, Cu, Zn, Cr and low contamination for Mg (**Fig.4.2.3. b**). Similarily, contamination factors of metals in SL reservoir revealed considerable contamination for Pb; and moderate to considerable contamination for Mn and moderate contamination for Fe, Al, Cu, Zn and Cr and low contamination for Ni (**Fig. 4.2.3. b**). Lead is one of the most contaminant, when present in significant quantity constitute a source of pollution causing a threat to the aquatic life (**Nambaje *et al.*, 2016**). The main source of lead into the aquatic systems, that causes lead deposition in the sediment, is mainly from lead pipes and waste batteries (**Showqi *et al.*, 2018**). Domestic sewage, industrial effluents, and vehicular emissions are the major anthropogenic sources of Pb (**Pandey and Singh, 2017**). The strong affinity of cobalt for manganese and iron hydroxides has been will described by several authors (**Achyuthan and Richardmohan, 2002**). Mobility of Co is intermediate and is controlled by adsorption and co-precipitation with Fe and Mn oxides (**Anitha and Kumar, 2014**).

a.



b.

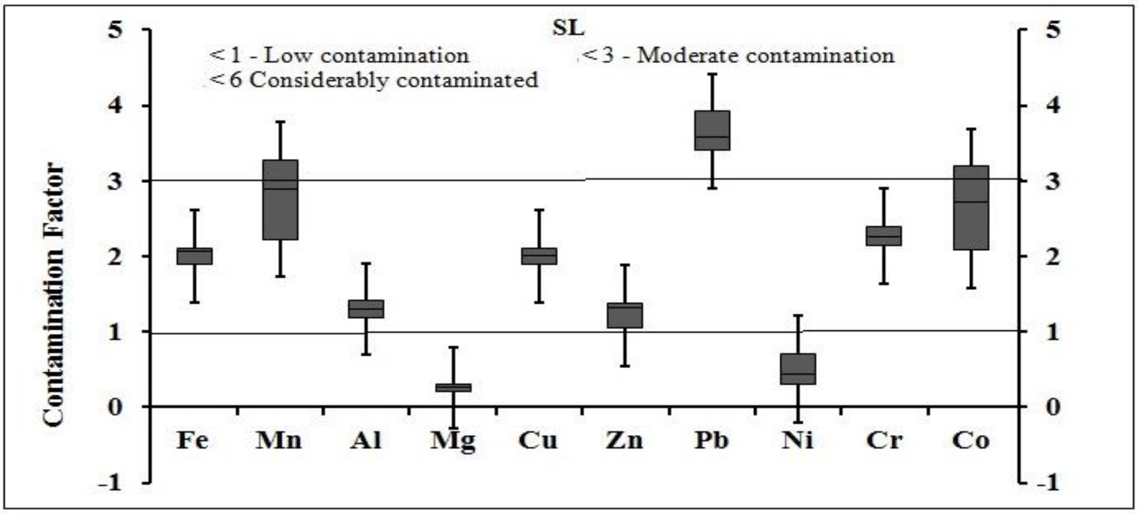
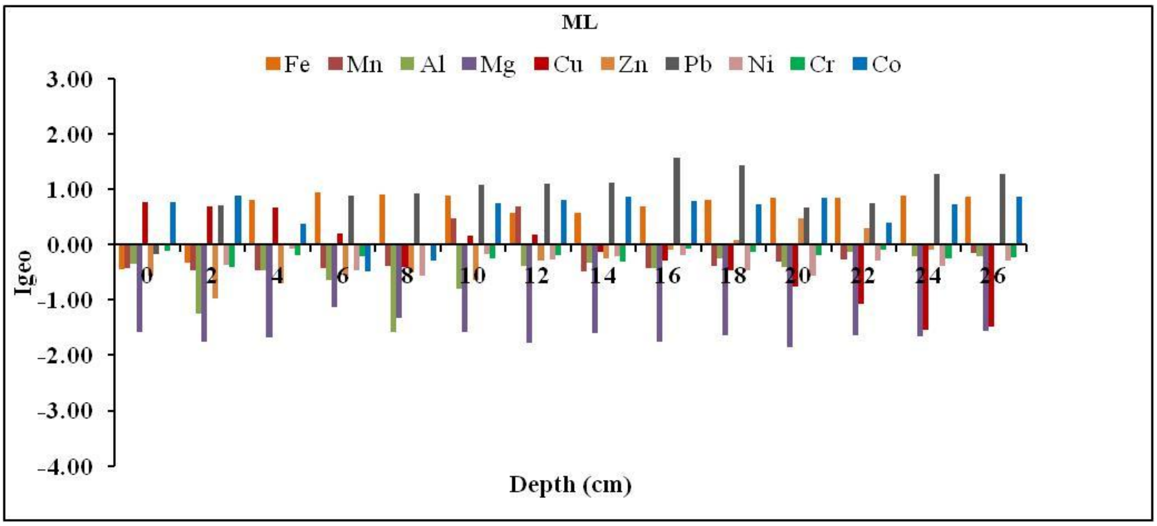


Fig.4.2.3. b. Contamination factor for major elements and trace metals in core collected from a. Mayem Lake (ML) and b. Selaulim Dam (SL), Goa-West coast of India

c. Geo-accumulation Index (Igeo)

Quantification of metal accumulation in the study area is done by calculating Igeo values. Igeo values in ML sediment core is considered to be moderately polluted with Pb from the bottom of the core to 10cm depth and thereafter unpolluted to moderately polluted up to the surface of the core; unpolluted to moderately polluted with Fe, Cu and Co, Whereas, it was unpolluted to moderately polluted with Cu (from 12cm up to the surface of the core). Mn, Al, Mg, Zn, Ni and Cr did not show any pollution (**Fig.4.2.3. c**). Geo-accumulation index obtained for top sediments confirms the anthropogenic influence of metals due to the release of material from iron ore mine dumps (**Girap, 1997**). The Igeo values in SL core showed moderate pollution with Pb and Co; unpolluted to moderately polluted with Fe, Mn, Cu and Cr, whereas Al, Mg, Zn and Ni did not show any pollution (**Fig.4.2.3. c**).

a.



b.

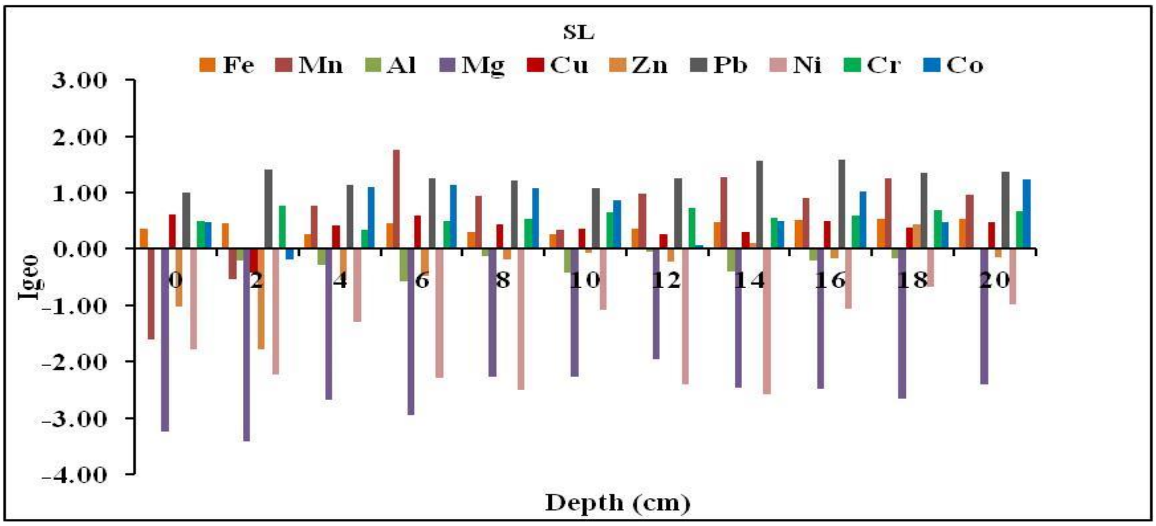


Fig.4.2.3.c Geo-accumulation Index for major elements and trace metals in core collected from a. Mayem Lake (ML) and b. Selaulim Dam (SL), Goa-West coast of India

d. Pollution Load Index (PLI)

PLI values in ML and SL cores varied from 1.4 to 2.28 (2.20) and 1.47 to 4.36 (2.79) respectively. These results showed that ML and SL cores are polluted as PLI values are greater than 1. The down core variation of PLI (Fig. **4.2.3.d**) in ML and SL cores though showed a decreasing trend from bottom up to 2cm depth and thereafter showed a slight increasing trend up to the surface of the core, indicating high pollution in the in the past.

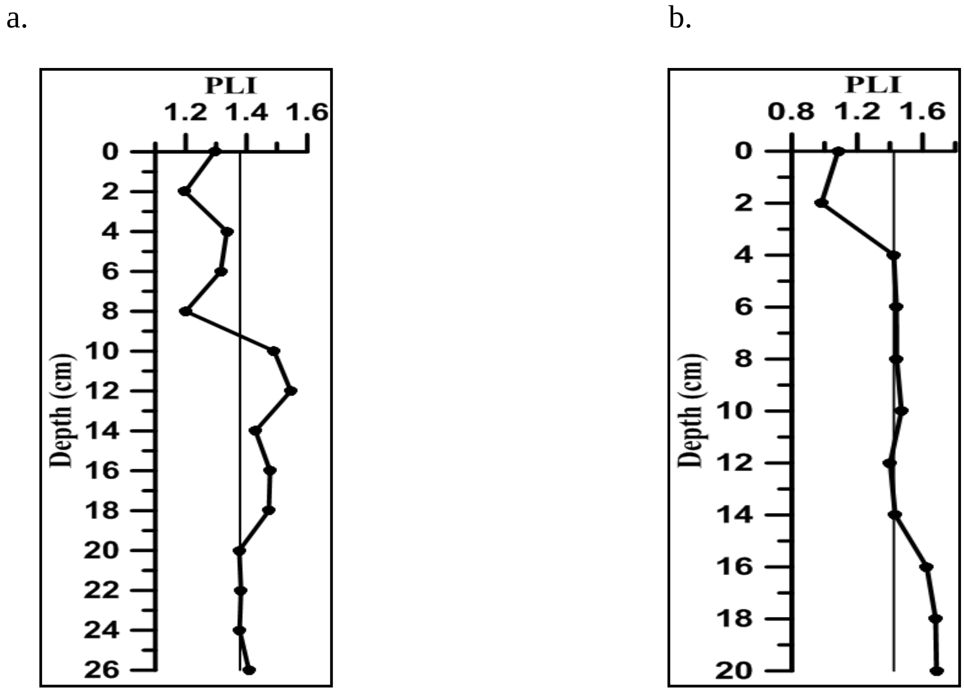


Fig. **4.2.3.d** Down core variation of PLI in sediment core of a. Mayem Lake (ML) and b. Selaulim Dam (SL) of Goa-West coast of India

4.2.4 Factor Analysis

A principal component analysis (PCA) was also performed to identify the relationships between variables (**Amor *et al.*, 2019**). In the present study, eigen values greater than 1 are selected. The varimax rotation has been employed to transform the analysis matrix and to limit the number of variables loaded in each factor. In ML core Factor 1 account for 38.22% of total variance. It showed significant strong positive loadings for Fe, OC, TP and Zn, which indicates that organic matter involved in accumulation and incorporation of these metals into sediments. Factor 2 in the core exhibits 21.11% of total variance, it showed significant strong positive loadings on silt. The total variance of 11.03 % is shown in Factor 3 that showed positive loading on sand indicating their lithogenic source. Factor 4 showed 8.83% total variance and did not show any loading (**Table 4.2.1.d)**. On the other hand, in SL core Factor 1 exhibited 34.95% of total variance with a strong positive loadings of silt, OC, TP, Mg and Zn indicating their common source of origin i.e with finer sediment /organic carbon. Factor 2 showed 19.56% of total variance, it showed significant positive loading on Cu and Co indicates its anthropogenic origin. Factor 3 accounts for 12.41% of total variance, it showed a strong positive loading on Fe and Pb indicating mining /terrigenous source, whereas factor 4 exhibits 11.73 % of total variance and did not show any loading. However, Factor 5 accounted for 10.01% of total variance and showed positive loading on for Ni indicating its anthropogenic source (**Table 4.2.1.d**). Rivers continuously receive trace amounts of heavy metals from terrigenous sources such as weathering of rocks. Continuous or intermittent but relatively higher input of heavy metals to rivers and streams is linked to anthropogenic sources such as urban and industrial waste water, fossil fuel combustion, and atmospheric deposition (**Sekabira et *al.*, 2010; Pandey *et al.*, 2013 and Singh and Pandey, 2014**).

Table 4.2.1.d Factor Analysis matrix after varimax rotation for core of a. Mayem Lake (ML) and b. Selaulim Dam (SL), Goa-West coast of India

a.

Parameters	Factor 1	Factor 2	Factor 3	Factor 4
sand	0.08	-0.36	**0.81**	0.18
silt	0.32	**0.81**	-0.34	0.13
clay	-0.40	**-0.75**	-0.01	-0.23
OC	**0.86**	0.25	0.08	-0.20
TP	**0.84**	0.48	0.11	0.08
Fe	**0.76**	-0.40	-0.08	0.12
Mn	0.03	0.11	0.07	0.67
Al	0.50	0.43	0.61	-0.17
Mg	0.01	**-0.91**	-0.04	-0.02
Cu	**-0.96**	-0.03	0.03	-0.08
Zn	**0.81**	0.41	-0.11	-0.35

Pb	0.60	0.11	-0.09	0.58
Ni	-0.52	0.27	0.69	-0.05
Cr	0.32	-0.23	0.01	-0.47
Co	-0.06	0.92	0.11	0.27
Expl.Var	4.86	3.97	1.67	1.40
Prp.Totl	0.32	0.26	0.11	0.09
% Total variance	38.22	21.11	11.03	8.83

b.

Parameters	**Factor 1**	**Factor 2**	**Factor 3**	**Factor 4**	**Factor 5**
sand	**-0.75**	-0.16	-0.39	0.34	-0.19
silt	**0.75**	0.08	0.34	-0.22	0.37
clay	-0.19	0.29	0.14	-0.44	-0.81
OC	**0.87**	-0.17	0.12	0.21	**0.08**
TP	**0.78**	0.47	-0.18	0.04	0.28
Fe	-0.02	-0.07	**0.95**	-0.12	0.17
Mn	0.43	0.39	0.48	0.52	-0.16
Al	0.06	-0.14	-0.01	**-0.97**	-0.06
Mg	**0.90**	-0.04	-0.22	-0.01	-0.23
Cu	0.19	**0.88**	-0.07	-0.09	0.09
Zn	**0.82**	0.17	0.28	0.11	0.36
Pb	0.17	-0.23	**0.83**	0.16	-0.11
Ni	0.15	0.17	0.11	-0.15	**0.85**
Cr	0.22	**-0.81**	0.24	-0.19	0.17
Co	0.12	**0.86**	0.02	0.11	0.06
Expl.Var	4.37	2.82	2.36	1.75	1.94
Prp.Totl	0.29	0.19	0.16	0.12	0.13
% Total variance	34.95	19.56	12.41	11.73	10.01

It is evident from the above observations on water reservoirs that the texture of sediment in ML reservoir is dominated by clayey silt whereas, SL is dominated by sandy silt. OC in both the reservoirs exhibited almost similar values. ML exhibited higher concentration of Fe, Zn and Ni which can be attributed to intensive mining activities at the vicinity of Mayem Lake. Whereas, SL exhibited high concentration of Mn, Al, Cu, Pb and Cr which is ascribed to anthropogenic activities. Pearson's correlation coefficients showed significant association of metals with finer sediments as well as organic carbon in both the cores indicating the influence of organic matter in trapping of metals. Enrichment factors showed Moderate enrichment for Fe and Pb in ML core and Mn and Pb in SL core. Enrichment of Fe and Mn was ascribed to mining dumps and runoff from the mining areas, whereas enrichment of Pb in the sediments was due to anthropogenic activities derived from combustion of fossil fuels in industries, in boat and other vehicles, and use of anti-fouling paints. Contamination factors and geo accumulation index also revealed that both the cores are highly contaminated with Pb due to anthropogenic activities which can be a threat to the aquatic life. Geo-accumulation index of metals indicated that ML core is moderately polluted with Pb and SL core with Pb and Co whereas both cores are unpolluted to moderately polluted by Fe and Mn which could be due to runoff from mining dumps, Vehicular emission and domestic sewage. The results of PLI studies indicated that ML and SL sediment cores are polluted. Factor analysis revealed that OC and texture of the sediment are the main factors influencing Zn and Pb concentrations in the two basins. While the major source of Mn in both the rivers comes from mining/ anthropogenic source, the main source for Al and Ni in the study region is identified as lithogenic origin. Copper in the study region is mostly derived from anthropogenic activities.

The distribution of major elements and trace metals in different water reservoirs follows the trend (decreasing)

Water Reservoir	Major elements	Trace metals
Mayem Lake (ML)	Fe > Al > Mn > Mg	Zn > Cr > Ni > Cu > Pb > Co
Selaulim Dam (SL)	Al > Fe > Mn > Mg	Cr > Zn > Cu > Pb > Co > Ni

Although the distribution trends for major elements and trace metals are different for ML and SL reservoirs. It is interesting to note that ML and SL water reservoirs registered highest concentrations of Fe and Al and lowest concentration of Mg and Mn. Relative high concentrations of Fe and Al can be attributed to terrigenous/anthropogenic sources of these metals. On the other hand trace metals registered highest concentrations of Zn and Cr in the study region and was attributed to anthropogenic input of the metals. The difference in the abundance of metals between ML and SL can be attributed to difference in geological terrain, physicochemical conditions of the water column and discharge of industrial and domestic sewage.

4.3 AGRICULTURAL FIELDS

Three sediment cores were collected from Mayem agricultural field (MF), Sanvordem agricultural field (SF) and Pernem agricultural field (PF) of Goa, West coast of India. The sediment components, the down core variation of different components, Organic Carbon (OC), Total Phosphorus (TP), major elements (Fe, Mn, Al, and Mg) and trace metals (Cu, Zn, Pb, Ni, Cr, and Co) have been reported.

4.3.1 Mayem Agricultural Field (MF)

4.3.1.1 Sediment components

The data on sand, silt, and clay (%) in MF core is presented in the table **(Table 4.3.1.a).** The MF core recorded the highest silt content (63.56) with a range of 2.58-32.05; moderate content of sand (23.87) that ranged from 46.54-84.87 and lower clay content (12.57) with a range of 8.54-23.34. Silt showed maximum values and sand showed minimum values at 8cm depth of the sediment core. Heavy rainfall during the monsoons leads to surface run-off of heavy metals and siltation in fields thereby causing huge agricultural losses. The state of Goa is the region of heavy monsoon, the deposition of silt and run-offs of overburden piled up at the various mining sites comes down in the agricultural fields during monsoon. The run-off from the mine dumps on the steep hills has created problems for the fertility of the soil (**Talule and Naik, 2014**). The core exhibits sandy silt type sediment texture (**Fig. 4.3.1.a)**. The downcore variation of sand showed a decreasing trend from the bottom up to 8cm depth and thereafter it showed an increasing trend up to the surface of the core. Distribution of silt compensates the variation of sand throughout the length of the core, whereas clay showed an irregular trend. The fine silt particles from the exposed overburdens and mines carried out along with run-off spread in the surrounding agricultural fields thereby affecting the low lying paddy fields.

Table 4.3.1.a Data on the sediment components, Organic Carbon (OC) and Total Phosphorus (TP) in sediment core of Mayem agricultural field (MF), Goa-West coast of India

Depth (cm)	Sand	Silt	Clay (%)	OC	TP
0	30.12	46.54	23.34	2.05	0.024
2	26.37	63.07	10.56	1.99	0.027
4	19.28	69.33	11.39	1.93	0.009
6	21.95	65.20	12.85	1.90	0.028
8	2.58	84.87	12.54	1.93	0.027
10	22.66	68.80	8.54	2.22	0.010
12	32.05	56.14	11.81	2.63	0.030
14	27.11	58.96	13.94	2.69	0.031
16	31.61	58.54	9.86	1.99	0.030
18	25.00	64.16	10.85	1.52	0.028
Avg	**23.87**	**63.56**	**12.57**	**2.09**	**0.024**
Min	2.58	46.54	8.54	1.52	0.009
Max	32.05	84.87	23.34	2.69	0.031

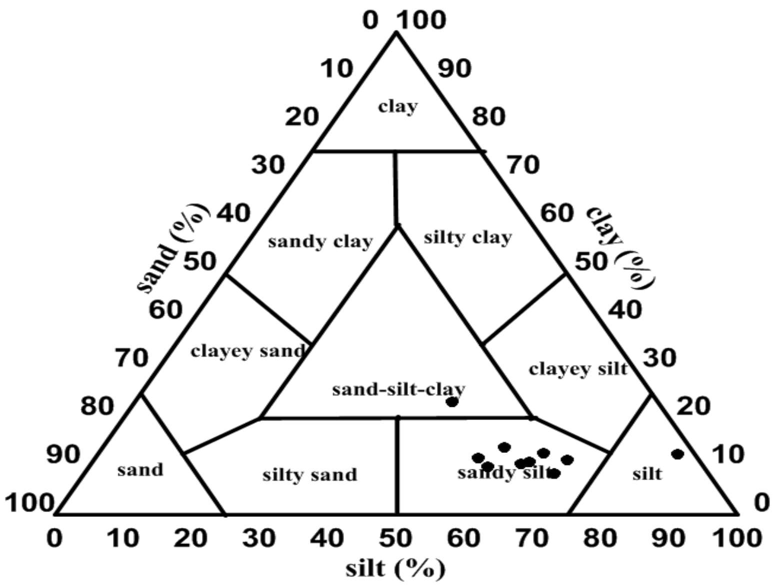


Fig. 4.3.1.a. Ternary diagram for sediment texture classification of the sediment core of Mayem agricultural Field (MF), Goa-West coast of India (**Pejrup, 1988**)

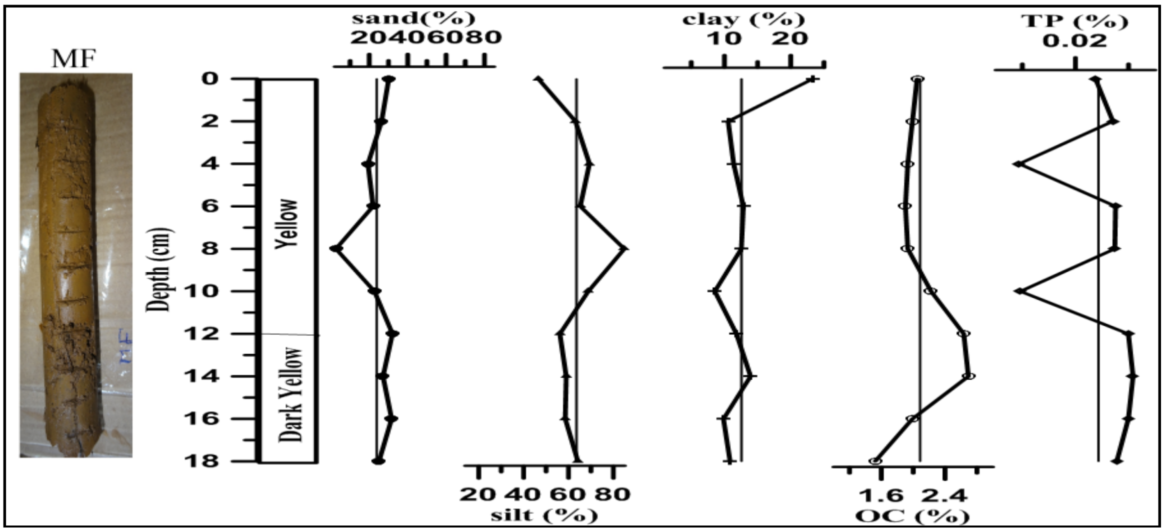


Fig. 4.3.1.b Down core variation of sand, silt, clay, Organic carbon (OC) and Total phosphorus (TP) in sediment core of Mayem agricultural Field (MF), Goa-West coast of India

4.3.1.2 Organic Carbon (OC)

OC (%) content in MF core varies from 1.52 to 2.69 with an average of 2.09 (**Table 4.3.1.a**). It showed higher concentration at 14cm depth of the sediment core. Relative high content of OC reflects the decrease of the soil grain size. The higher OC content was found in the sediments that had lower sand contents and the highest silt and clay contents (**Barkouch and Pineau, 2016**). The core showed yellow to dark yellow color indicating that organic material has been oxidized (**Daniels *et al.*, 2004**)The down core variation of OC showed an increasing trend from the bottom up to 14cm depth and thereafter it showed a decreasing trend up to the surface of the core (**Fig. 4.3.1.b**).

4.3.1.3 Total Phosphorus (TP)

TP (%) concentration in MF core ranged from 0.009-0.031 (0.024). At 4cm depth TP recorded minimum concentration (**Table 4.3.1.a).** Lower concentration of TP in the core may be due to less usage of phosphorous enriched fertilizer compounds (**Chahal *et al.*, 2014**). The down core variation of TP showed a slightly increasing trend from the bottom up to 14cm depth and thereafter it showed an irregular trend (**Fig. 4.3.1.b**).

Low phosphorus in soil may also be due to its presence in the insoluble state (**Yaseen *et al.*, 2015**).

4.3.1.4 Major Elements (Fe, Mn, Al and Mg)

The data on major elements (%) in MF sediment core is presented in the table (**Table 4.1.1.b.).** Fe (26.27) and Mn (0.78) showed higher average values that ranged from 20.14-32.79 and 0.51-1.10 respectively. Whereas, Al registered slightly higher values (9.61) with a range of 7.05-11.95 and lower average values are registered by Mg (0.96) that ranged from 0.51-2.21 when compared to average Shale values (**Turekian and Wedehpohl, 1961**). The values of Fe and Mn are in broad agreement with those reported by **Chahal *et al.*, (2014)** from Amritsar Punjab. The down core variation of Fe showed an irregular trend from the bottom up to the surface of the core. Mn and Al showed a sharp decreasing trend from the bottom up to the surface of the core. However, Mg showed similar values from bottom up to 12cm depth and thereafter it showed an irregular trend up to the surface of the core (**Fig. 4.3.1.c**). It is estimated that variation of Fe is randomly distributed over the core depth with varying concentrations and is correlated with the quantity of run-off and the deposition of soil layer which confirms that the concentration build-up in soil relates to proportional run-off during the monsoon season and also indicating the influence of mining dumps at the vicinity of it (**Fig. 4.3.1.d**). Mn concentration in the core was randomly distributed with a minimum (0.52) at 4cm depth and maximum (1.10) at 6cm depth of the core so; the similar pattern of the run-off was recorded in Fe concentration at 8cm depth. The core showed minimum variation in Al concentration close to the world's Shale value, the Al percentage variation at 14cm depth showed higher values than the normal variation (**Rane and Matta, 2019**). In general the distribution of major elements in MF core follows the order (decreasing) Fe > Al >Mg > Mn.

Table 4.3.1.b Data on major elements and trace metals in a sediment core of Mayem agricultural Field (MF), Goa-West coast of India

Depth (cm)	Major Elements (%)				Trace metals (µg g-1)					
	Fe	**Mn**	**Al**	**Mg**	**Cu**	**Zn**	**Pb**	**Ni**	**Cr**	**Co**
0	27.44	0.57	7.05	0.51	22.00	140.57	186.33	105.33	247.66	72.67
2	27.62	0.93	9.26	0.60	22.66	136.24	137.33	83.67	250.00	66.67
4	21.25	0.52	7.81	2.21	23.33	165.57	75.33	97.67	187.33	79.00
6	24.56	1.10	8.78	0.73	23.33	154.24	129.33	108.00	321.33	91.67
8	32.79	0.71	9.69	0.65	22.33	189.90	187.00	108.33	302.66	69.67
10	23.55	0.58	9.65	2.01	18.00	141.24	119.33	51.67	268.33	81.33
12	29.16	0.72	10.48	0.74	25.66	142.57	147.33	56.33	320.66	61.67
14	20.14	0.90	11.95	0.67	26.00	154.24	119.33	68.33	268.00	62.33
16	27.95	0.87	10.46	0.80	27.66	161.90	102.67	130.00	311.66	69.67
18	28.25	0.92	10.96	0.69	28.00	132.24	157.00	131.00	313.33	66.67
Avg	**26.27**	**0.78**	**9.61**	**0.96**	**23.90**	**151.87**	**136.10**	**94.03**	**279.10**	**72.13**
Min	20.14	0.52	7.05	0.51	18.00	132.24	75.33	51.67	187.33	61.67
Max	32.79	1.10	11.95	2.21	28.00	189.90	187.00	131.00	321.33	91.67
Std Dev	3.86	0.19	1.47	0.61	3.01	17.33	35.11	28.25	43.20	9.38
Avg Shale	4.72	0.08	8.0	1.5	45	95	20	68	90	19

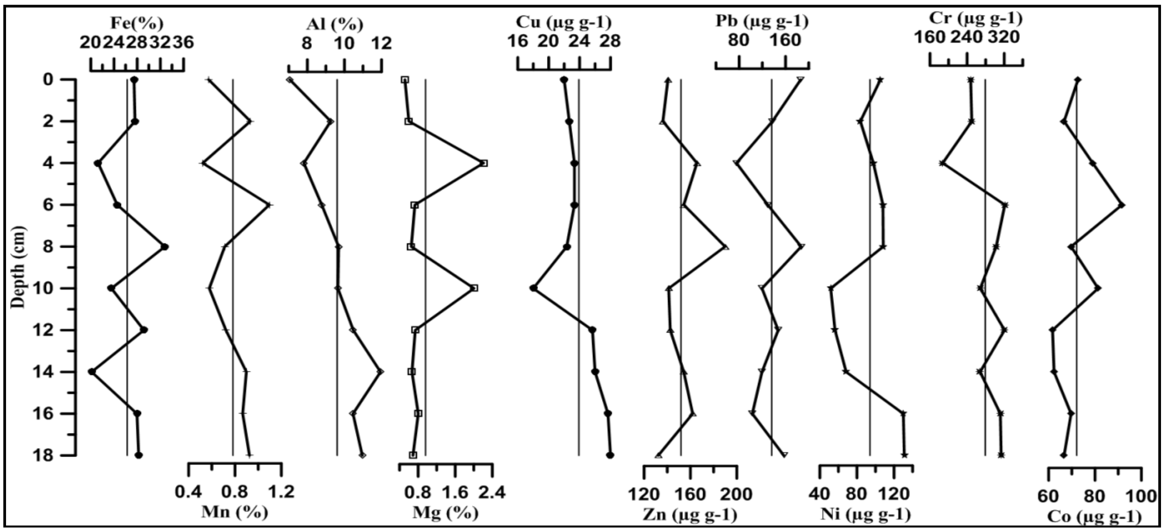


Fig. 4.3.1.c Down core variation of major elements (Fe, Mn, Al, and Mg) and trace metals (Cu, Zn, Pb, Ni, Cr, and Co) in sediment core of Mayem agricultural Field (MF), Goa-West coast of India

Fig 4.1.1.d Photograph showing exposed overburdens and mines on the slope above Mayem agricultural Field (MF), Goa-West coast of India

4.3.1.5 Trace Metals (Cu, Zn, Pb, Ni, Cr and Co)

Data on trace metals (µgg^{-1}) in MF core is presented in the table (**Table 4.3.1.c).** Zn values ranged from 132.24-189.90 (151.87); Pb 75.33-187.00 (136.10), Ni 51.67-131.00 (94.03), Cr 187.33-321.33 (279.10) and Co from 61.67-91.67 (72.13) in MF core recorded higher average concentrations, whereas Cu registered lower values (23.90) with a range of 18.00-28.00 as compared to average Shale values (**Turekian**

and Wedepohl, 1961). The values of Cu, Zn and Pb are in good agreement with those reported by **Chahal *et al.*, (2014)** from Amritsar, Punjab. About 60% of the total iron-ore reserves of Goa came from the Northern zone which included BicholimTaluka and Mayem lies in this taluka (**Kandrika and Dwivedi, 2003**). Heavy metals from mining sites may reach agricultural soils through leaching. Also during the rainy season, large quantities of tailing and waste containing heavy metals are carried by run-off to the agricultural fields near the mining sites which lead to the elevated levels of heavy metals in the soils (**Juwarkar *et al.*, 2004**). The high concentration of Zn in soil could be due to the use of chicken manure, fertilizers and metal-based pesticides (**Kayastha, 2014**). **Singh *et al.*, (2004**) have reported 3-15 fold higher concentration of Pb in wastewater irrigated area. A higher concentration of Cr may be due to high cation exchange capacities of manganese oxides that act as strong scavengers for heavy metals such as Cr (**Bartlett, 1991 and Kim and Dixon, 2002**). Major sources of Ni in the soil was attributed to wastewater that is discharged from ceramics, steel and alloys and other metal processing industries (**Mondol *et al.*, 2011**). Mine tailing indiscriminately dumped become materials for soil formation which on weathering releases into soils the composing metals with levels depending on the total metal concentration, speciation, geochemical characteristics, and mineralization. (**Jung, 2001; Ezeh and Chukwu, 2011 and Jian-Min *et al.*, 2007**). **Zhou *et al.*, (2007)** reported the presence of Cu, Zn, and Pb from mine tailings that contributed levels as high as 567, 1140, and 191 $\mu g g^{-1}$ respectively to the soil. Weathering also leads to oxidation of sulfide-bearing minerals which cause acid mine drainage (AMD) characterized by the release of metals leading to a high concentration of heavy metals, acidity, and salinity of soil in agricultural lands in mining sites. The down core variation of Cu, Ni and Cr showed a decreasing trend from the bottom up to the surface of the core, whereas Zn, Pb, and Co exhibited an irregular trend (**Fig. 4.3.1.c)**. In general the distribution of trace metals in MF core follows the order (decreasing) Cr > Zn > Pb > Ni > Co > Cu.

4.3.1.6 Pearson's Correlation

The data on Pearson's Correlation in MF core is presented in the table (**Table 4.3.1.c**.). Silt showed a positive correlation with Zn indicating its association with finer sediments (**Abílio *et al*., 2006**). TP showed a positive correlation coefficient with Mn, Mg, Cu, and Cr indicating that they have a common source of origin i.e anthropogenic source. Fe showed a significant positive correlation indicating their common association. The Fe-oxyhydroxide phase is a good scavenger of Pb and it is one of the major controlling factors for its distribution in the sediment cores. OC and Metals such as Al, Ni, Co did not show any significant correlation.

Table 4.3.1.c Data on Pearson's correlation between different sediment components (sand, silt, clay), OC, TP, major elements (Fe, Mn, Al, and Mg) and trace metals (Cu, Zn, Pb, Ni, Cr, and Co) in sediment core of Mayem agricultural Field (MF), Goa-West coast of India (n=9)

Param	**sand**	**silt**	**clay**	**OC**	**TP**	**Fe**	**Mn**	**Al**	**Mg**	**Cu**	**Zn**	**Pb**	**Ni**	**Cr**	**Co**
sand	1.00														
silt	**-0.92**	1.00													
clay	0.15	-0.54	1.00												
OC	0.32	-0.31	0.08	1.00											
TP	0.21	-0.25	0.17	0.14	1.00										
Fe	-0.27	0.21	0.05	-0.32	0.45	1.00									
Mn	0.14	-0.03	-0.23	-0.15	**0.70**	0.05	1.00								
Al	0.12	0.10	-0.50	0.35	0.51	-0.01	0.46	1.00							
Mg	-0.17	0.31	-0.41	-0.02	**-0.93**	-0.54	-0.60	-0.27	1.00						
Cu	0.36	-0.27	-0.09	-0.07	**0.67**	0.12	0.49	0.54	-0.46	1.00					
Zn	**-0.74**	**0.66**	-0.07	-0.03	-0.01	0.18	-0.15	-0.04	0.10	-0.04	1.00				
Pb	-0.24	-0.01	0.54	-0.13	0.43	**0.72**	0.01	-0.09	**-0.66**	-0.10	-0.04	1.00			
Ni	-0.15	0.07	0.14	**-0.80**	0.28	0.35	0.31	-0.15	-0.31	0.49	0.24	0.14	1.00		
Cr	0.05	0.03	-0.20	-0.01	**0.68**	0.54	0.59	0.54	-0.58	0.40	-0.01	0.39	0.20	1.00	
Co	-0.25	0.23	-0.04	-0.37	-0.52	-0.31	0.01	-0.56	0.45	-0.51	0.13	-0.27	0.12	-0.11	1.00

4.3.2 Sanvordem Agricultural Field (SF)

4.3.2.1 Sediment Components

The data on the sand, silt, and clay (%) of the SF core is presented in the table (**Table 4.3.2.a.).** SF core recorded higher average values for sand 63.49-77.59 (70.16); moderate silt 17.34-29.19 (23.50) and lower values of clay 2.59-9.70 (6.31). It is interesting to note that at 14 cm depth sand registered higher values and silt showed lower values. The core exhibited a silty sand type of texture (**Fig. 4.3.2.a).** Down core variation of sand showed an increasing trend from the bottom up to the surface of the core, whereas the distribution of silt compensates the variation of sand throughout the length of the core and clay showed an irregular trend (**Fig. 4.3.2.b**).

Table 4.3.2.a Data on the sediment components, Organic Carbon (OC) and Total Phosphorus (TP) in sediment core of Sanvordem agricultural Field (SF), Goa-West coast of India

Depth (cm)	**Sand**	**Silt**	**Clay (%)**	**OC**	**TP**
0	67.59	27.32	5.09	1.01	0.025
2	65.13	28.44	6.43	0.59	0.014
4	70.56	23.10	6.34	0.41	0.012
6	72.72	17.58	9.70	0.38	0.012
8	71.26	26.15	2.59	0.32	0.013
10	71.46	20.92	7.62	0.29	0.013
12	72.02	21.95	6.03	0.41	0.012
14	77.59	17.34	5.07	0.35	0.012
16	69.80	22.98	7.22	0.35	0.011
18	63.49	29.19	7.33	0.32	0.003
Avg	**70.16**	**23.50**	**6.34**	**0.44**	**0.013**
Min	63.49	17.34	2.59	0.29	0.003
Max	77.59	29.19	9.70	1.01	0.025

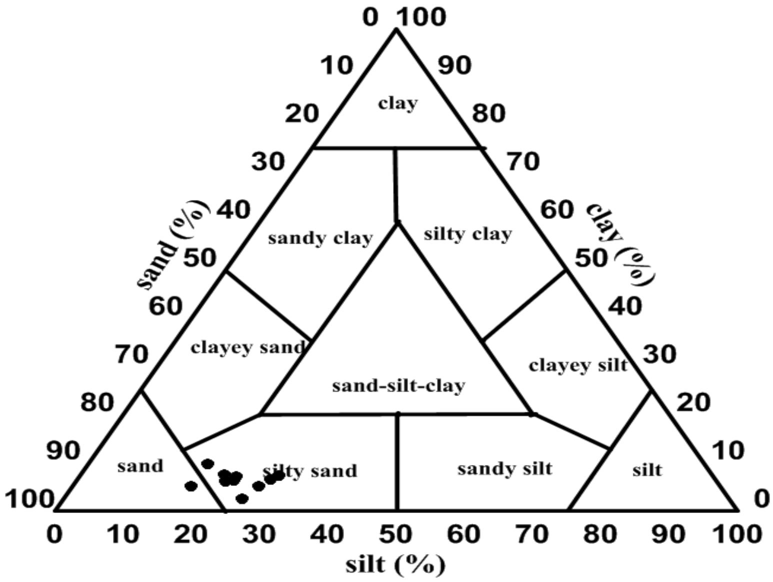


Fig. 4.3.2.a. Ternary diagram for sediment texture classification of the sediment core for Selaulim Dam (SF), Goa-west coast of India (**Pejrup, 1988**)

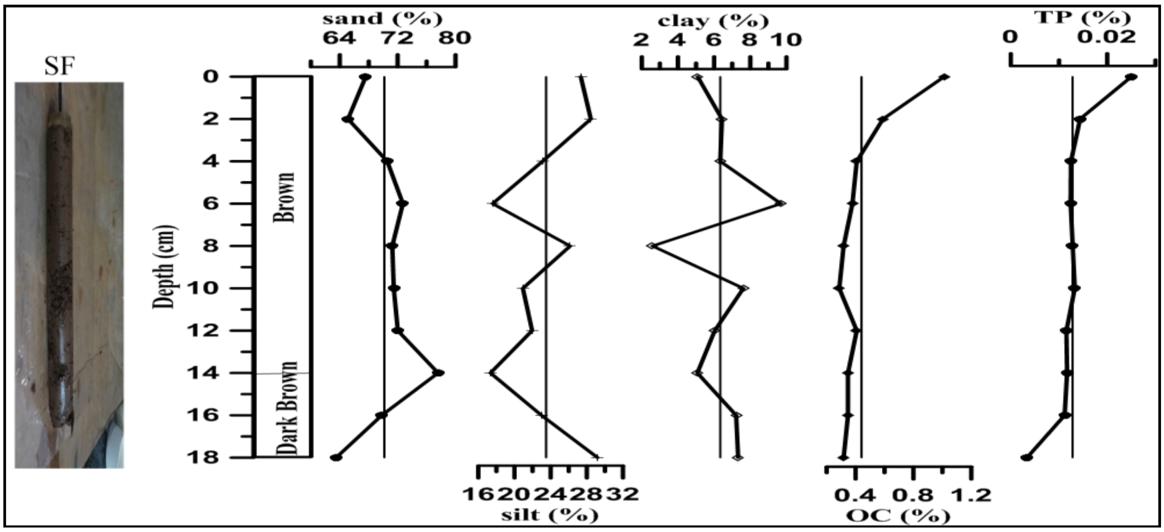


Fig. 4.3.2.b Down core variation of sand, silt, clay, Organic Carbon (OC) and Total Phosphorus (TP) in a sediment core of Sanvordem agricultural Field (SF), Goa-West coast of India

4.3.2.2 Organic Carbon (OC)

OC content (%) of core (**Table 4.3.2.a)** ranges from 0.23–1.01(0.40%). OC showed higher concentration at the surface of the core. The average percentage of OC is low and it is supported by brown color of the core indicating that the sediments have been deposited in oxidizing environment (**Daniel *et al.*, 2004**). If OC level in sediment is greater than 0.8% it is rated as good quality of soil (**Saxena, 1987**) and if a level of OC is greater than 0.75% it indicates good fertility (**Ghosh *et al.*, 1983**). Soil texture affects OC because of the stabilizing properties that clay has on organic matter (**Yaseen *et al.*, 2015**). A small difference in clay percentage may result minimal differences in OC concentration in the soil (**Chodak and Niklinska, 2012**), variations of OC depends upon land use, soil type and terrain (**Han *et al.*, 2010**), which have a great impact on soil nutrient status (**Wong, 2003**). OC in association with primary soil particles is considered to be a reliable indicator for monitoring soil quality and land degradation (**Rajan *et al.*, 2010**). The down core variation of OC showed an increasing trend from the bottom up to the surface of the core (**Fig. 4.3.2.b)**.

4.3.2.3 Total Phosphorus (TP)

TP (%) in the SF core is presented in the table (**Table 4.3.2.a.)**. The core recorded lower concentrations (0.013) of TP that ranged from 0.003-0.025, that may due to the fact that the phosphate ion is extremely reactive, and therefore tends to form insoluble or slightly soluble compounds if a suitable counter ion is available (**Sharpley, 1995**). TP recorded almost same concentration throughout the length of the core. Most TP in the soil is in the particulate form, as precipitates of iron, aluminum or calcium phosphates, bound to soil minerals (clay, calcite, aluminum hydroxides, etc.), or occluded within soil granules (**Wang *et al.*, 2010**). A significant portion of P losses can be in the dissolved form (**Baker *et al.*, 2007)** The down core variation did not show any trend in the core except at the bottom and the surface, where it showed an increasing trend (**Fig. 4.3.2.b**).

4.3.2.4 Major Elements (Fe, Mn, Al and Mg)

The data on concentration and average values of major elements (%) in SF sediment core are presented in the table (**Table 4.3.2.b).** It is found that the average concentration of Fe in the core is 8.83 with the variation in the concentration over the core depth is from 6.13-11.21; Mn concentration varied from 0.02-0.09 (0.07); Al showed variation from 5.81-8.96 (7.42) and Mg registered an average value of 0.57 that varied from 0.46-1.01. Fe showed higher concentration at 8cm and Mn, Al and Mg at the surface of the sediment core. The values of Mn are in broad agreement with those reported by **Ratnakar and Shikha, (2018)** from Lucknow, Uttar Pradesh. Fe showed higher concentration indicating the influence of iron ore transportation through trucks via the road at the vicinity of the agricultural land. The spilled off ore gets washed into the agricultural land during the monsoon. However, Mn, Al, and Mg registered lower values than average Shale values (**Turekian Wedepohl, 1961**). The down core variation of Fe, Mn, Al, and Mg showed an increasing trend from the bottom up to the surface of the core (**Fig. 4.3.2.c**). In general the distribution of major elements in sediment core followed the (decreasing) order Fe > Mn > Al >Mg.

Table 4.3.2.b Data on major elements and trace metals in a sediment core of Sanvordem agricultural Field (SF), Goa-West coast of India

Depth (cm)	**Major Elements (%)**				**Trace metals (µg g-1)**					
	Fe	**Mn**	**Al**	**Mg**	**Cu**	**Zn**	**Pb**	**Ni**	**Cr**	**Co**
0	9.63	0.09	8.96	1.01	32.00	87.24	66.00	31.00	215.00	28.33
2	9.69	0.08	5.97	0.58	21.66	82.90	63.33	21.33	209.00	41.33
4	7.56	0.08	8.63	0.72	23.00	91.90	79.33	34.00	199.66	42.67
6	10.73	0.09	8.82	0.54	31.66	89.24	45.67	42.00	208.00	39.00
8	11.21	0.08	7.89	0.52	30.00	99.90	34.00	47.33	145.67	39.00
10	6.13	0.05	6.92	0.47	11.66	53.90	57.67	27.00	138.33	51.67
12	8.72	0.02	6.82	0.46	11.66	42.57	59.33	35.00	140.33	29.67
14	7.63	0.05	7.66	0.51	8.33	37.90	64.00	45.67	146.00	39.67
16	8.76	0.04	5.81	0.49	11.33	32.90	64.67	40.33	180.33	32.67
18	8.25	0.07	6.75	0.46	19.00	38.90	66.00	26.33	207.00	34.00
Avg	**8.83**	**0.07**	**7.42**	**0.57**	**20.03**	**65.74**	**60.00**	**35.00**	**178.93**	**37.80**
Min	6.13	0.02	5.81	0.46	8.33	32.90	34.00	21.33	138.33	28.33
Max	11.21	0.09	8.96	1.01	32.00	99.90	79.33	47.33	215.00	51.67
Std Dev	1.54	0.03	1.15	0.17	9.09	26.69	12.39	8.73	32.66	6.92
Avg Shale	4.72	0.08	8.0	1.5	45	95	20	68	90	19

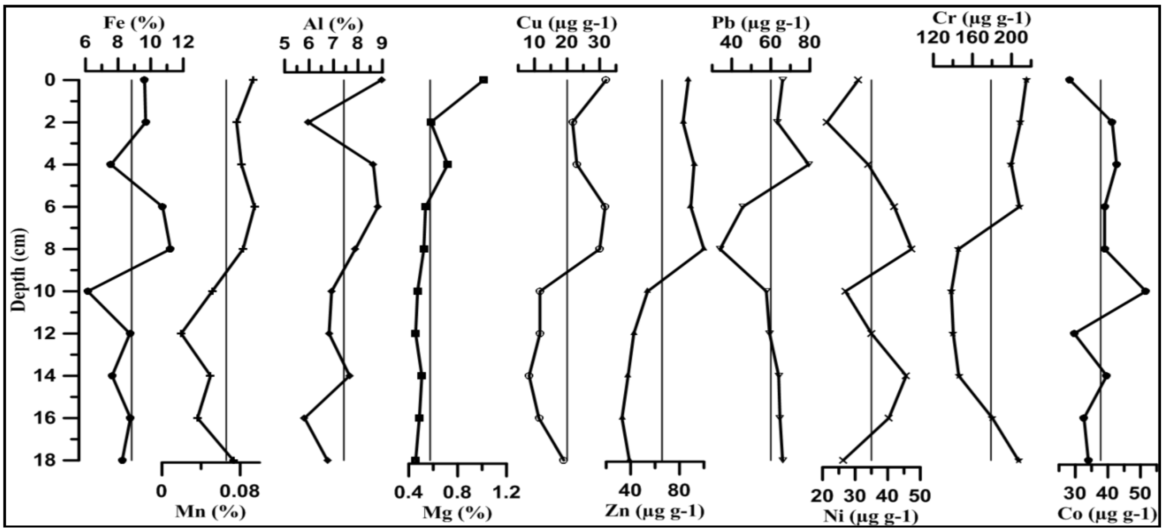


Fig. 4.3.2.c Down core variation of major elements (Fe, Mn, Al, and Mg) and trace metals (Cu, Zn, Pb, Ni, Cr, and Co) in sediment core of Sanvordem agricultural Field (SF), Goa-West coast of India

4.3.2.5 Trace Metals (Cu, Zn, Pb, Ni, Cr and Co)

Data on concentration and average of trace metals (μgg^{-1}) Cu, Zn, Pb, Ni, cr ans Co in SF core is presented in the table (**Table 4.3.2.b).** Higher average concentration is shown by Pb that ranged from 34.00-79.33(60.00); Cr 138.33-215.00 (136.00), and Co 28.33-51.67 (72.13), whereas, Cu ranged from 8.33-32.00 (20.00); Zn 32.90-99.90 (65.74) and Ni 21.33-47.33 (35.00) registered lower average concentrations as compared to average Shale values (**Turekian and Wedepohl, 1961**). Cu and Cr showed higher concentration at the surface of the core, Zn and Ni showed at 8cm, Pb showed at 4cm and Co at 10cm depth of the sediment core. The values of Zn, Ni and Pb are in good agreement with those reported by **Kayastha, (2014)** from Nepal. Heavy metals from mining sites may reach agricultural soils through leaching. Also during the rainy season, large quantities of mine tailing and waste containing heavy metals are carried by runoff to the agricultural fields near the mining sites which lead to the elevated levels of heavy metals in the soils (**Juwarkar *et al.*, 2007**). Iron ore mines act as an important source of metals; mainly Fe and Mn, and also, contributes for trace metals into the environment (**Yellishettya *et al.*, 2008: Xu *et al.*, 2006 and Zang and Liu, 2000**). A higher concentration of Pb may be due to aerial emission from the combustion of petrol containing tetraethyl lead; this contributes substantially to the content of Pb in soils in urban areas and in those adjacent to major roads (**USEPA Report, 1996**). A higher concentration of Cr may be due to its use to protect the wood from decay or fungi and termites (**Hingston, 2001**). It is also used in manufacturing leather goods, paint, cement, mortar, and anti-corrosives (**Thor *et al.*, 2011**). Co may probably be due to availability of Mn and Fe which is more affected by oxidation and reduction than that of other trace elements, but reduction caused by high moisture content or flooding can increase the availability of S, Cu, Mo, Ni, Zn, Pb, V and Co (**Mitchell *et al.*, 1963)**. An application of cobalt chloride ($CoCl_2.6H_20$) to the soil may increase the Co content in sediment and the residual effect of Co on fertilization was also reported (**Rossiter *et al.*, 1948**). Cu and Zm showed an increasing trend from bottom upto the surface of the core, Pb and Cr showed a decreasing trend from bottom upto 8 cm depth and thereafter it showed an increasing trend upto the surface of the core, whereas Ni and Co showed an irregular trend from botoom of upto the surface of the core (**Fig. 4.3.2.c**). In general the distribution of trace metals in sediment core followed the order (decreasing) Cr > Pb > Co > Zn > Ni > Cu.

4.3.2.6 Pearson's Correlation Coefficient

A correlation coefficient of metals in the SF core is presented in the table (**Table 4.3.2.c**). Mg showed a significant positive correlation with TP and OC indicating that they have a common source of origin i.e biogenic source. On the other hand, Cu showed a significant positive correlation with Fe, Mn, Al, and Zn indicating that their common source of origin i.e terrigenous. Cr showed a significant positive correlation with Mn indicating that their common source of origin i.e anthropogenic. It is interesting to note that Pb, Ni, and Co did not show any correlation indicating that they have different modes of deposition metals.

Table 4.3.2.c Data on Pearson's correlation between different sediment components (sand, silt, clay), OC, TP, major elements (Fe, Mn, Al, and Mg) and trace metals (Cu, Zn, Pb, Ni, Cr, and Co) in sediment core of Sanvordem agricultural Field (SF), GoaWest coast of India (n=9)

Param	**sand**	**silt**	**clay**	**OC**	**TP**	**Fe**	**Mn**	**Al**	**Mg**	**Cu**	**Zn**	**Pb**	**Ni**	**Cr**	**Co**
sand	1.00														
silt	**-0.90**	1.00													
clay	-0.12	-0.33	1.00												
OC	-0.33	0.40	-0.20	1.00											
TP	0.07	0.06	-0.28	**0.84**	1.00										
Fe	-0.15	0.24	-0.23	0.27	0.23	1.00									
Mn	-0.31	0.30	-0.01	0.40	0.32	0.48	1.00								
Al	0.31	-0.25	-0.10	0.35	0.46	0.24	**0.64**	1.00							
Mg	-0.21	0.30	-0.23	**0.90**	**0.83**	0.18	0.56	0.61	1.00						
Cu	-0.31	0.33	-0.10	0.48	0.44	**0.73**	**0.89**	**0.66**	0.59	1.00					
Zn	-0.11	0.21	-0.23	0.38	0.51	0.57	**0.81**	0.63	0.54	**0.87**	1.00				
Pb	-0.24	0.13	0.21	0.26	0.01	-0.63	-0.16	-0.11	0.32	-0.36	-0.31	1.00			
Ni	**0.75**	-0.57	-0.31	-0.32	-0.04	0.35	-0.07	0.35	-0.16	0.05	0.04	-0.49	1.00		
Cr	**-0.64**	0.44	0.38	0.53	0.17	0.31	**0.67**	0.23	0.53	0.58	0.37	0.37	-0.41	1.00	
Co	0.23	-0.30	0.18	-0.47	-0.16	-0.43	0.11	-0.03	-0.30	-0.16	0.18	-0.08	-0.14	-0.28	1.00

4.3.3 Pernem Agricultural Field (PF)

4.3.3.1 Sediment Components

The data on the sand, silt, and clay (%) of the PF core is presented in the table (**Table 4.3.3.a).** The PF core recorded higher values of sand (66.39) that range from 42.94-84.09; moderate silt (28.25) which ranged from 14.05-52.37 and lower values of clay (5.35) that varied from 1.86-7.97. It is interesting to note that sand recorded lower concentration at the bottom while it exhibited higher concentration at the surface of the core. The down core variations from the bottom up to 8cm depth the core exhibited silty sand and from 8cm up to the surface of it exhibited the sand type of texture (**Fig. 4.3.3.a.)**. Down core variation of sand showed an increasing trend from the bottom up to the surface of the core, whereas silt compensates sand throughout the length of the core, clay showed an irregular trend from the bottom up to the surface of the core (**Fig. 4.3.3.b)**.

Table 4.3.3.a Data on the sediment components, Organic Carbon (OC) and Total Phosphorus (TP) in sediment core of Pernem agricultural Field (PF), Goa-West coast of India

Depth (cm)	**Sand**	**Silt**	**Clay (%)**	**OC**	**TP**
0	80.54	14.35	5.10	1.29	0.023
2	84.09	14.05	1.86	1.29	0.021
4	76.35	18.26	5.39	1.26	0.018
6	74.01	20.06	5.94	1.24	0.024
8	69.73	23.15	7.12	1.29	0.022
10	67.28	29.15	3.57	1.29	0.024
12	59.72	32.31	7.97	1.24	0.022
14	64.00	31.59	4.42	1.21	0.022
16	45.25	47.17	7.58	1.18	0.022
18	42.94	52.37	4.69	1.15	0.023
Avg	**66.39**	**28.25**	**5.36**	**1.24**	**0.022**
Min	42.94	14.05	1.86	1.15	0.018
Max	84.09	52.37	7.97	1.29	0.024

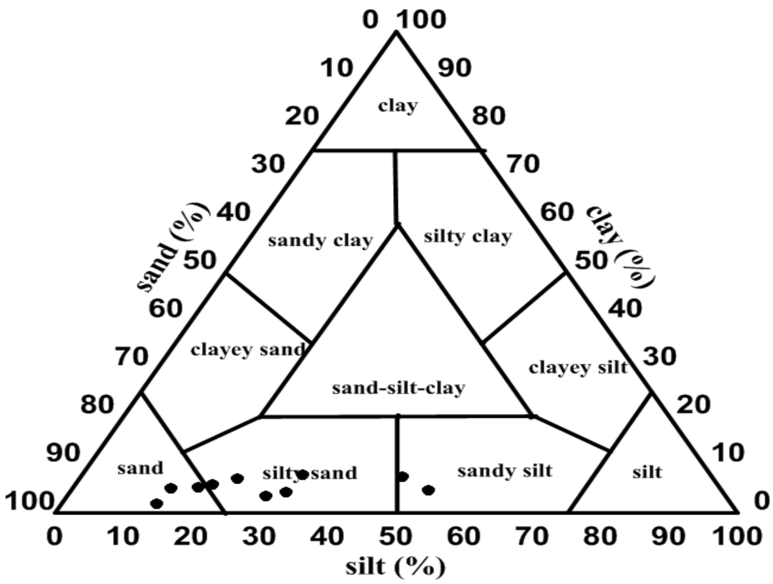


Fig. 4.3.3.a. Ternary diagram for sediment texture classification of the core for Pernem agricultural Field (PF), Goa-West coast of India (**Pejrup, 1988**)

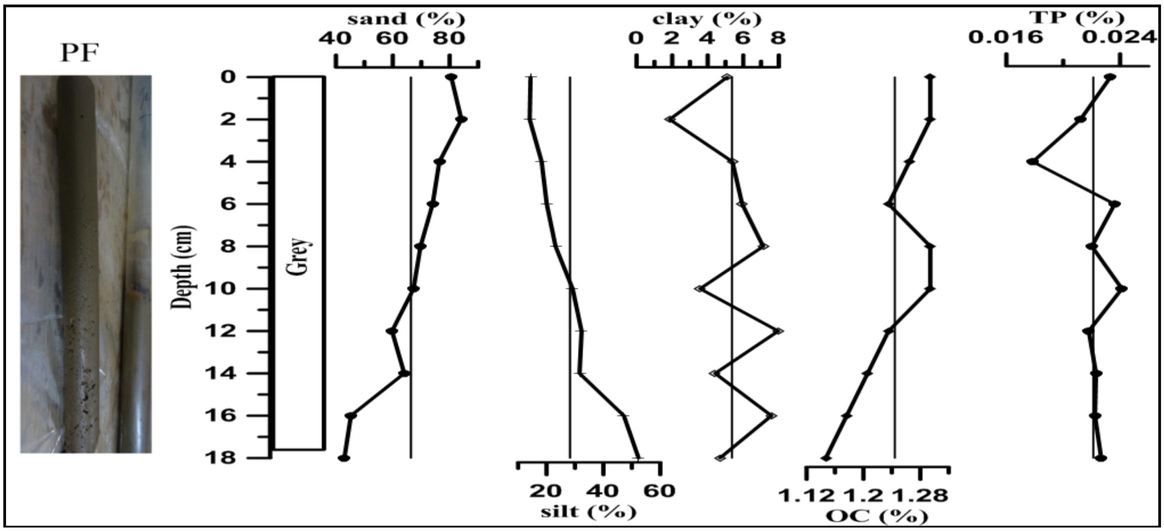


Fig. 4.3.3.b Down core variation of sand, silt, clay, Organic Carbon (OC) and total phosphorus (TP) in a sediment core of Pernem agricultural Field (PF), Goa-West coast of India

4.3.3.2 Organic Carbon (OC)

OC (%) in the PF core is presented in the table (**Table 4.3.3.a.).** It ranged from from1.09-1.29 (1.22). It showed higher concentrations at top 4cm depth of the sediment core. The down core variation showed an increasing trend from the bottom up to the surface of the core (**Fig. 4.3.3.b**). This may probably be due to the higher amount of humic substances present in the sediments by decomposition of garbage wastes dumped on the soil and also due to the addition of domestic wastes. This is also supported by Grey color of the core. Soil texture affects Soil Organic Carbon (SOC) because of the stabilizing properties that clay has on organic matter (**Yaseen *et al.,* 2015**).

4.3.3.3 Total Phosphorus (TP)

Data on TP (%) in PF core varied from 0.018-0.024 with an average of 0.022 **(Table 4.3.3.a).** Most of the sediment samples in the core showed almost similar values (0.02 %). Lower values of TP in sediment samples maybe because of less usage of phosphorous enriched fertilizer compound to the soil and also due to its presence in an insoluble state or due to lack of organic matter in the soil (**Yaseen *et al.,* 2015**). The down core variation of OC from the bottom up to 12cm depth and from 12cm up to 4cm showed an irregular trend and thereafter up to the surface of the core it exhibited an increasing trend (**Fig. 4.3.3.b)**.

4.3.3.4 Major Elements (Fe, Mn, Al and Mg)

The data on concentration and average values of major elements in PF core is presented in table (**Table 4.3.3.b)** The average concentration of Fe (%) in the PF core varied from 0.12-0.22 (0.17%); Mn from 0.12-0.20(0.16%); Al from 7.79-11.18 (9.93) and Mg registered values between 1.12-1.83 with an average of 1.52. Fe and Al showed higher concentration at the surface, Mn showed at 6cm and Mg showed at the bottom of the core. Mn registered higher values, Fe and Al showed comparatively lower values compared to average shale values (**Turekian and Wedehpohl, 1961**). While Mg showed values similar to shale values. The values of Fe and Mn are in broad agreement with those reported by **Lokhande *et al.,* (2014)** from Bharitola. The down core variation of Fe and Mg showed a decreasing trend from the bottom up to 4cm depth and thereafter it showed an increasing trend up to the surface of the core. Whereas, Mn showed an increasing trend from the bottom up to 6cm depth and thereafter it showed a decreasing trend up to the surface of the core. However, Al showed a decreasing trend from the bottom up to 8cm and thereafter it exhibited an increasing trend up to the surface of the core. Mg showed a decreasing trend from the bottom up to 4cm depth and thereafter it exhibited an increasing trend (**Fig. 4.3.3.c**). In general the distribution of major elements in sediment core followed the (decreasing) order Al > Mg > Fe > Mn.

Table 4.3.3.b Data on major elements and trace metals in a sediment core collected from Pernem agricultural Field (PF) Goa, India

Depth (cm)	**Major Elements (%)**				**Trace metals (μg g-1)**					
	Fe	**Mn**	**Al**	**Mg**	**Cu**	**Zn**	**Pb**	**Ni**	**Cr**	**Co**
0	0.20	0.15	8.30	1.79	51.33	101.33	39.00	105.00	74.00	46.33
2	0.17	0.14	7.61	1.31	44.33	92.67	38.67	80.67	70.67	35.00
4	0.12	0.15	7.85	1.12	22.33	64.67	32.67	98.33	90.00	54.33
6	0.15	0.20	6.99	1.47	52.00	97.00	38.00	81.00	73.33	45.00
8	0.17	0.17	6.76	1.46	124.00	94.00	35.00	78.67	89.33	42.00
10	0.17	0.17	7.54	1.56	55.00	93.00	26.33	77.00	71.33	63.67
12	0.16	0.16	7.79	1.47	48.00	82.33	17.33	75.33	71.00	42.00
14	0.16	0.14	7.63	1.56	49.00	112.67	33.67	79.33	72.33	41.00
16	0.18	0.16	6.96	1.69	47.67	92.33	34.33	82.67	79.67	34.33
18	0.19	0.12	7.41	1.83	50.00	95.33	32.67	77.33	86.67	51.67
Avg	**0.17**	**0.16**	**7.48**	**1.52**	**54.37**	**92.53**	**32.77**	**83.53**	**77.83**	**45.53**
Min	0.12	0.12	6.76	1.12	22.33	64.67	17.33	75.33	70.67	34.33
Max	0.20	0.20	8.30	1.83	124.00	112.67	39.00	105.00	90.00	63.67
Std Dev	0.02	0.02	0.47	0.21	26.09	12.44	6.57	9.92	7.94	8.99
Avg Shale	4.72	0.08	8.0	1.5	45	95	20	68	90	19

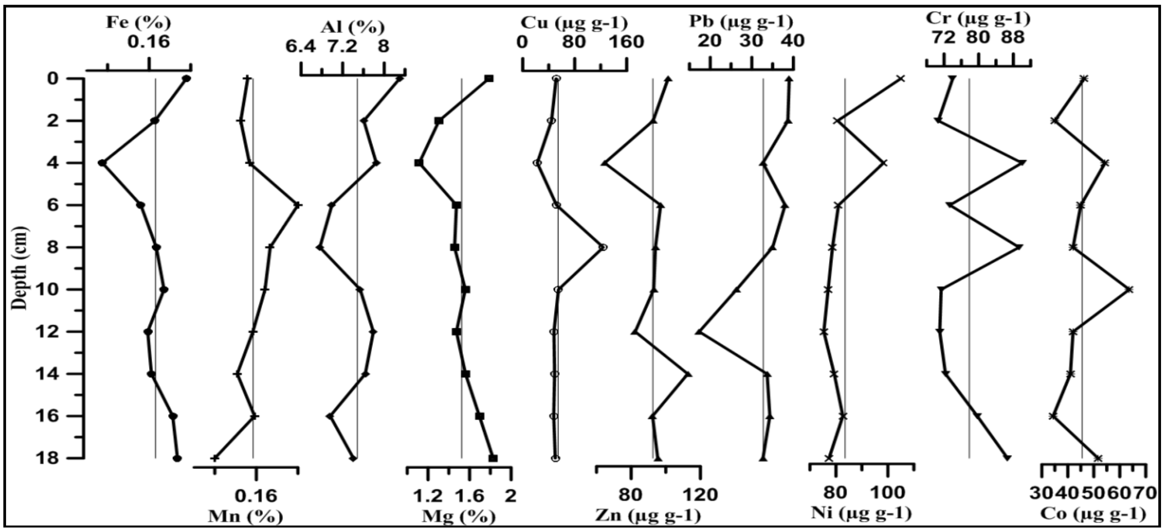


Fig. 4.3.3.c Down core variation of major elements (Fe, Mn, Al, and Mg) and trace metals (Cu, Zn, Pb, Ni, Cr, and Co) in sediment core of Pernem agricultural Field (PF) Goa, India

4.3.3.5 Trace Metals (Cu, Zn, Pb, Ni, Cr and Co)

Data on trace metals (µgg^{-1}) in PF core is presented in the table (**Table 4.3.3.b).** The concentration of Cu in the core varied from 22.33-124.00 (53.78); Zn from 64.67-112.67(93.22); Concentration of Pb varied from 17.33-99.33 (63.69%); Ni ranged from 112.67-181.00 (156.75); Cr varied from 187.33-321.33 (279.10) and Co ranged from 34.33-63.67 (45.53). Except for Zn and Cr, all trace metals in the PF core showed higher values as compared to average shale values (**Turekian and Wedepohl, 1961**). Cu showed higher concentration at 8cm, Zn showed at 14cm, Pb and Ni showed at the surface of the core, Cr showed at 4cm and Co showed at 10cm depth of the sediment core. The values of Cu, Zn, Pb, Cr and Co are in broad agreement with those reported by **Krailertrattanachai *et al.,* (2019)** from Thailand**.** Soil contamination with metals could be mainly due to wastewater irrigation, application of sludge, chicken manure, diammonium phosphate (DAP), urea and pesticides in the farmland (**Kayastha 2014**). The road surface runoff water also contains Cu and Pb, which can accelerate contamination of these metals in the roadside areas (**Ignatavicius *et al.,* 2017 and Ghosh and Maiti, 2018**). The down core variation of Cu did not show any trend except at 8cm depth where it showed an increased peak; Zn and Co showed an irregular trend; Pb showed a decreasing trend from bottom up to 12cm depth and thereafter it showed an increasing trend; whereas

Ni did not show any trend from bottom up to 6cm depth and thereafter it showed an irregular trend. However, Cr showed a decreasing trend from the bottom up to 10cm depth and thereafter it showed an irregular trend. However, a significant rise in the concentration of all trace metals except Cr in PF core may probably be due to excessive runoff and soil deposition (**Fig. 4.3.3.c**.). In general the distribution of trace metals in sediment core followed the (decreasing) order Zn > Ni > Cr > Cu > Co > Pb.

4.3.3.6 Pearson's Correlation Coefficient

The correlation coefficient in the PF core is presented in the table (**Table 4.3.3.c**). Sand showed a positive correlation with OC; whereas Fe showed a good positive correlation with TP, Mg, and Zn. indicating their common source of origin. On the other hand, Al, Pb, Cu, Ni, Cr, and Co did not show any significant correlation indicating that they are derived from different modes of origin.

Table 4.3.3.c Data on Pearson's correlation between different sediment components (sand, silt, clay), OC, TP, major elements (Fe, Mn, Al, and Mg) and trace metals (Cu, Zn, Pb, Ni, Cr, and Co) in sediment core of Pernem agricultural field (PF) Goa, India (n=9)

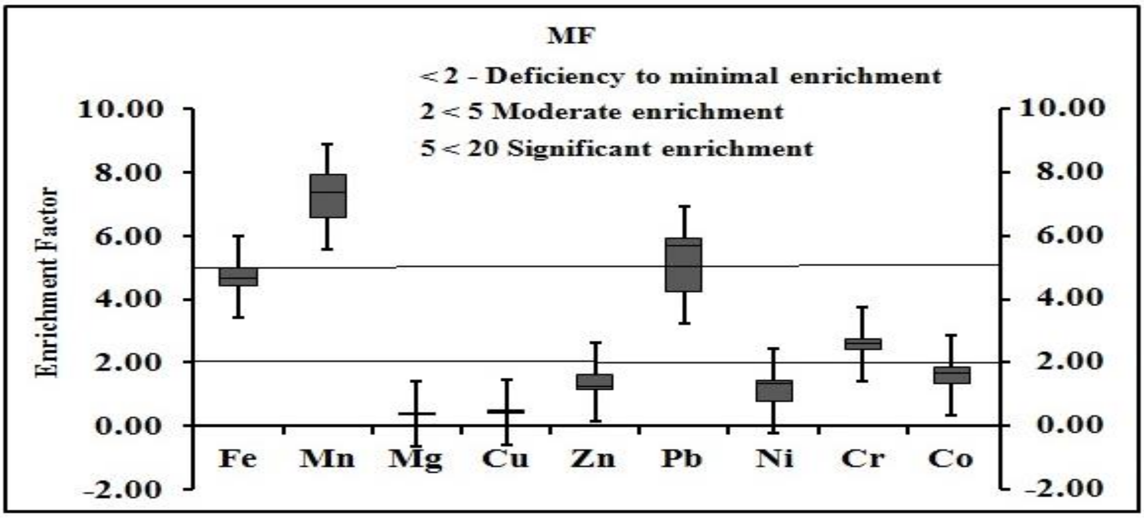
Param	**sand**	**silt**	**clay**	**OC**	**TP**	**Fe**	**Mn**	**Al**	**Mg**	**Cu**	**Zn**	**Pb**	**Ni**	**Cr**	**Co**
sand	1.00														
silt	**-0.99**	1.00													
clay	-0.44	0.32	1.00												
OC	**0.86**	**-0.87**	-0.29	1.00											
TP	-0.19	0.21	-0.04	-0.07	1.00										
Fe	-0.35	0.38	-0.06	-0.18	0.75	1.00									
Mn	0.36	-0.42	0.33	0.41	0.25	-0.27	1.00								
Al	0.37	-0.34	-0.34	0.26	-0.19	-0.01	-0.45	1.00							
Mg	-0.57	0.58	0.13	-0.47	0.73	**0.90**	-0.29	-0.01	1.00						
Cu	-0.01	-0.03	0.30	0.27	0.32	0.28	0.31	-0.58	0.15	1.00					
Zn	-0.10	0.14	-0.22	-0.17	**0.75**	**0.67**	-0.06	-0.12	**0.64**	0.31	1.00				
Pb	0.37	-0.34	-0.37	0.11	0.03	0.15	0.07	-0.15	0.06	0.10	0.35	1.00			
Ni	0.47	-0.49	-0.05	0.33	-0.34	-0.10	-0.05	0.59	-0.07	-0.32	-0.24	0.44	1.00		
Cr	-0.25	0.22	0.31	-0.19	-0.52	-0.26	-0.17	-0.32	-0.13	0.28	-0.45	0.17	0.20	1.00	
Co	0.04	0.00	-0.24	0.18	0.08	-0.15	0.03	0.26	-0.01	-0.15	-0.27	-0.29	0.12	0.17	1.00

4.3.4 Pollution Indices

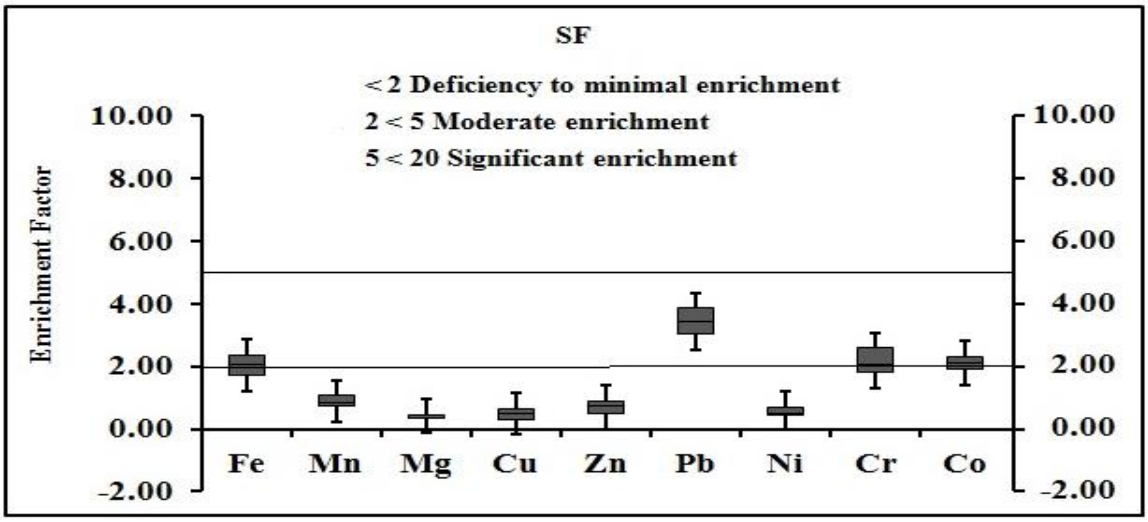
4.3.4.1 Enrichment Factor (EF)

Enrichment factor (EF) was used to assess metal contamination in the sediments of MF, SF, and PF (**Fig. 4.3.4.1.a, b, c**). In MF core, Mn and Pb showed significant enrichment, Fe and Cr showed moderate enrichment suggesting significant anthropogenic inputs, whereas Cu, Zn, and Ni showed deficiency to minimal enrichment (**Fig. 4.3.4.1.a**). Enrichment factor for SF core showed moderate enrichment for Fe, Pb, Cr, and Co, whereas Mn, Mg, Cu, Zn and Ni showed deficiency to minimal enrichment (**Fig. 4.3.4.1.b**). However, in PF core Mn and Co showed moderate enrichment and Fe, Mg, Cu, Zn, Pb, Ni, and Cr showed deficiency to minimal enrichment (**Fig. 4.3.4.1.c**). Significant moderate enrichment of Fe, Pb, and Cr in MF and SF cores can be attributed to anthropogenic inputs while other elements (Mn, Cu, Zn, and Ni) may be of crustal origin. According to **Zang and Liu,** (**2000**) if EF values are between 0.05 and 1.5 it indicated that the metal was from crustal materials / natural processes and EF values > 1.5 it is more likely to be anthropogenic.

a.



b.



c.

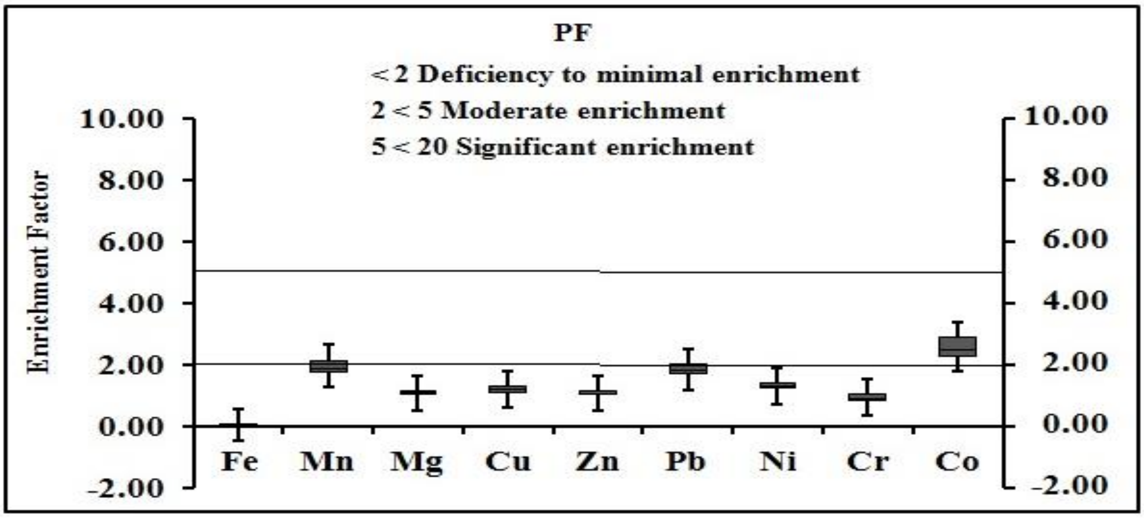
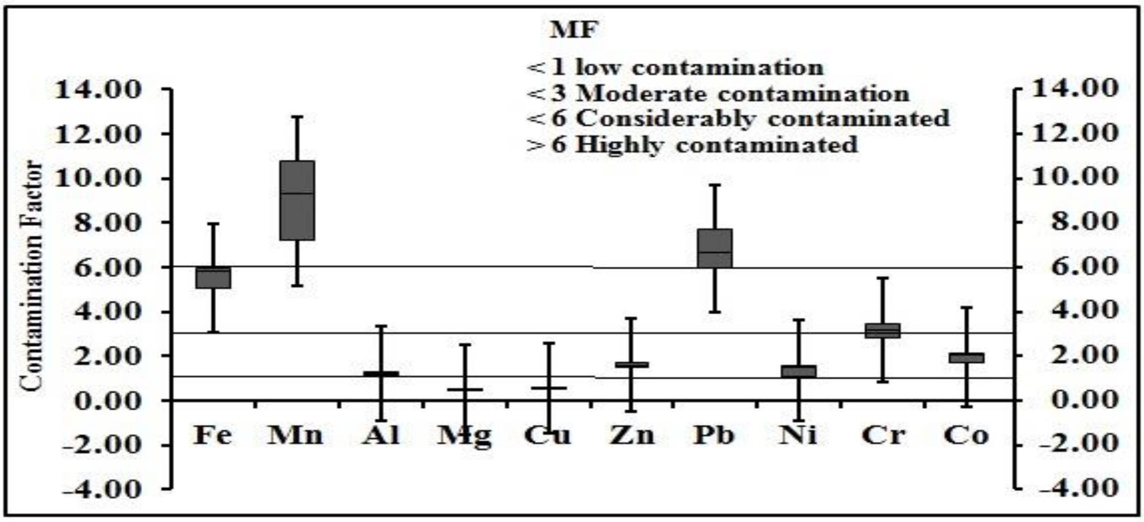


Fig. 4.3.4.1 Enrichment factor for major elements and trace metals in cores collected from a. Mayem agricultural Field (MF), b. Sanvordem agricultural Field (SF) and c. Pernem agricultural Field (PF), Goa-West coast of India

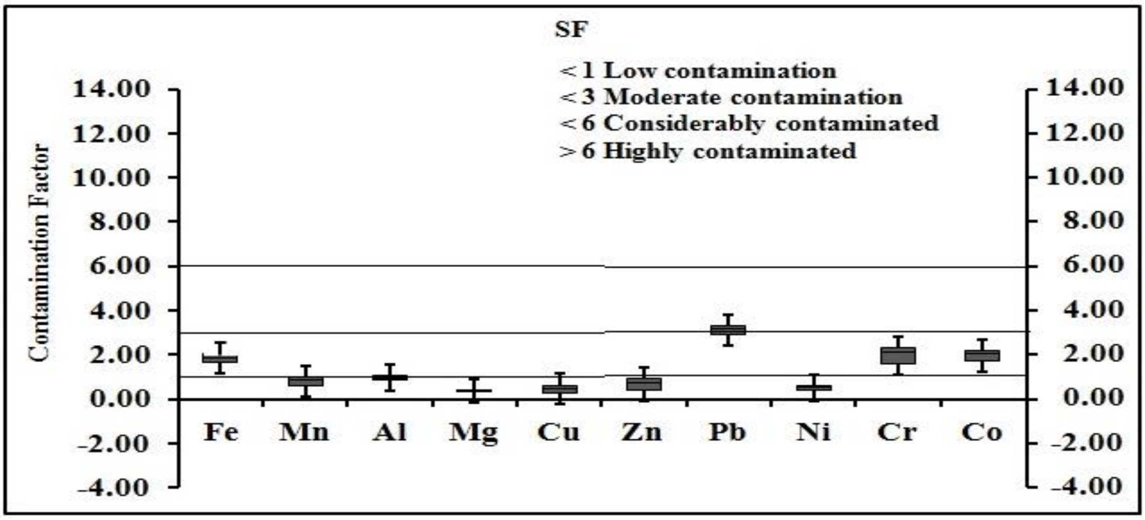
4.3.4.2 Contamination Factor (CF)

Contamination factors for MF core indicated that it is highly contaminated with Mn and Pb; considerably contaminated with Fe and Cr; moderately contaminated with Al, Zn, Ni, and Co. However Cu and Mg showed low contamination (**Fig. 4.3.4.2.a**). In SF core Pb showed considerable contamination; moderately contaminated with Fe, Cr and Co whereas Mn, Al, Mg, Cu, Zn and Ni showed low contamination (**Fig. 4.3.4.2.b**). However, in PF core, Mn, Pb, Ni and Co showed moderate contamination and Fe, Al, Mg, Cu, Zn, and Cr showed low contamination (**Fig. 4.3.4.2.c**). High contamination for Mn and Pb and considerable contamination for Fe and Cr in MF sediment core can be attributed to enormous mining activities and discharge of wastes. Iron ore mines acts as an important source of mainly Fe and Mn, and also contributes for trace metals into the environment (**Ratha *et al.*, 1995**; **Yellishettya *et al.*, 2008 and Xu *et al.*, 2006**). Moderate contamination of Al may be due to the use of aluminum salts in treating wastes from the mining pits. Considerable contamination of Pb in SF sediment core may be due to runoff from mining waste which included trace elements and minerals often associated with iron deposits (**Jung, 2008**). On the other hand, low contamination of Fe in PF core revealed that this area is not affected by mining activities. The soil contained various functional groups which are effective agents for heavy metal sorption. Their interactions affect the properties and processes in the soil which are determined by the level of Fe, Al, and Mn oxides and hydroxides, rainfall distribution, erosion, soil drainage, redox potential, texture, and organic matter and clay content. The dominant process at any specific time determines the heavy metal retention capacity (**Jian-Min *et al.*, 2007 and Yaylali-Abanuz, 2011**). Pb production and operation facilities without a waste-gas treatment system, battery production and scrap battery recovery facilities and iron–steel industries are the other sources of lead. Moreover, among the heavy metals, Pb was the most immobile element and its content in soil was closely associated with clay minerals, Mn-oxides, Al and Fe hydroxides, and organic material (**Mondol *et al.*, 2011**) Cr behavior in soil was regulated by soil pH and redox potential (**Rabee *et al.*, 2011**).

a.



b.



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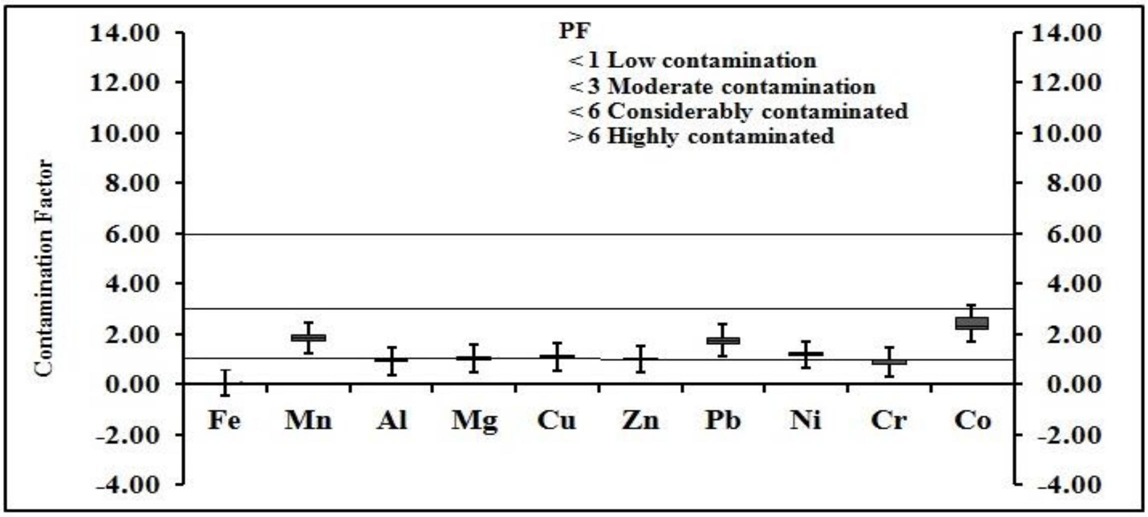
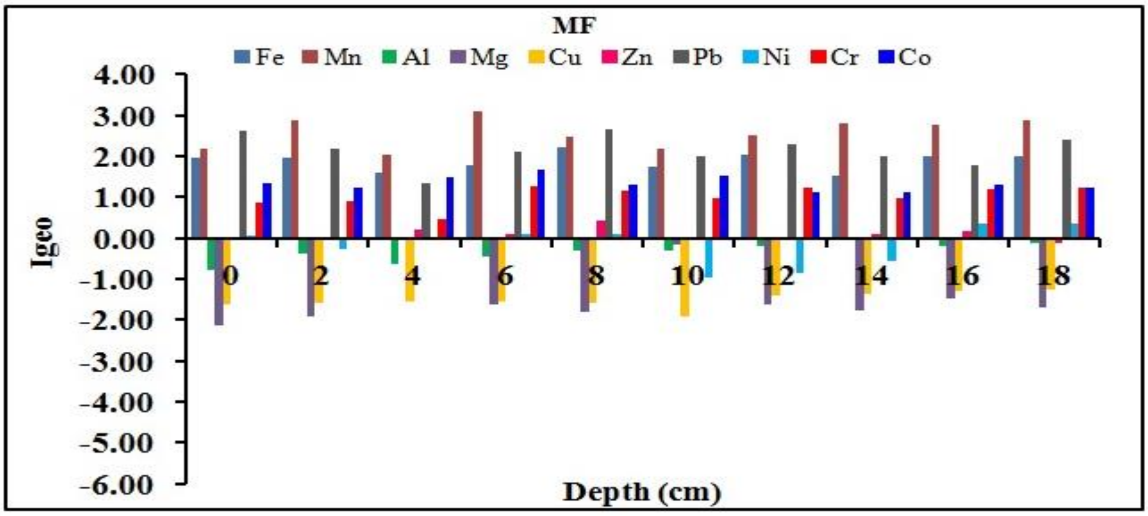


Fig. 4.3.4.2 Contamination factor for major elements and trace metals in cores collected from a. Mayem agricultural Field (MF), b. Sanvordem agricultural Field (SF) and c. Pernem agricultural Field (PF), Goa-West coast of India

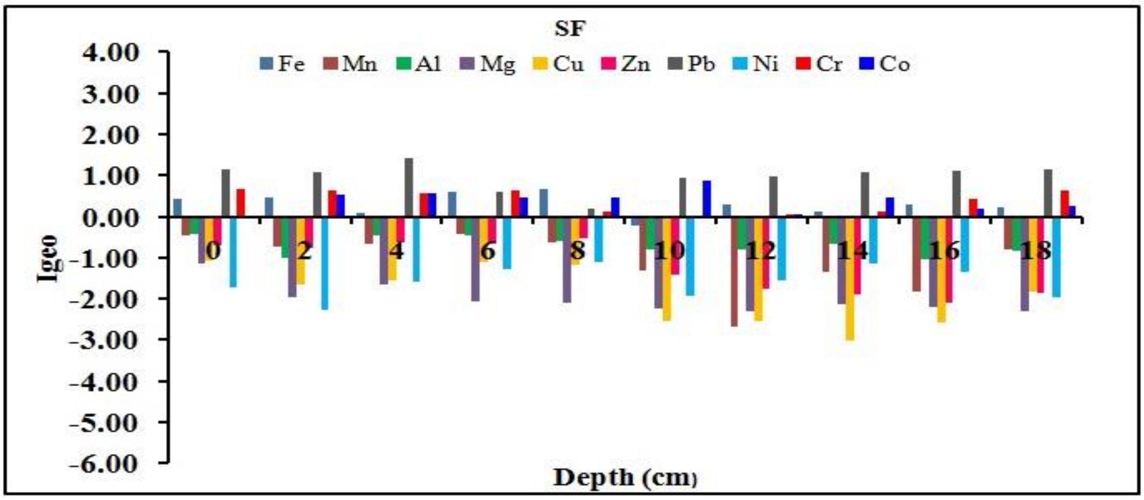
4.3.4.3 Geo-accumulation Index (Igeo)

The I-geo grades for the study area sediments varied from metal to metal and site to site (**Rabee *et al.,* 2011**). Geo-accumulation Index is presented in figure (**Fig. 4.3.4.3 a.b.c)**. MF core is moderate to strongly polluted with Mn; moderately polluted with Fe and Cr; unpolluted to moderately polluted with Zn and unpolluted with Al, Cu, Pb, and Ni (**Fig. 4.3.4.3.a**). Whereas, SF sediment core is moderately polluted with Pb (class 2); unpolluted to moderately polluted with Fe and Cr (class 1) and unpolluted (class 0) with Mn, Al, Cu, Zn, and Ni (**Fig. 4.3.4.3.b)**. However, the PF core was unpolluted to moderately polluted with Mn and Pb and unpolluted with Fe, Al, Cu, Zn, Ni, and Cr (**Fig. 4.3.4.3.a**). The moderate contamination of Cr might be associated with the presence of liquid manure, composted materials, and agrochemicals such as fertilizers and pesticides (**Krishna and Govil, 2004**). The increase of Pb in sediments is caused by the use of the combustion of petroleum and diesel and other traffic activities (**Veersingham *et al.*, 2014**). Dispersal of Fe mining wastes rich in Pb, Zn, and Cd is the likely source of these metals in soils (**Boon and Soltanpour, 1992**). Mine tailing indiscriminately dumped become materials for soil formation which on weathering releases into soils the composing metals with levels depending on the total metal concentration, speciation, geochemical characteristics, and mineralization. (**Jung, 2001; Ezeh and Chukwu, 2012 and Jian-Min *et al.*, 2007**). According to **Jung (2008),** metals dispersed from mine waste are likely retained in the lower areas used for agriculture with their mobilization in solution at the surface favoring down slope**. Zhou *et al.*, (2007)** reported the presence of Cu, Zn, and Pb from mine tailings that contributed levels as high as 567, 1140, 2.48 and 191 $\mu g g^{-1}$respectively to the soil.

a.



b.



c.

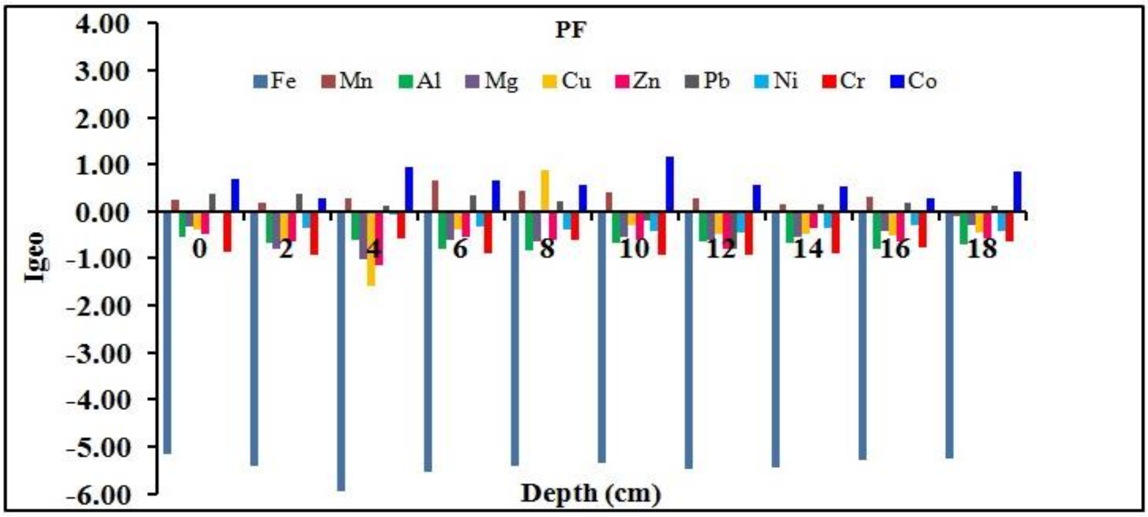


Fig. 4.3.4.3 Geo-accumulation Index (Igeo) for major elements and trace metals in cores collected from a.Mayem agricultural Field (MF), b. Sanvordem agricultural Field (SF) and c. Pernem agricultural Field (PF), Goa-West coast of India

4.3.4.4 Pollution Load Index (PLI)

PLI values in MF, SF and PF sediment cores varied from 2.02 to 2.83 (2.47); 0.75 to 1.25(1.00) and 0.66 to 0.87(0.76), respectively. These results of PLI indicated that MF and SF cores are polluted (PLI >1) and PF core is unpolluted (< 1). Higher PLI values of MF and SF cores can be attributed to enrichment of pollutants due to the steep slopes of dumps and unconsolidated nature of their constituents, dump materials get washed down the slope either filling up the low-lying agricultural land of Mayem area and due to transportation of ore by roads in the Sanvordem area.

The down core variation of PLI in MF, SF and PF core is presented in **Fig. 4.3.4.4.a.b.c**. MF core showed a decreasing trend from the bottom up to 14cm depth and thereafter it showed an increasing trend up to 8cm and from 8cm up to the surface of the core it showed a decreasing trend (**Fig. 4.3.4.4.a)**. Whereas SF core showed a decreasing trend from the bottom up to 12cm depth and thereafter it showed an increasing trend up to the surface of the core (**Fig. 4.3.4.4.b)**. However, PF core showed a decreasing trend from the bottom up to 12cm depth and thereafter it showed an irregular trend up to the surface of the core with an increased peak at 8cm and a decreased peak at 4cm depth of the core (**Fig. 4.3.4.4.c)**.

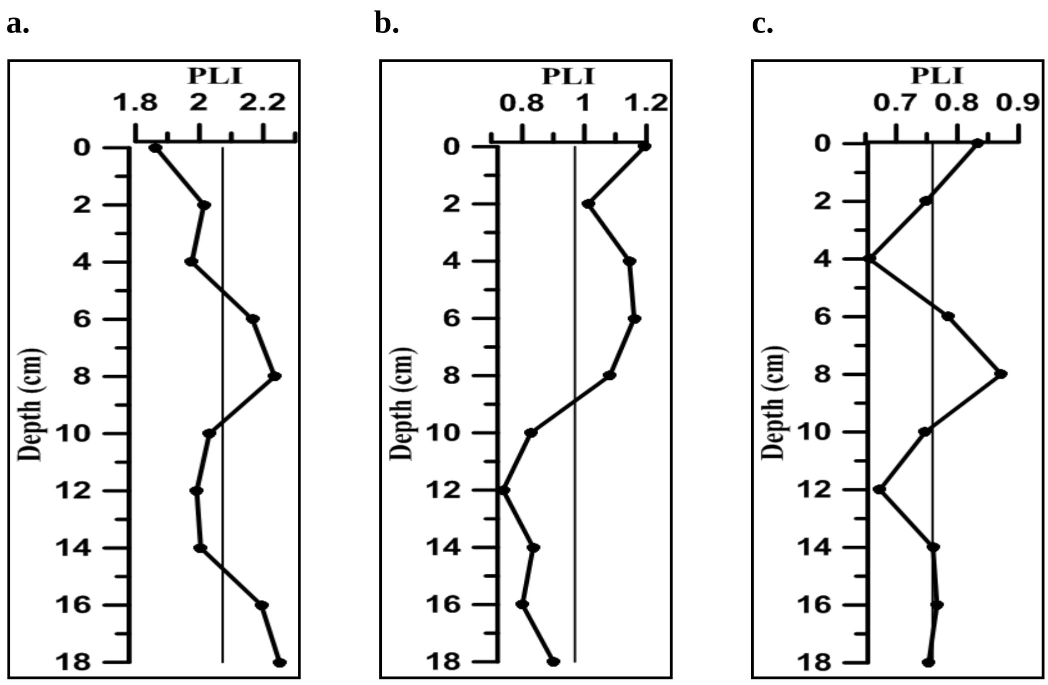


Fig. 4.3.4.4 Down core variation of PLI in sediment cores of a. Mayem agricultural Field (MF), b. Sanvordem agricultural Field (SF) and c. Pernem agricultural Field (PF), Goa-West coast of India

4.3.5 Factor Analysis

The varimax factor analysis was performed on data set of cores the metal concentration along with Organic Carbon (OC), Total phosphorus (TP) and textural parameters of sediments for three cores MF, SF and PF in order to identify the major factors that determine the distribution of metals in sediment. The numbers of factors are selected on the basis of criteria given by **Kaiser, (1960)**, with Eigen values >1 was retained. The factor analysis of the present data set was sorted by the contribution of significant variables. The results of sorted rotated factor loading scores along with Eigen values and percentage of variances were shown in the table (**Table 4.3.5**).

Five factors were obtained for MF core with Eigen values >1. The loadings between different parameters in the principal factors, are given in the table (**Table 4.3.5.a**.). In MF core, Factor 1 accounted for 31.25% of the total variance shows significant positive loadings for Fe and Pb. Factor 2 showed 21.02% of total variance shows significant positive loadings for silt and Zn suggests an association of this metal with finer fractions. Factor 3 accounted for 16.18% of the total variance and showed strong positive loading on Mn and Cr. Factor 4 showed 12.33% of the total variance and showed strong loading on Ni, whereas Factor 5 accounted for the 7.42% of total variance with a good loading on Cu. Mn and Cr did not show high loading values in any component, indicating that these metals had different sources of pollution. Pb has long been linked primarily to traffic activities due to the utilization of leaded gasoline (**Day *et al.*, 1975 and Paoli *et al.*, 2013**). Additionally, traffic activities also contribute to the concentration of Zn in the soil. It has been reported that tire wear contributes significantly to Zn in the agricultural top soil in cities (**Zanders, 2005**).

Five factors were extracted with Eigenvalues >1 for SF core. It is presented in the table (**Table 4.3.5.b**.). Factor 1 accounted for 37.49% of the total variance shows significant positive loadings for Fe Mn, Cu, and Zn. Factor 2 showed 21.73% of the total variance shows significant positive loadings for silt. Factor 3 accounted for 13.25% of the total variance and showed a strong positive loading on OC, TP, and Mg. Factor 4 showed 11.85% of the total variance and showed strong loading on clay, whereas Factor 5 accounted for 7.98% of the total variance and did not show any positive loading. Fertilizers, super phosphates contain the highest level of Cu and Zn as impurities (**Gimeno-Garcia, 1996**).

Five factors with Eigenvalues >1 were obtained for the PF core is presented in table (**Table 4.3.5.c**). Factor 1 accounted for 30.52% of the total variance it shows significant positive loadings for sand and OC. Factor 2 showed 20.15% of total variance with strong positive loading of TP, Fe, Mn, and Zn, which indicates the role of Fe-oxide in adsorption of metals. Factor 3 showed 16.18% of total variance with strong loading on Al, Factor 4 accounted for 10.85% of total variance with strong positive loading on Ni and Cr. Whereas Factor 5showed 8.21% of total variance with a strong positive loading on Co. Zn, Fe, and Cr sources can be related either to their use in agriculture or in various industrial process (**Mann *et al.*,** 2002).

Table 4.3.5 Factor analysis matrix after varimax rotation for a. Mayem agricultural Field (MF), b. Sanvordem agricultural Field (SF) and c. Pernem agricultural Field (PF), Goa-West coast of India

a.

Parameters	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
sand	-0.16	**-0.91**	0.08	-0.10	0.23
silt	-0.10	**0.94**	0.17	0.04	-0.21
clay	0.57	-0.40	-0.59	0.12	0.03
OC	-0.06	-0.19	-0.05	**-0.86**	0.30
TP	0.55	-0.18	0.51	0.10	0.57
Fe	**0.76**	0.31	0.16	0.18	0.09
Mn	0.09	-0.19	**0.83**	0.29	0.12
Al	-0.12	0.10	0.67	-0.33	0.57
Mg	**-0.76**	0.25	-0.35	-0.14	-0.39
Cu	-0.05	-0.20	0.35	0.38	**0.80**
Zn	0.02	**0.82**	-0.17	0.13	0.18
Pb	**0.97**	0.05	-0.03	-0.02	-0.05
Ni	0.16	0.10	0.06	**0.95**	0.18
Cr	0.45	0.02	**0.79**	0.02	0.11
Co	-0.26	0.06	0.00	0.32	**-0.81**
Expl.Var	3.07	2.88	2.71	2.18	2.39
Prp.Totl	0.20	0.19	0.18	0.15	0.16
% Total variance	31.25	21.02	16.18	12.33	7.42

b.

Parameters	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
sand	-0.15	**-0.95**	0.00	-0.17	-0.15
silt	0.17	**0.92**	0.11	-0.24	0.18
clay	-0.05	-0.02	-0.25	**0.89**	-0.10
OC	0.17	0.29	**0.86**	0.00	0.28
TP	0.23	-0.08	**0.86**	-0.21	0.02
Fe	**0.74**	0.01	-0.07	-0.21	0.59
Mn	**0.87**	0.18	0.29	0.19	-0.12
Al	0.58	-0.46	0.52	0.13	-0.06
Mg	0.30	0.13	**0.93**	0.04	0.09
Cu	**0.93**	0.13	0.29	0.04	0.16
Zn	**0.87**	0.04	0.33	-0.14	-0.19
Pb	-0.55	0.29	0.46	0.46	-0.13
Ni	0.19	**-0.81**	-0.17	-0.28	0.31
Cr	0.42	0.47	0.31	0.63	0.24
Co	0.10	-0.10	-0.25	0.01	**-0.94**
Expl.Var	4.02	3.09	3.37	1.74	1.63
Prp.Totl	0.27	0.21	0.22	0.12	0.11
% Total variance	37.49	21.73	13.25	11.85	7.98

c.

Parameters	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
sand	**0.96**	-0.17	0.17	0.08	-0.09
silt	**-0.96**	0.20	-0.10	-0.09	0.07
clay	-0.37	-0.17	-0.61	0.03	0.17
OC	**0.92**	-0.07	-0.06	0.04	0.19
TP	0.03	**0.90**	-0.19	-0.33	0.11
Fe	-0.22	**0.91**	0.03	0.07	-0.04
Mn	0.53	-0.07	-0.63	-0.27	0.06
Al	0.24	0.00	**0.83**	0.13	0.34
Mg	-0.45	**0.86**	0.02	0.13	0.09
Cu	0.15	0.32	**-0.80**	0.11	-0.06

Zn	0.01	**0.84**	0.00	-0.16	-0.38
Pb	0.33	0.24	0.02	0.56	-0.62
Ni	0.38	-0.09	0.37	**0.72**	0.11
Cr	-0.33	-0.38	-0.39	**0.73**	0.09
Co	0.10	0.00	0.11	0.10	**0.84**
Expl.Var	3.79	3.50	2.47	1.65	1.49
Prp.Totl	0.25	0.23	0.16	0.11	0.10
% Total variance	30.52	20.15	16.18	10.85	8.21

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The present study has generated data on major elements and trace metals concentration in soil from three agricultural fields of Goa. The soil is a long term sink for the group of potentially toxic elements often referred to as heavy metals, including zinc, copper, lead. These metals are usually small plant uptake compared to the total quantities entering the soil from different sources. The high contamination of heavy metals found in soil was closely related to the pollutants in irrigation water, agricultural soil fertilizers, and dust. Monitoring of heavy metals in soil should be performed and alternative options should be carried out in order to prevent excessive accumulation of these heavy metals in the human food chain and ultimately cause risk to human health (**Kayastha, 2014**). Several reports have clearly documented the various human activities as a major cause for heavy metal contamination of the soil ecosystem (**Al-Khashman and Shawabkeh, 2006 and Kasassi *et al.*, 2008**) which include mining processes, iron and steel industries, transportation, open disposal of waste, and use of inorganic fertilizers, pesticides on to the agricultural lands (**Hansen *et al.*, 2002 and Lado *et al.*, 2008**). Heavy metals from mining sites may reach agricultural soils through leaching. Also during the rainy season large quantities of tailing and waste containing heavy metals are carried by runoff to the agricultural fields near the mining sites **(Escarré *et al.*, 2010 and Duruibe *et al*., 2009).**

Of the three agricultural fields, MF core recorded the higher silt content. Whereas SF and PF showed higher sand content. Thus MF exhibited sandy silt texture and SF showed silty sand texture. On the other hand, PF exhibited silty sand texture. MF core recorded higher Concentration of OC as compared to SF and PF core. TP values in all the three cores were low. The concentration of organic carbon and available phosphorus have been found low as compared to normal soils, thereby, indicated deterioration of soil quality, hence not found to be environmentally safe for plantation, vegetation and agricultural purposes. MF is more enriched with metals such as Fe, Mn, Zn, Pb, Ni, Cr and Co as compared to SF and PF. Build up of metals in soil relates to proportional run-off during the monsoon season also indicating the influence of mining dumps in the vicinity of it.

MF is more enriched with Fe, Mn, Pb and Cr due to large scale extraction of minerals from Fe-Mn ores and dumping of mine wastes which are at an elevation above the agricultural land. Contamination factors revealed that MF is highly contaminated with Mn and Pb and considerable contamination of Pb in SF core due to the run-off from the mining-related activities. Geo-accumulation index (Igeo) of metals indicated that MF core was highly polluted by Mn due to anthropogenic factor; SF core was moderately polluted by Pb. Pollution load index indicated that MF and SF sediment cores were polluted (PLI > 1). PF core did not show any pollution. This study revealed that past mining has a considerable impact on the sediment quality of Mayem agricultural Field (MF) and Sanvordem agricultural Field (SF). Iron ore mines act as an important source of major metals; mainly Fe and Mn, and also, contributes for trace metals into the environment (**Yellishettya *et al.*, 2008; Xu *et al.*, 2006 and Zang and Liu, 2000**). Pb is a non-essential element, is toxic, and not required by organisms at any level (**Singh *et al.*, 2010**).

However, the distribution of major elements and trace metals in different agricultural fields follows the trend (decreasing)

Agricultural fields	Major elements	Trace metals
Mayem agricultural field (MF)	Fe > Al > Mg > Mn	Cr > Zn > Pb > Ni > Co > Cu
Sanvordem agricultural field (SF)	Fe > Al > Mg > Mn	Cr > Pb > Co > Zn > Ni > Cu
Pernem agricultural field (PF)	Al > Mg > Fe > Mn	Zn > Ni > Cr > Cu > Co > Pb

It is interesting to note that MF and SF agricultural fields recorded the similar trend distribution of major elements i.e Fe > Al > Mg > Mn except PF agricultural field. This may probably due to the influence of mining related activities. These two fields (MF and SF) are influenced by mining activities. On the other hand, PF agricultural field showed lower concentration of Fe and Mn indicating that this area is not influenced by mining activities. Relative high concentration of Al and Mg can be attributed to terrigenous effect. However, the distribution trend for trace metals for 3 regions are different and was ascribed to difference in geological terrain, physicochemical conditions of the soil and influence of fresh water containing domestic wastes.

Goa is one of the highest iron and manganese producing states in India. Legal and illegal mining activities were concentrated in Bicholim, Sattari, Sanguem and Quepem talukas of Goa. Mining practice in Goa has been by open-cast method. Exhaustive mining activities have produced a large amount of hazardous wastes. The overburden produced to access the ore has posed a major problem in handling of ore and its storage.

Mining activities have caused contamination of water and soil leading to environmental degradation. During monsoon, run-off from the mining areas leads to increase in the suspended load of the river flowing through the mining areas and also transportation of ores by barges through Mandovi and Zuari River. A substantial amount of suspended particles from the mining wastes get deposited in due course of time. Mining associated activities such as ore loading, transportation, effluents from processing plants and barge-building activities pollute water resources. Mandovi and Zuari Rivers were heavily used for transportation of large quantities of ferro-manganese ores from mines located in the up streams. The run-off from the mining areas has caused siltation of adjoining rivers, lakes and agricultural fields. The Pollution due to high loads of pollutants, mainly from the mine wastes are devoid of plant growth and supportive nutrients and hence pose danger to agricultural soil. The mining activities have also affected the Selaulim Dam on the Guleli River in Sangeum taluka, which supplies drinking water to the southern part of the state of Goa. More than 20 mines are operating in the vicinity of the dam.

Earlier studies mostly carried out on the Mandovi- Zuari river systems mainly focuses on biological, geochemical and mineralogical aspects by different authors. However, information on metal contamination and their distribution in sediments of Bicholim, Kushavati and Terekhol River, Mayem Lake and Selaulim Dam are scanty. However no work has been carried out on the agricultural fields affected by past mining in Goa.

The long term contamination history and impact of past mining activities in sediments are sparsely understood. So an attempt has been made to study geochemistry of sediment cores and would help to establish the background levels of the toxic metals for pollution assessment with reference to past mining in Goa.

Hence the present study has been undertaken in order to assess the metal contamination during past mining in Goa with the following objectives.

i) To study the effect of past mining on the rivers running through mine areas of Goa.

ii) To study the influence of past mining on lakes/dam of Goa

iii) To study the influence of past mining on agricultural fields of Goa

In order to achieve the objectives, ten sediment cores were collected representing rivers (Bicholim, Mandovi, Kushavati, Zuari and Terekhol), water reservoirs (Mayem Lake and Selaulim Dam) and agricultural fields (Mayem agricultural field, Sanvordem agricultural field and Pernem agricultural field) and were analyzed for various sedimentological and geochemical parameters. It included analysis of sediment components, organic carbon, total phosphorus, major elements (Fe, Mn, Al and Mg) and trace metals (Cu, Zn, Pb, Ni, Cr and Co). The color of the sediment core was used to reveal about its weathering history. Isocon plots were plotted and used to compare the parameters and also to understand metal enrichment areas. Statistical analysis like Pearson's correlation and Factor Analysis were employed to understand the association and metal input sources. Pollution indices like Enrichment Factor, Contamination Factor, Geo-accumulation Index and Pollution Load Index were computed to understand the Pollution level in the sediments cores collected from different environments.

1. Impact of past mining on the Rivers

The study on distribution of sediment components from riverine sediments in general, indicated higher percentage of silt in BR (Bicholim River) and ZR (Zuari River) core is attributed to its deposition under very violent hydrodynamic conditions, whereas MR (Mandovi River), KR (Kushavati River) and TR (Terikhol River) exhibited higher percentage of sand is attributed to higher fresh water discharge. BR, and TR core exhibited sandy silt texture. Whereas, MR and KR showed silty sand texture. However, ZR exhibited clayey silt texture. Hydrodynamic conditions prevailed during deposition of sediments indicated that BR, MR and TR core sediments are deposited under relatively to extremely violent conditions, whereas KR and ZR sediments were deposited under relatively violent conditions. OC values in BR and KR core are comparatively lower than MR, TR and ZR sediments. Texture played an important role in controlling the OC content, this is also supported by yellowish to brown colour in BR and KR core which also indicates that organic material has been oxidized and leached to some degree. However, MR ZR, and TR core exhibited grey colour indicating that they are derived from reducing environment. All the cores exhibited comparatively lower concentration of total phosphorus.

BR and KR cores showed higher concentration major elements Fe, Mn and Al as compared to MR, ZR and TR cores, this was attributed to iron and manganese ore mines in the vicinity of the these rivers. However, MR and ZR cores registered comparatively higher values for Mg than BR, KR and TR core which may be due to larger marine input in addition to the digenetic precipitation. In general, the distribution of major elements in different rivers is as follows (decreasing order): Bicholim River Fe > Mn > Al >Mg; Mandovi River Fe > Mn > Mg > Al; Kushavati River Fe > Mn > Al >Mg; Zuari River Fe > Mn > Mg > Al and Terekhol River Al > Mg > Fe >Mn. BR and KR showed similar distribution trend which may be due to large-scale extraction of minerals from Fe-Mn ores and dumping of mine wastes. BR, and KR cores registered higher concentration of all the trace metals, this may probably be due to iron ore mining and processing along the banks of this rivers. Whereas MR showed higher concentration of Pb, Co and ZR core registered higher concentration Pb, Ni, Cr and Co this may probably be due to shipping activities and industrial effluents. However, TR core showed higher concentration of Cu, Pb, Ni, Cr and Co this can be contributed to dumping of ship waste, sewage, solid waste and municipal waste at Redi Port. The distribution of trace metals (decreasing order) in different rivers is as follows: Bicholim River Cr > Zn > Ni > Cu > Pb > Co ; Mandovi River Cr > Zn > Pb > Cu > Co > Ni; Kushavati River Cr > Ni > Cu >Zn > Pb > Co; Zuari River Cr > Zn > Ni > Pb > Cu > Co and Terekhol River Cr > Cu > Ni > Zn > Co > Pb. Variations in concentration of trace metals in different rivers was ascribed to difference in geographical terrain, mining activities, physic chemical conditions of water column and discharge of industrial and domestic wastes. Pearson’s correlation coefficients showed significant association of metals with finer sediments as well as organic carbon in all the cores indicating the influence of organic matter in trapping of metals. Fe-oxyhydroxide phase is a good scavenger of metals.

Enrichment factor showed significant enrichment of Fe and Mn in BR and KR sediment cores which may be due to high level of iron and manganese in the surrounding ore-bearing areas as these rivers flow through the ore-bearing terrain that might be picking up the elements. Whereas, moderate enrichment of Pb, and Cr in BR, MR, KR and ZR core can be attributed to anthropogenic inputs, while other elements (Cu, Zn, Ni and Co) may be of crustal origin. On the other hand, moderate enrichment of Cu, Cr and Co in TR core may be due to anthropogenic input. Contamination factors revealed that Bicholim and Kushavati river areas are highly contaminated by Fe and Mn this may be due to the run-off from mining-related activities. Considerable contamination by Mn, and Pb is observed in MR and ZR core. The increase of Pb in sediments is caused by the use of anti-fouling paints, combustion of petroleum and diesel in the boat, ferry and other traffic activities. High contamination of Mn is due to Fe–Mn ore deposits and human-induced activity in handling and transportation of these ores through the river and ore transportation by barges. However Co showed considerable contamination in TR core.

Geo accumulation index (Igeo) of metals indicated that BR and KR cores are moderately polluted by Fe and Mn and it is believed to be due to anthropogenic input; MR and ZR cores are moderately polluted by Mn and Pb. The ore deposits brought from the mines are stored at several loading points on the shore of the river and transported through barges to the port for export. TR core is moderately polluted by Co. Pollution load index indicated that the Bicholim River is the most polluted river (PLI value 2.07), whereas the Terekhol River is least polluted (PLI value 1.02). The pollution load index of five rivers varied in the order of (decreasing) BR > KR > ZR > MR > TR Hence, our study showed that past mining has an adverse impact on the sediment quality of Bicholim and Kushavati rivers as these rivers are flowing through the mining areas of Goa and receives runoff from adjacent Fe-Mn ore mines and dumps of mine wastes during the monsoon. Factor loading revealed that the texture of the sediment and intensity of mining activities and anthropogenic input are major factors responsible for trace metals accumulation in both the rivers. However, the difference in the accumulation of pollutants in both rivers (BR and KR) can be related to the difference in the mining activities and the anthropogenic input of metal. It is therefore concluded that exhaustive iron-ore mining in the past had a considerable impact on the sediment quality of rivers.

2. Impact of past mining on the Lake / Dam:

ML (Mayem Lake) and SL (Saululim Dam) sediment core registered higher content of silt, this may be due to run off from the mining wastes in the vicinity of these reservoirs. The texture of sediment in ML reservoir is dominated by clayey silt. Whereas, SL core is dominated by sandy silt. OC in both the reservoirs exhibited lower values. This is supported by yellow and brown color of these cores indicating that the material has been oxidized and leached to some degree. ML and SL core exhibited higher concentration of major elements Fe, Mn and Al which is ascribed to anthropogenic activities. However, Mg exhibited lower values in both the cores. In general, the distribution of major elements in Mayem lake and Selaulim dam reservoirs is as follows (decreasing order): Fe > Mn > Al > Mg. Relative high concentrations of Fe and Mn was attributed to intensive mining activities at the vicinity of these reservoirs. All the trace metals showed higher concentration in both the cores except Ni in SL core is ascribed to anthropogenic activities. The distribution of trace metals in both the water reservoirs is as follows (decreasing order): Mayem Lke Zn > Cr > Ni > Cu > Pb > Co and Selaulim Dam Cr > Zn > Cu > Pb > Co > Ni. Pearson's correlation coefficients showed significant association of metals with finer sediments as well as organic carbon in both the cores indicating the influence of organic matter in trapping of metals.

Enrichment factors showed moderate enrichment for Fe and Pb in ML core and Mn and Pb in SL core. Enrichment of Fe and Mn was ascribed to mining dumps and runoff from the mining areas, whereas enrichment of Pb in the sediments was due to anthropogenic activities derived from combustion of fossil fuels in industries, in boat and other vehicles, and use of anti-fouling paints. Contamination factor revealed that ML core is considerably contaminated with Pb, whereas SL core is considerably contaminated with Mn, Pb and Co may be due to anthropogenic activities which can be a threat to the aquatic life. Geo-accumulation Index showed that ML core is moderately polluted with Pb, whereas SL core is moderately polluted with Pb and Co. This may be due to domestic sewage and vehicular emissions.

The results of PLI studies indicated that ML and SL sediment cores are polluted. Factor analysis revealed that OC and texture of the sediment are the main factors influencing Zn and Pb concentrations in the two reservoirs. While the major source of Mn in both the reservoirs comes from mining, anthropogenic source, the main source for Al and Ni in the study region is identified as lithogenic origin. Copper in the study region is mostly derived from anthropogenic activities. The difference in the abundance of metals between ML and SL can be attributed to difference in geological terrain, physicochemical conditions of the water column and discharge of industrial and domestic sewage. These variations in ML and SL might be due to intensive mining, and anthropogenic activities such as burning of fossil fuels, operational boats, and discharge of municipal wastes in the Mayem Lake. Accordingly, it is important that heavy metal contaminants, especially Pb needs to be carefully monitored in the study area. The information obtained in this study could be useful in the development of effective management strategies for control of heavy metal pollution in the limnetic ecosystems of west coast of Goa.

3. Impact of Past mining on the Agricultural fields:

The soil is a long term sink for the group of potentially toxic elements including zinc, copper, and lead. Various human activities as a major cause for heavy metal contamination of the soil ecosystem which include mining processes, transportation, open disposal of wastes, and use of inorganic fertilizers, pesticides on to the agricultural lands. Heavy metals from mining sites through leaching may reach agricultural soils, rivers and water reservoirs during the rainy season as runoff. Soil pollution with heavy metals has become a critical environmental concern due to its potential adverse ecological effects. However, they are considered as soil contaminants due to their toxicity. Monitoring of heavy metals in soil should be performed and alternative options should be carried out in order to prevent excessive accumulation of these heavy metals in the bottom dwelling aquatic organisms and crop plants and ultimately pose risk to human health.

Of the three agricultural fields, MF (Mayem Agricultural field) core recorded the higher silt content and exhibited sandy silt texture. Whereas, SF (Sanvordem Agricultural field) and PF (Pernem Agricultural field) showed higher sand content and exhibited silty sand texture. MF core recorded higher concentration of OC as compared to SF and PF. This is supported by yellow and brown color of the core indicating that the material has been oxidized and leached to some degree. These materials tend to be lower in pH and less fertile. TP values in all the three cores were low. The concentration of organic carbon and available phosphorus have been found low as compared to normal soils, thereby, indicated deterioration of soil quality, hence not found to be environmentally safe for plantation, vegetation and agricultural purposes.

MF and SF core showed higher concentration of Fe, Mn and Al and lower values for Mg. On the other hand, PF core registered higher values for Al, whereas Fe, Mn and Mg registered comparatively lower values. The distribution of major elements (decreasing order) in MF and SF follows the same trend: Fe > Mn > Al > Mg; as these are located at the vicinity of mining areas. While PF follows different pattern Al > Mn > Mg > Fe. All trace metals except Cu registered higher values in MF core, whereas Pb, Cr and Co showed higher values in SF core. However PF core registered higher values for Cu, Pb, Ni and Co. Higher concentration of trace metals in MF and SF core may probably be due to mining wastes containing heavy metals are carried by run off during monsoon to the low lying agricultural fields. The distribution of trace metals (decreasing order) in all the three agricultural fields is as follows: Mayem agricultural field Cr > Zn > Pb > Ni > Co > Cu; Sanvordem agricultural field Cr > Pb > Co > Zn > Ni > Cu and Pernem agricultural field Zn > Ni > Cr > Cu> Co > Pb. Pearson's correlation showed association of metals with finer sediments indicating that they are of anthropogenic origin.

Enrichment factor for MF core showed significant to moderate enrichment with Fe, Mn, Pb and Cr, Whereas Fe, Pb and Cr showed moderate enrichment in SF core this may be due to large scale extraction of minerals from Fe-Mn ores and dumping of mine wastes which are at an elevation above the agricultural land. PF core showed moderate enrichment with Mn, Pb and Co. Contamination factors revealed that MF is highly contaminated with Mn and Pb and considerable contamination of Pb in SF core is due to the run-off from the mining-related activities. Geo-accumulation index (Igeo) of metals indicated that MF core was highly polluted by Mn due to anthropogenic factor; SF core was moderately polluted by Pb. However PF core was unpolluted to moderately polluted with Mn, Pb and Co. Pollution load index indicated that MF and SF sediment cores were polluted (PLI > 1). PF core did not show any pollution. This study revealed that past mining has a considerable impact on the sediment quality of Mayem agricultural Field (MF) and Sanvordem agricultural Field (SF). Iron ore mines act as an important source of major metals; mainly Fe and Mn, and also, contributes for trace metals into the environment. Contamination of agricultural soils with heavy metals is a critical challenge in scientific community. Heavy metals are generally present in agricultural soil at low levels. Due to their toxicity, they have hazardous effect not only on crop plants but also on human health. Open-cast mining activities usually yield large quantities of waste materials, higher concentrations of pollutants which make the soil severely infertile that may inhibit plant growth.

Sediment contamination due to heavy metal is one of the burning issues in term of growing environmental concern; such contaminants are usually caused by anthropogenic activities such as iron ore mining. In state of Goa past iron ore mining activities have created an adverse impact on the sediment quality of Bicholim and Kushavati rivers as these rivers are flowing through the mining areas of Goa. Bicholim River is a tributary of River Mandovi whereas Kushavati River is a tributary of Zuari River owing to which these two rivers also get polluted. Mayem Lake and Selaulim Dam and Mayem agricultural field and Sanvordem agricultural field also have been affected by iron ore mining in the past causing siltation of these environments. Considering the distribution of metals, measurement of their levels in soil ecosystem it can be concluded that time to time analysis of heavy metals not only can help us to assess how strongly they are retained in soil. This study is also useful to estimate the level of metal contamination in agriculture soil to assure crop quality and also help reduce the contamination in the Silting watershed by identifying the major pollution sources. Furthermore, for the best management of the native soil resources, it is very important to have information about the pollution hazards and heavy metals concentration of the study area.

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List of Publications

1. Rane, N. T., & Matta, V. M. (2019). Impact of Past Iron Ore Mining on the Sediment Cores of Rivers of Goa. West-coast of India. Research Journal of Environmental and Earth Sciences, 11(1):1-13.

2. Rane NT and Matta VM (2019). Assessment of metal contamination in sediment cores of Zuari and Kushavati rivers with reference to past mining in Goa, West-coast of India. Environment and Ecology, 37(3):704-714.

3. Rane NT and Matta VM (2019). Geochemistry of sediment archives of agricultural lands with reference to past mining in Goa, West-Coast of India. International Journal of Scientific Research and Reviews, 8(1):2808-2835.

Paper Presentation

1. Poster presentation on Metal concentrations in sediment cores of water reservoirs of Goa- West coast of India at National conference held on 16th and 17th March 2017 on New frontiers in Life Sciences and Environment, Goa University.

2. Paper presentation on Impact of past mining on water reservoirs of Goa at National conference on Ecosystem Conservation and Sustainable Development held on 27th to 29th November 2018 at AET Institutes Bengaluru, Karnataka.

3. Paper presentation on Impact of past mining on metal contamination in Mayem lake in Goa, West-coast of India at National Conference on Biodiversity: Conservation Issues and Management Strategies held on 21st and 22nd December 2018 at Gokhale Centenary College Ankola, Uttar Kannada.

4. Paper presentation on Assessment of metal contamination through different pollution indices in Mayem lake, Goa at National Conference on Ecological Imbalances: Causes and Solutions held on 21st and 22nd March 2019 at Veerashaiva College Bellary Karnataka.

Awards/Honours

1. Awarded **second position** for paper presentation titled "Impact of past mining on water reservoirs of Goa" at National conference in Bangaluru, Karnataka.

2. Awarded **First position** for paper presentation titled "Assessment of metal contamination through different pollution indices in Mayem lake, Goa" at National conference in Bellary, Karnataka.