Studies on Metal Toxicity in the surface sediments of North and South Goa beaches along the West Coast of India

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GLENNIS JOYCE DA COSTA

Roll Number: 22P0400006

ABC ID :243895073987

PR Number: 201702550

Under the Supervision of

Dr. VISHNU MURTY MATTA

School of Earth, Ocean & Atmospheric Sciences

Marine Science

Goa University

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Examined by

Seal of the School

DECLARATION BY STUDENT

I hereby declare that the data presented in this Dissertation report entitled, "Studies on Metal Toxicity the surface sediments of North and South Goa beaches along the West Coast of India" is based on the results of investigations carried out by me in the Marine Science at the School of Earth, Ocean and Atmospheric Sciences, Goa University under the Supervision of Dr. Vishnu Murty Matta and the same has not been submitted elsewhere for the award of a degree or diploma by me. Further, I understand that Goa University or its authorities will be not be responsible for the correctness of observations/experimental or other findings given the dissertation.

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Seat No: 22P0400006

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This is to certify that the dissertation report **"Studies on Metal Toxicity in the surface sediments of North and South Goa beaches along the West Coast of India"** is a bonafide work carried out by **Ms. Glennis Joyce Da Costa** under my supervision in partial fulfilment of the requirements for the award of the degree of Master's in the Discipline of Marine Sciences at the School of Earth, Ocean and Atmospheric Sciences, Goa University.

30/04/2024

Dr. Vishnu Murty Matta

Discipline of Marine Sciences,

School of Earth, Ocean and Atmospheric Sciences

Date:

21/5/24

Sr. Prof. Sanjeev C. Ghadi, School Stamp
Senior Professor and Dean
Marine Sciences

School of Earth, Ocean and Atmospheric Sciences

Date:

Place: Goa University, Taleigão Plateau, Goa

SEOAS, GOA UNIVERSITY TALEIGAO PLATEAU GOA

School Stamp

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PREFACE

In the era of rapid industrialization and urbanization, coastal environments are increasingly vulnerable to pollution and contamination. Goa, known for its pristine beaches, faces the challenge of maintaining its coastal ecosystems amidst growing human activities. Understanding the dynamics of organic carbon content and metal pollution in beach sediments is crucial for effective coastal management and conservation efforts. This study delves into the assessment of organic carbon content, metal distribution, and pollution indices in the surface beach sediments of North and South Goa beaches. By analyzing various pollution indices, this study aims to provide insights into the current state of contamination and potential ecological risks posed to these coastal ecosystems.

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LIST OF ABBREVIATIONS

Entity	Abbreviation
AR	Arambol
CA	Calangute
MI	Miramar
H	Harbour
MA	Majorda
CO	Colva
TOC	Total Organic Carbon
Ni	Nickel
Co	Cobalt
Cu	Copper
Zn	Zinc
Mn	Manganese
Fe	Iron
AAS	Atomic Absorption Spectrophotometer
CF	Contamination Factor
PLI	Pollution Load Index
Cd	Contamination Degree
mCd	Modified Contamination Degree
Cp	Pollution Contamination Index
E^i_r	Ecology Risk Index
T^i_r	Potential Ecological Risk Factor
n	number
%	Percentage
C_n	Concentration of metal in the sediment
B_n	concentration of the same metal in the upper crust
GPS	Global Positioning System
°C	Degree Celsius
cm	Centimeter

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LIST OF EQUATIONS

1. % of TOC = 10 (1-T/S) x F
2. Igeo = log2 (Cn / 1.5* Bn)
3. $CF = C_{metal}/C_{background}$
4. PLI = n√ (CF1 × CF2 × CF3 ×…×CFn)
5. Cd=∑ni = 1 CFi
6. mCd = 1//n x ∑ni=1 CFi
7. $Cp = Metal_{(Sample\ max)} / Metal_{(Background)}$
8. $RI = \Sigma E^{i}_{r}$
9. $\Sigma E^{i}_{r} = T^{i}_{r}$

ABSTRACT

The study investigates the organic carbon content, metal distribution, and pollution indices in the surface beach sediments of North and South Goa beaches. Three beaches from each region were selected for analysis, encompassing urbanized, rural, and fishing zone settings. Sediment samples underwent sedimentological and geochemical analyses to assess total organic carbon and metal concentrations. Pollution indices, including Geoaccumulation Index (Igeo), Contamination Factor (CF), Pollution Load Index (PLI), Contamination Degree (Cd), Modified Contamination Degree (mCd), Pollution Contamination Index (Cp), and potential ecological risk, were computed to evaluate contamination levels and ecological risks. Results indicated varying levels of organic carbon content and metal pollution across the studied beaches. While urbanized areas exhibited lower organic carbon content, fishing zones and rural settlements showed relatively stable levels. Pollution indices revealed moderate contamination levels in some areas but overall indicated low to moderate contamination and lower ecological risks. This study provides valuable insights for coastal management and underscores the importance of monitoring and conservation efforts in Goa's coastal ecosystems.

CHAPTER 1: INTRODUCTION

1.1 BACKGROUND

The coastal regions of India, particularly along the west coast, are characterized by scenic landscapes, diverse ecosystems, and rich cultural heritage. The coastal regions play a vital role in supporting marine biodiversity, sustaining fisheries, and providing recreational opportunities for people.

The coastal state of Goa, situated on the western coast of India along the Arabian Sea, is renowned for its stunning beaches, vibrant culture, and thriving tourism industry. However, beneath the surface of its pleasant shores lies a growing environmental concern: the presence of trace metals in beach sediments. The coastal environment of Goa is not only a paradise for tourists but also a crucial ecosystem supporting a myriad of marine life and habitats. Mangrove forests, estuaries, coral reefs, and sandy beaches form integral components of Goa's coastal landscape, providing essential services such as shoreline protection, nutrient cycling, and habitat provision for countless species.

In addition to its natural splendour, Goa's coastal environment plays a vital role in supporting the state's economy and livelihoods. Fishing communities rely on coastal resources for sustenance, while the tourism industry attracts Goa's pristine beaches and water-based activities. Moreover, the coastal environment serves as a place for cultural activities, festivals, and traditional practices that are deeply intertwined with the coastal way of life.

However, the pristine beauty of these coastal environments is increasingly threatened by various anthropogenic activities, leading to concerns about environmental degradation and pollution. Goa's beaches face numerous challenges, including pollution, habitat degradation, overfishing, and coastal erosion. Urbanization, industrialization, and increasing tourism pressure have led to environmental degradation and loss of biodiversity in some areas.

The geochemical studies of surface sediments along the coastal zone of India has been extended in the recent decades due to the growing awareness of coastal pollution and its impact on the ecosystem. The west coastal zone of India encompasses diverse ecosystems, ranging from mangrove forests and estuaries to sandy beaches and rocky shores. However, alongside its natural beauty, the west coast is facing growing environmental challenges, including pollution from various sources.

The coastal environment is a dynamic ecosystem subjected to continuous changes by the natural processes as well as the anthropogenic activities leading to the enrichment of trace metals compared to their background concentrations. Apart from the geogenic sources, the increasing population and developmental activities in the coastal regions induce the generation of huge amounts of solid waste containing different metals and their disposal into the seawater posing serious environmental risks.

Beaches hold significant importance within the Earth's ecosystem, serving as depositional sites for sediments and popular destinations for tourists worldwide, attracted by their proximity to water and the array of recreational activities they offer. These sediments act as significant repositories of metals, accumulating them over short and long periods from both land and sea sources, making beaches ideal for studying metal concentrations and pollution levels. Contamination of beaches commonly originates from chemicals and debris, with higher metal concentrations indicating increased toxicity. While metals like iron (Fe), zinc (Zn), copper (Cu), and magnesium (Mg) are essential for biological functions, their abundance can lead to toxicity.

The beach sediments are integral components of coastal ecosystem, providing habitats for various marine organisms and serving as crucial barriers against erosion. Despite their importance, these sediments are increasingly vulnerable to contamination from a range of sources, including natural processes and human activities. Beaches form one of the most contaminated sedimentary environments due to wide range of anthropogenic activities, including tourism and recreational activities.

Metals are introduced into the aquatic environment from different sources like geological weathering, industrial processing of ores and metals, the use of metals and metal components, leaching of metals from garbage and solid waste dumps as well as animal and human excretions However, the influence of anthropogenic activity is the major source for enrichment of the metals in these sediments. The human activities have significantly interfered with natural conditions and processes of the beach, mainly during the last few decades. The environmental pollution caused by uncontrolled human-induced activities is occurring on a vast and unprecedented scale around the globe. The intensive mining activities in mineralized zones leads to disposal of tailings and the discharge of effluents. Almost all metals, including the essential micronutrients, are toxic to aquatic organisms as well as humans if exposure levels are sufficiently high **(Singh et al. 2008).**

Metal contamination in beach sediments poses significant risks to marine ecosystems and human health. These sediment act as sinks for pollutants and can serve as indicators of environmental quality. It can adsorb persistent and toxic metals, often reaching concentrations significantly higher than that observed in the water column

(Krishnakumar et al. 2003). When the effluent loaded water in the marine environment comes in contact with the coastal region, a large part of the pollutant, in one form or other, settles down, or is adsorbed by the oceanic sediments. Over the recent years, there has been a prominent increase in human-induced metal contamination to the marine sediments. Once these metals are released into the marine environment, they are transferred to the sediments through the processes of adsorption onto the suspended matter and subsequent sedimentation. These adsorption and sedimentation processes of metals mainly depend on the composition including grain size, carbonate content, level of organic matter, Fe-Mn oxy-hydroxides, etc. **(Jonathan et al. 2003).**

The geochemistry of organic carbon in sediments involves the study of the distribution, composition, sources, and transformations of organic carbon within sedimentary environments. Organic carbon in sediments originates primarily from the deposition and accumulation of organic material derived from terrestrial, marine, and freshwater sources. The geochemical processes governing organic carbon dynamics in sediments include sedimentation, burial, diagenesis, and microbial degradation.

The composition of organic carbon in sediments varies depending on its source, with contributions from a diverse array of organic matter sources such as terrestrial vegetation, marine phytoplankton, and microbial biomass. Organic carbon undergoes diagenetic transformations during burial, leading to the formation of kerogen, bitumen, and other organic compounds. Diagenetic processes, including thermal maturation, microbial degradation, and mineralization, influence the abundance and stability of organic carbon in sediments.

The geochemical cycling of organic carbon in sediments is mediated by microbial activity, which drives organic matter decomposition and mineralization under anaerobic and aerobic conditions. Microbial processes, such as sulfate reduction, methanogenesis, and organic matter oxidation, play a significant role in organic carbon turnover and the production of greenhouse gases, such as methane and carbon dioxide.

Among the numerous pollutants impacting the beaches of Goa, trace metals have emerged as a major concern in coastal environment due to their persistence, toxicity, and potential adverse effects on marine life and human health and can enter the coastal environments through a variety of pathways **(Ramkumar et al. 2023).** Trace metals entering aquatic ecosystems from various sources can accumulate in significant amounts and become part of the aquatic food chain. When metal ions dissolve in water, they can be absorbed by aquatic plants and animals, potentially leading to toxicity if the concentration becomes high enough. The concentrations of metals in aquatic organisms are often higher than those in the surrounding water. This has raised concerns that metals may become more concentrated at higher trophic levels in aquatic food chains, a phenomenon known as biological magnification. This accumulation not only affects the life cycles of aquatic organisms but also poses potential hazards to humans who consume them. In some regions, the presence of these metals in the environment has reached levels that threaten the health of both aquatic and terrestrial organisms **(Singh et al. 2008).**

Goa's susceptibility to metal pollution is due to its diverse socio-economic activities, including tourism, fisheries, and industrial development. Goa has a history of extensive mining operations for iron ore, manganese ore, and bauxite has left a significant impact on the environment. Open-cast mining, a prevalent practice in Goa, generate substantial waste, estimated at around three tons for every ton of ore extracted. This substantial waste generation has cascading effects, as trace metals originating from mining activities accumulate within beach sediments. **Nayak and Dessai (2002)**. Consequently, trace metals from these mining activities accumulate in beach sediments, persisting for extended periods and posing potential risks as contaminants.

The relationship between organic carbon content and metal toxicity in sediments is a complex and dynamic interplay that significantly influences the environmental fate and bioavailability of metals. Organic carbon serves as a crucial binding agent in sediments, interacting with metals through complexation, adsorption, and precipitation processes. High organic carbon content in sediments can reduce metal toxicity by sequestering metals and limiting their availability for uptake by benthic organisms. This occurs through the formation of metal-organic complexes and the adsorption of metals onto organic matter surfaces, which reduces the concentration of free metal ions in pore waters. Additionally, organic carbon can enhance the stability of metal complexes, reducing their reactivity and potential toxicity to biota.

Conversely, the presence of high organic carbon content can also exacerbate metal toxicity under certain conditions. Organic matter serves as a substrate for microbial activity, promoting anaerobic conditions in sediments and facilitating metal mobilization through microbial-mediated processes such as sulfate reduction and metal complex dissolution. Under anoxic conditions, organic matter degradation can lead to the release of metal-bound sulfides, which can increase the bioavailability of metals such as cadmium, lead, and mercury, posing risks to benthic organisms and ecosystem health. Furthermore, organic carbon can influence metal toxicity indirectly by altering sediment pH, redox conditions, and microbial community composition, which in turn affect metal speciation and availability.

The interrelationship between organic carbon content and metal toxicity in sediments is influenced by various environmental factors, including sediment characteristics, hydrodynamic conditions, and anthropogenic activities. The intricate relationship between the organic carbon content and the metal contamination in the sediments is essential for evaluating the ecological risks linked to metal contamination in sediments and formulating efficient management strategies to alleviate the effects of metal pollution on aquatic ecosystems.

1.2 Aim and Objectives

Aim: To study metal contamination in the surface sediments of north and south Goa beaches along the west coast of India.

Objectives:

- To study the organic carbon content in the surface beach sediments of North and South Goa beaches.
- To understand the distribution of total metals in the surface beach sediments of North and South Goa beaches.
- To assess the pollution indices of beach sediments.

1.3 Scope

1. Analysis of Organic Carbon Content

- Investigate influencing factors and comparing the concentrations of organic content across different locations to understand variations and potential sources.

2. Distribution of Total Metals

- Investigating the seasonal and spatial distribution patterns of total metals, and identifying the factors influencing their distribution
- Analysing spatial variations in metal concentrations to identify hotspots and potential sources of contamination.

3. Assessment of Pollution Indices

- Comparing pollution indices among different beach sites to identify areas of concern and prioritize management efforts.

CHAPTER 2: LITERATURE REVIEW

Santhiya et al. (2011) reported the concentration of Partially Extracted Trace Metals (PETMs) such as Fe, Mn, Cr, Cu, Ni, Co, Pb, Zn, and Cd in beach sediments along the south-east coast of India across 57 different locations in Chennai Metropolitan City. The results depicted high concentration of PETMs such as Pb and Ni in beach sediments influenced by industrial regions as compared to those influenced by tourism.

Usmani et al. (2015) examined trace metal pollution in water, sediment, and bivalves in the Mandovi and Chapora Estuaries of Goa, west coast of India. The trace metal concentrations in the water and sediment of the Mandovi Estuary were higher compared to Chapora indicating the influence of anthropogenic activities as the primary source of metal input in the Mandovi Estuary leading to the accumulation of trace metals.

Alagarsamy (2006) examined trace metal concentrations in surface sediments of the Mandovi Estuary, west coast of India. The study showed varying concentrations of Fe, Mn, Co, Cu, Zn, and Pb with the lowest levels typically observed during the monsoon compared to the pre- and post-monsoon periods. The enrichment of metals in sediments was determined using the Geoaccumulation Index. The results revealed that the surface sediments of the Mandovi Estuary were moderately to strongly contaminated with Fe and Mn. The Cu and Zn showed the influence of organic wastes from the municipal sewage entering the estuary.

Gaonkar et al. (2021) examined metal enrichment and contamination in the surface sediment of the Mandovi Estuary in Goa, India indicating various sources such as iron-ore mining, industry, fishing, and agriculture contributing to metal input. Heavy riverine runoff during the monsoon influenced the distribution of certain metals Mn, Zn and Pb. Sediment grain size and organic matter were identified as key factors influencing metal distribution. Pollution indices such as Geo-accumulation index, Contamination Factor, and Potential Contamination Index indicated the presence of contamination with Cr, Pb in the surface sediments of the Mandovi Estuary.

Karloniene et al. (2021) assessed the influence of coastal geodynamic processes on the distribution of trace metals in sandy beach sediments along the south-eastern Baltic Sea coast in Lithuania. The trace metal concentration varied between coastal regions, with the mainland coast being dominated by elements such as Ca, Mg, Mn and Ti, while the Curonian Spit coast shows higher levels of Fe, Pb, As, Co, Cr, Ni, Al. Additionally, high trace metal concentrations were observed in erosion-dominated areas on the mainland coast, whereas on the spit coast, concentrations increased in areas with relict coarse sand and active sediment loading.

Krishnakumar et al. (2013) studied trace metal concentrations in beach and estuarine sediments along the Velanganni Coast in South India, aiming to understand metal pollution resulting from urbanization and industrialization impacted by activities such as untreated effluent discharge and solid waste transportation and incineration. The sediment quality was assessed using various indices, including enrichment factor, geo-accumulation index (Igeo), pollution load index, and sediment quality guidelines. Results indicated that Cd, Cr, Ni, Zn, Pb, Mn, and Cu were present in varying concentrations, with Cd showing the highest enrichment.

Bhutia et al. (2023) studied metal speciation in sediments and bioaccumulation by edible bivalves in aquatic systems along the coast of Goa, India. The total metal concentrations of Mn and Zn, varied between months due to physicochemical factors and additional metal sources. Sediments at certain stations showed moderate contamination levels for Zn, Cu, and Co. The metal concentrations in bivalves exceeded permissible limits, indicating potential toxicity. The results highlighted the role of total organic carbon in sediments in metal speciation and bioavailability, as organic matter can bind with metals, altering their chemical forms and availability for uptake by bivalves.

Kumar et al. (2016) studied the elemental distribution and trace metal contamination in surface sediments across eight ecosystems along the southeast coast of India. Major elements like Ca, Mg, K, Ti, and trace metals including Cr, Mn, Co, Al, Fe, Ni, Cu, Zn, Cd, and Pb were analyzed. Pollution indices, such as contamination factor, geo-accumulation index, probable effect level, enrichment factor, and pollution load index, were calculated to assess pollution levels indicating moderate metal contamination along the coast, with the exception of cadmium. The organic carbon content was observed as a critical factor influencing the distribution and contamination levels of trace metals in surface sediments.

Gandhi et al. (2020) studied the concentration of acid leachable trace metals (ALTMs) and their ecological risk in beach sediments along the Coromandel Coast of south India. Thirty-six samples collected from both low and high tide zones reported enrichment of ALTMs due to natural processes due to anthropogenic influences. The distribution of ALTMs, predominantly Fe, Cr, Mn, Pb, Ni, Cu, Co, and Zn indicated their origin from natural processes such as leaching, weathering, and fluvial action with significant influence from textural characteristics, organic matter, and calcium carbonate content on metal distribution in the beach sediments.

Alagarsamy and Zhang (2009) assessed thirty-five surface sediment samples from the Indian continental shelf, collected at the mouths of major rivers discharging into both the east and west coasts. The distribution and concentration of selected major elements like Al, Ca, Fe, K, Ti, Mg, and Na and trace elements including Ba, Co, Cr, Cu, Ga, Ni, P, and V in coastal sediments revealed the importance of geochemical processes and possible environmental consequences of potential pollution due to nearby industrial activities. The Metal enrichments in proximity to urban areas on both the east and west coasts were attributed to industrialized areas with high concentrations of Cu and Co.

Ramkumar et al. (2003) studied heavy metal contamination in popular tourist beaches of Kerala State, Southern India, highlighting their susceptibility to various anthropogenic activities, including tourism. The concentration of metals and pollution levels were studied across four tropical tourist beaches, with bulk geochemical and mineralogical analyses conducted on sediment samples to assess environmental status and risk using various indices.

Nagarajan et al. (2013) assessed metal concentrations in sediments from tourist beaches in Miri City, Sarawak, Malaysia, aiming to identify enrichment of partially leached trace metals (PLTMs) across six different beaches. The study revealed analysis of forty-three sediment samples with varying concentrations of PLTMs, with enrichment observed predominantly on the southern side of the study area indicating high concentration of Cr, Cu, Pb, and Ni compared to environmental standards indicated potential ecological risks. Comparative analysis with other regions suggested external inputs of Co, Cr, Cu, Ni, and Zn emphasizing the importance of understanding trace metal distributions, pollution indices, and organic carbon content in coastal sediments for effective risk mitigation.

Ladislao et al. (2015) examined trace metal contamination and toxicity in coastal sediments of West Bengal, eastern India. The study revealed decrease in concentration of trace metals like Cr, Cu, Ni, Pb, As, Cd, and Ag in the surface sediments of Hugli River Estuary (HRE) and Sundarban Mangrove Wetland (SMW) The pollution indices such as Geo-accumulation index (Igeo) and Contamination factor (CF) values highlighted significant pollution by Ag, Cd, and Pb at Nurpur in the HRE. The Potential Ecological Risk Index (RI) ranged from low to serious ecological risk levels, with a positive correlation between metals and organic carbon observed. Assessment based on Sediment Quality Guidelines (SQGs) indicated adverse effects on sediment-dwelling organisms due to trace metal contamination.

Sundar et al. (2021) examined metals and trace elements in Kanyakumari beach sediments of southernmost India. The study revealed significant enrichment and contamination of Th, Zr, Mo, Ti, and U originating from metamorphic lithologies and heavy mineral deposits. Most elements showed positive correlations, suggesting natural sources, whereas the presence of Cd associated with P indicated potential anthropogenic influence from the fishing industry. High concentrations of Zn, Cr, and Ni pose a potential risk to coastal aquifers, with indications of bioavailability to seawater. The geo-accumulation index reflected variable abundances of these elements at different sites.

Singh et al. (2008) examined trace metal content in sediment samples collected from the Zuari River in Goa, India, throughout different seasons. The study reported concentrations of Zn, Fe, Mn, Cd, Co, Cu, and Cr across ten sampling stations during pre-monsoon, monsoon, and post-monsoon periods. The results depicted high concentration of trace during the Monsoon season, except for Cd and Fe, which peaked during the post-monsoon period. The elevated levels of Fe during the Post-monsoon and Monsoon seasons, compared to Pre-monsoon was attributed to mining, shipping activities, and increased river runoff.

Liu et al. (2005) assessed the impact of sewage irrigation on heavy metal distribution and contamination in Beijing, China, revealing a potential hazard due to the accumulation of heavy metals in agricultural soils. Metal concentrations including Cd, Cr, Cu, Zn, and Pb were assessed in samples from irrigated farming areas. Pollution load indices indicated metal contamination in the soils, with Cd, Cu, Zn, and Pb showing enhanced pollution levels compared to reference values. The results reported homogeneous distribution of metals in the irrigation area indicating heavy metal transfer from soils to plants posing risks to human health.

Bramha et al. (2014) studied heavy metal content in beach sediments along the southeast coast of India across seven locations from Kalpakkam to Mamallapuram. Pollution indices such as Enrichment Factor (EF), Geo-accumulation Index (Igeo), Contamination Factor (CF), Pollution Load Index (PLI), and Modified Degree of Contamination (mCd) were calculated to assess metal contamination levels. The results depicted metal contamination of Cr, Cu, Pb, and Cd, showing moderate to severe enrichment. Mamallapuram exhibited particularly high Cd contamination. The sediment pollution levels were low according to (PLI) and (mCd), except at location M1, which showed moderate contamination. However, Ni and Cr levels exceeded probable effect limit values, indicating potential adverse effects. The metals did not exceed the effect range median indicating low sediment toxicity.

Wong et al. (2006) assessed trace metal contamination in sediments of Guiyu in China. The results revealed elevated levels of Cd, Cu, Ni, Pb, and Zn river sediments indicating an increase in concentrations of Copper, Lead and Zinc in the non-residual fractions of contaminated sediments compared to those in uncontaminated sediments

Bhatkhande et al. (2022) studied metal enrichment in mudflat sediments of the Chapora Estuary of Goa, in west coast of India and its potential impact on the edible bivalve *Saccostrea cucullata*. The results indicated varying metal concentrations in Chapora Estuary sediments due to hydrodynamics, metal sources, and sand mining. Fe oxides, clay and organic carbon played significant roles in trace metal distribution. Moderate Mn contamination was observed in core (C-3), with severe contamination in certain spots. The bioavailability of metals indicated a high risk to biota, particularly for Mn. The metal concentrations in *Saccostrea cucullata* exceeded permissible limits, suggesting toxicity and unsuitability for human consumption.

Gao et al. (2012) studied sediment grain size and trace metals in the surface sediments of intertidal Bohai Bay, China. The results showed that sediment grain size played a crucial role in regulating the fractionation and distribution of metals. The clayey silt sediments showed higher concentrations of metals than the sand and silty sand cores.

Fernandes and Nayak (2014) assessed concentration and distribution of metals viz., Fe, Mn, Cu, Co, Cr, Pb and Zn in the intertidal sediments of Ulhas Estuary and Thane Creek. The results revealed the significant role of grain size and organic matter as metal carriers. The Ulhas Estuary displayed greater metal contamination levels as compared to the Thane Creek.

Veerasingam et al. (2015) conducted a study in the Mandovi Estuary on the west coast of India to investigate the depositional patterns of metals and assess contamination levels indicating concentrations of trace metals such as Co, Pb, Mn, Cu, Cr, and Zn in the sediments. The results indicated enrichment of trace metals in the surface sediments and decrease in concentration with depth suggesting excess of anthropogenic loading especially from mining activities.

Jonathan et al. (2004) studied the major and minor elements in the recent sediments of the Gulf of Mannar along the southeast coast of India. The study showed the enrichment of metals viz., Zn, Pb, Ni, Cu, Cd and Cr along the Gulf of Mannar. The study revealed metal contamination by riverine sources and nearby industries.

Mesquita and Kaisary (2007) studied the distribution of metals like Fe and Mn in water, suspended particulate matter and sediments from the Zuari Estuary. The higher concentration of Fe and Mn was noted in the middle estuary and was attributed to the input from mining activities.

Dessai and Nayak (2008) studied metals in the surface sediments in the Zuari Estuary for pre-monsoon, monsoon and post monsoon seasons. The results indicated severe pollution by Mn, followed by Co and least from Cu, Zn, Cr and Fe.

Adjei-Boateng (2010) conducted a comparative evaluation of metals in the clam Galatea paradoxa and in the sediments of the Volta Estuary, Ghana. The study showed significant variations in metal concentrations between tissues and sediments. However, Fe concentration in tissues of the different clam size classes from the two sampling stations was similar.

Kesavan et al. (2010) estimated the concentration of heavy metals in sediment and biota (*Telescopium telescopium*) from the Vellar Estuary. The concentration of the metals exhibited the following decreasing order Fe > Mg > Zn > Cu in the sediments.

The concentration of metals showed a decreasing order of Mg > Fe > Zn > Cu in tissues and shells of the biota.

CHAPTER 3: MATERIALS AND METHODS

3.1 Introduction

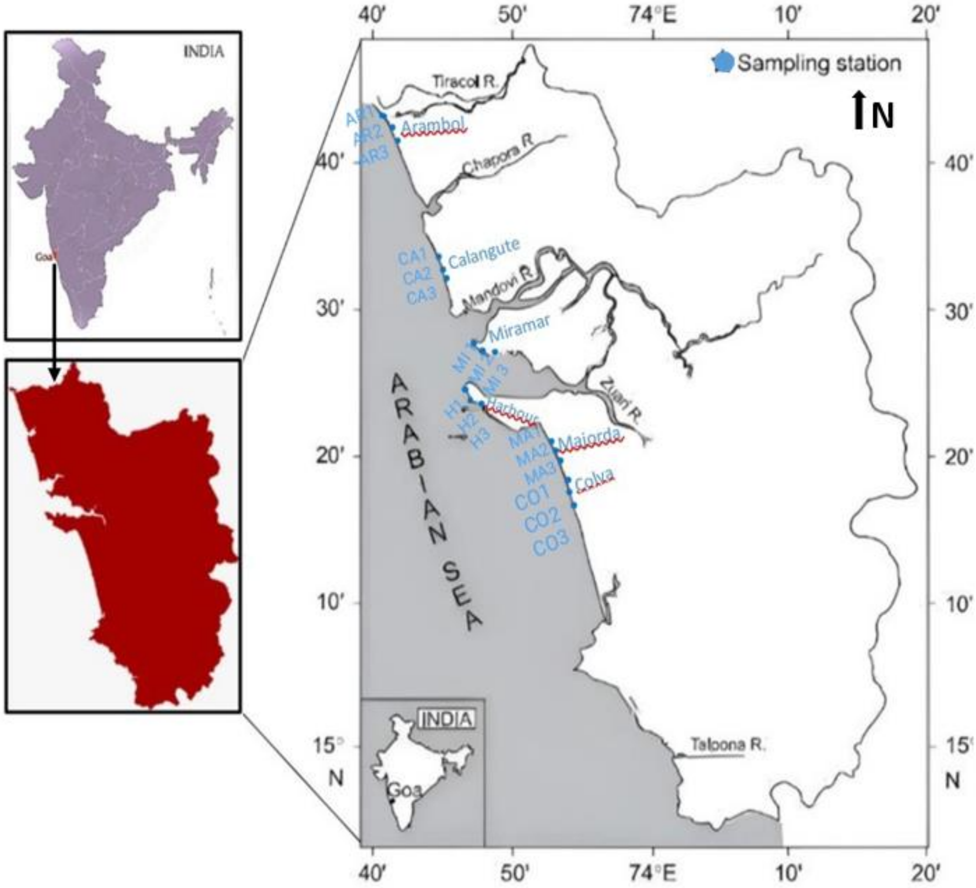
A sample of a specific quantity represents the biogeochemical processes prevailing in the environment. The samples are collected from a desired site(s), stored and then analysed for several parameters, upon reaching the laboratory. The analysis must be carried out using the standard analytical procedure to obtain accurate results which represent not just the environment but the issues pertaining in the environment. Thus, the materials, methods and the techniques used must be of internationally accepted standards.

3.2 Sampling

A total of 18 surface sediment (~ 5 cm) samples were collected by using a plastic scoop from six beaches of Goa, west coast of India. It included three beaches from North Goa namely Arambol, Calangute and Miramar, and three beaches Harbour, Majorda and Colva from South Goa. Three samples were collected from each beach: one from the extreme left side, one from the extreme right, and one from the center. Care was taken to avoid any contamination. The location of the sampling stations was noted down using the Global Positioning System (GPS). The collected samples were packed in pre-labelled zip-lock polythene bags and stored in an ice-box. Later, samples were carried to the laboratory and freezed (-20°C) until further analysis. The samples were then dried in the oven at 60°C to eliminate the moisture content from the sediment. Upon complete dryness the sediment samples were powdered using agate mortar and pestle prior to its analysis.

3.3 Study Area

Fig. 3.1 Map showing sampling locations



Goa has a coastline of 105 km long coast, more than 70km comprise linear and wide sandy beaches all backed by 1 - 10 meters high dunes; sandy pockets and secluded coves backed by rocky cliff are also found the sea front is marked by a combination of beaches, rocky shores and headlands. The coastline includes beaches with white sand, beaches with palm trees, and beaches with water sports.

The study includes the selected North Goa beaches and South Goa beaches namely Arambol beach, Calangute beach, Miramar beach and Bogmalo beach, Majorda beach, Colva beach respectively. The stations for the study were selected based on the amount of anthropogenic influence to the region.

Arambol Beach, also referred to as Harmal Beach, is located in the Pernem taluka of the North Goa district, stretching approximately 2.5 km along the coastline. Positioned as one of the northernmost beaches in Goa, it is bordered by Keri Beach to the north and Mandrem Beach to the south. Notably, one end of the beach boasts the presence of Pailem Sweet Water Lake, originating from natural hot springs, alongside a small hillock. Unlike many other beaches in Goa, Arambol Beach maintains a relatively low level of commercialization, making it an ideal study site due to its minimal anthropogenic influence. Despite the ongoing urbanization and tourist activities, Arambol retains its charm, offering visitors a serene and tranquil environment amidst its natural beauty. Its attractions, including the Pailem Sweet Water Lake, contribute to its appeal, attracting visitors seeking a laid-back coastal experience.

Selected for its significant anthropogenic impact, Calangute Beach epitomizes one of the busiest and most commercialized coastal stretches in Goa. Renowned for its lively atmosphere and diverse water sports opportunities, such as parasailing and water skiing, Calangute allures a considerable influx of tourists in search of excitement and entertainment along its bustling shoreline.

Originally known as "Gasper Dias Beach," Miramar Beach is situated in the Tiswadi taluka of the North Goa district, where the Mandovi Estuary meets the Arabian Sea. Its proximity to the capital city of Panaji renders it a popular destination for both locals and tourists. Despite its commercialization with numerous hotels and resorts, Miramar Beach maintains its charm and allure, boasting picturesque views and a bustling ambiance along its shoreline. Positioned at the confluence of the Mandovi Estuary and the Arabian Sea, Miramar Beach experiences significant anthropogenic activities, rendering it an ideal location for study. However, its proximity to commercial shipping activities introduces additional anthropogenic influences, such as ballast waters from nearby ships and buoys.

Bogmalo Beach, situated near an industrial zone and port, represents a unique study site influenced by industrial activities. While not as heavily commercialized as other beaches, Bogmalo faces anthropogenic pressures from nearby industrial operations. The proximity to the port further adds to its anthropogenic influence, making it an important location for studying the impacts of industrialization on coastal environments.

Colva Beach is a prominent destination within the southern circuit of Goa. It offers visitors a vibrant coastal experience, featuring resort complexes, tourist cottages, discos, guest houses, and an assortment of food stalls. Alongside its recreational appeal, Colva Beach is also renowned as a major fishing destination, with numerous motor trawlers dotting its offshore waters, adding to its bustling maritime activity and scenic charm. Despite being surrounded by rural settlements, Colva Beach experiences significant anthropogenic influence due to its popularity among tourists. The beach serves as a designated study site due to this impact, with the discharge of sewage from seaside hotels contributing to environmental concerns. Additionally, the influx of tourists has led to the development of various amenities, but it has also increased pressure on the local ecosystem. Nonetheless, Colva remains a favored destination for both leisure and fishing activities along the picturesque coastline of Goa.

Located in South Goa, Majorda Beach is celebrated for its picturesque landscape and peaceful atmosphere. Physically, it features a wide expanse of sandy shorelines adorned with abundant palm trees, gently caressed by the tranquil waters of the Arabian Sea. Exciting water sports, including parasailing, jet skiing, and banana boat rides, are readily accessible, offering exhilarating experiences for beachgoers. Moreover, Majorda Beach is renowned for its vibrant nightlife, with beachfront bars and cafes providing a variety of refreshing beverages and live music, ideal for unwinding and socializing after a day of seaside activities.

Table 3.1The locations of sampling sites across beaches of Goa.

Sampling stations	Latitude	Longitude
Arambol Beach (AR 1)	15° 41' 31" N	73° 42' 03" E
Arambol Beach (AR 2)	15° 41' 20" N	73° 42' 08" E
Arambol Beach (AR 3)	15° 41' 07" N	73° 42' 12" E
Calangute Beach (CA 1)	15° 32' 52" N	73° 45' 14" E
Calangute Beach (CA 2)	15° 32' 35" N	73° 45' 19" E
Calangute Beach (CA 3)	15° 32' 25" N	73° 45' 22" E
Miramar Beach (MI 1)	15° 29' 05" N	73° 48' 24" E
Miramar Beach (MI 2)	15° 28' 59" N	73° 48' 28" E
Miramar Beach (MI 3)	15° 28' 53" N	73° 48' 30" E
Harbour Beach (H 1)	15° 22' 05" N	73° 50' 06" E
Harbour Beach (H 2)	15° 21' 47" N	73° 51' 20" E
Harbour Beach (H 3)	15° 21' 05" N	73° 51' 28" E
Majorda Beach (Ma 1)	15° 19' 52" N	73° 54' 6" E
Majorda Beach (Ma 2)	15° 19' 25" N	73° 54' 19" E
Majorda Beach (Ma 3)	15° 19' 2" N	73° 54' 35" E
Colva Beach (CO 1)	15° 17' 23 "N	73° 54' 27"E
Colva Beach (CO 2)	15° 17' 05"N	73° 54' 33"E
Colva Beach (CO 3)	15° 16' 30"N	73° 54' 46"E

3.4 Sedimentological Analysis

3.4.1Total Organic Carbon (TOC)

The estimation of TOC was carried out to understand the role of organic components of the sediment in transport, deposition and mobility of trace metals. The TOC was estimated using the Wallkey-Black (1974) method. The method involves exothermic heating using potassium dichromate ($K_2Cr_2O_7$) and oxidation with the concentrated sulphuric acid (H_2SO_4).

The chromic acid was used to clean all the glassware. 0.5 g of powdered sediment sample was weighed and taken in a 500 ml conical flask. To it, 10 ml of 1 N standard potassium dichromate solution, and 20 ml of sulphuric acid and silver sulphate mixture was added. The conical flask was gently swirled and was allowed to stand for 30 minutes. Thereafter, 200 ml of the MilliQ water was added to it followed by 10 ml of 85% orthophosphoric acid and 0.2 g of sodium fluoride. The conical flask was gently swirled to thoroughly mix the reagents with the sediment sample. Also, few drops of diphenylamine indicator were added to the flask. The solution was treated against 0.5 N ferrous ammonium sulphate till an end point (one drop end point) was attained showing brilliant green. The addition of silver sulphate prevented the oxidation of chlorine ions. The standardization blank was performed using the same procedure without the sediment sample.

The percentage of TOC was calculated using the following formula:

% of TOC 10 (1-T/S) x F

Where,

S-Standardization blank titration, ml of ferrous solution

T-Sample titration, ml of ferrous solution

F-(1.0 N) x 12/4000 x 100/Sample weight 0.6, when sample weight is exactly 0.5g

Where, 12/4000 = m. eq. wt. carbon

3.5 Geochemical Analysis

3.5.1Total Metal analysis

The concentration of total metals in sediment was determined following the method proposed by **Jarvis and Jarvis (1985)** which was later modified by **Sholkovitz (1990)** that involved the acid digestion of the sediment sample.

The chromic acid was used to clean all the glassware. 0.2 g of powdered sediment sample was weighed and transferred into a clean Teflon beaker. To it, 10 ml of acid mixture involving HF, HNO_3 and $HClO_4$, in the ratio 7:3:1 was added and dried on a hot plate at 150°C. After complete drying, additional 5 ml of the acid mixture was added and was kept for drying. Once the sample had completely dried, 2 ml of concentrated HCl was added to it and was further dried on a hot plate. The dried sample was extracted with 10 ml of 1:1 HNO_3: MilliQ water and was heated for few minutes. It was then cooled and the entire digested sample was filtered through a Whatmann filter paper into a 50 ml volumetric flask. The volume was made up to 50 ml with the MilliQ water. It was then transferred into a pre-cleaned plastic bottle and stored for the chemical analysis.

The concentration of trace metals viz., Fe, Mn, Zn, Cu, Co and Ni in the digested sediment samples was analysed using the flame Atomic Absorption Spectrophotometer (Thermo Scientific-iCE 3000 Series AAS model).

3.6 Pollution Indices

3.6.1 Geo-accumulation index (Igeo)

The Igeo values were calculated using the formula proposed by **Muller (1979)** as follows:

$$Igeo = \log2 (C_n / 1.5 * B_n)$$

Where, C_n is the concentration of metal in the sediment sample and B_n is the concentration of the same metal in the upper crust **(Wedehpohl 1995).** 1.5 is the background correction.

Muller (1979) proposed seven grades or classes for the Igeo along with the associated sediment quality as given in the Table 3.6.1

Table 3.6.1 Classes with respect to sediment quality and pollution intensity **Muller (1979).**

Pollution intensity	**Geo-accumulation index**	**Igeo Class**
Very strongly polluted	>5	6
Strongly to very strongly polluted	4-5	5
Strongly polluted	3-4	4
Moderately to strongly polluted	2-3	3
Moderately polluted	1-2	2
Unpolluted to moderately polluted	0-1	1
Practically unpolluted	<0	0

3.6.2 Contamination Factor (CF)

The contamination of metals in sediments was evaluated by computing the CF.

$$CF = C_{metal}/C_{background}$$

Where, C_{metal} = metal content in sediment and $C_{background}$ = background value of that metal in reference sediment (upper crustal value, **Turekian & Wedepohl 1961)**. The CF is classified into four categories **(Pekey et al. 2004)** as given in the Table 3.6.2

Table 3.6.2 Classification of Contamination Factor

Contamination Factor	**Contamination level**
CF < 1	Low contamination
1≤ CF < 3	Moderate contamination
3 ≤ CF < 6	Considerable contamination
CF > 6	Very high contamination

3.6.3 Pollution Load Index (PLI)

The pollution load index is used to calculate the overall pollution level of a certain location. It is often referred to as the evaluation of overall sediment toxicity. The following relationship can be used to compute the pollutant load index:

$$PLI = \sqrt[n]{(CF1 \times CF2 \times CF3 \times \ldots \times CFn)}$$

Where, CF denotes the contamination factor, CF_n is the contamination factor of the nth metal, and n denotes the number of metals being assessed as given in Table 3.6.3.

Table 3.6.3 Classification of pollution load index (PLI)

Pollution load index	**Pollution level**
≤ 1	No metal pollution in sediment
>1	Polluted sediment

3.6.4 Contamination degree (Cd)

Hakanson(1980) proposed a method for simplifying contamination control that makes use of a diagnostic tool called the contamination degree (Cd). The contamination degree is estimated by adding the contamination factor of each sample.

$$\mathbf{Cd = \sum_{i=1}^{n} CFi}$$

Where CFi is the contamination factor of the individual metal "i". The contamination degree is classified in Table 3.6.4.

Table 3.6.4 Classification of contamination degree (Cd)

Contamination degree	**Contamination level**
Cd < 6	Low degree of contamination
6 < Cd < 12	Moderate degree of contamination
12 < Cd < 24	Considerable degree of contamination
Cd > 24	High degree of contamination

3.6.5 Modified degree of Contamination (mCd)

The modified degree of contamination helps in determining the overall metal contamination in sediment samples. **Abrahim and Parkec (2008)** proposed an equation to estimate the modified degree of contamination, which was modified from **Hakanson, (1980)**.

$$mCd = 1//n \times \sum_{i=1}^{n} CFi$$

Where n denotes the number of investigating elements, i denotes the ith element, and CF denotes the contamination factor. Table7 shows the classification of the modified degree of contamination.

Table 3.6.5 Classification of Modified degree of contamination (mCd)

Modified degree of contamination	**Contamination status**
mCd < 1.5	Nil to a very low degree of contamination
1.5 ≤ mCd < 2	Low degree of contamination
2 ≤ mCd < 4	A moderate degree of contamination
4 ≤ mCd < 8	A high degree of contamination
8 ≤ mCd < 16	A very high degree of contamination
16 ≤ mCd < 32	An extremely high degree of contamination
mCd < 32	Ultra high degree of contamination

3.6.6 Potential contamination index (Cp)

The potential contamination index can be determined using the following method **Davaulter and Rognerud (2001).**

$$\mathbf{Cp = Metal_{(sample\ max)} / Metal_{(Background)}}$$

Where $(Metal)_{Sample\ max}$ is the highest concentration of a metal in sediment and $(Metal)_{Background}$ is the average concentration of the same metal at a background level. **Davaulter and Rognerud (2001)** classified Cp values into three categories. The classification of the potential contamination index is shown in 3.6.6.

Table 3.6.6 Classification of Potential contamination index (Cp)

Potential contamination index	**Contamination level**
Cp < 1	Low contamination
1 < Cp < 3	Moderate contamination
Cp < 3	Severe or very severe contamination

3.6.7 Potential ecological risk

Håkanson, (1980, 1988) proposed a potential ecological risk index approach from a sedimentological perspective to examine the features and environmental behaviour of metal pollutants in coastal sediments. This index's primary role is to identify contaminating agents and where contamination investigations should be prioritized. The potential ecological risk index (RI) was developed to measure the degree of metal pollution in sediments based on metal toxicity and environmental response.

$$\textbf{Risk Index (RI)} = \Sigma E^i_r$$

$$\Sigma E^i_r = T^i_r$$

RI represents the potential hazard of metal contamination, indicating the toxicity of a certain metal as well as the environmental sensitivity to contamination. The monomial potential ecological risk factor is El, the contamination factor is CF, and the toxicity response factor is T (Mn, Zn=1, Cr 2, Cu, Pb=5, Cd=30). **Håkanson, (1980)** introduced the classification that is used to characterize the risk parameters El and RI.

Table 3.6.7 Classification of Potential ecological risk factor (E^i_r)

Risk Index	**Ecological status**
$R_i < 95$	Low potential ecological risk
$95 < R_i < 190$	Moderate potential ecological risk
$190 < R_i < 380$	Considerable potential ecological risk
$R_i > 380$	Very high potential potential ecological risk

Table 3.6.8 Classification of Ecological risk index (R_i)

Potential Ecological risk	**Ecological status**
$E^i_r < 40$	Low potential ecological risk
$40 < E^i_r < 80$	Moderate potential ecological risk
$80 < E^i_r < 160$	Considerable potential ecological risk
$160 < E^i_r > 320$	High potential potential ecological risk
$E^i_r > 320$	Very high potential potential ecological risk

<u>**CHAPTER 4: RESULTS AND DISCUSSION**</u>

4.1 Sedimentological Analysis

4.1.1 Total Organic Carbon (TOC)

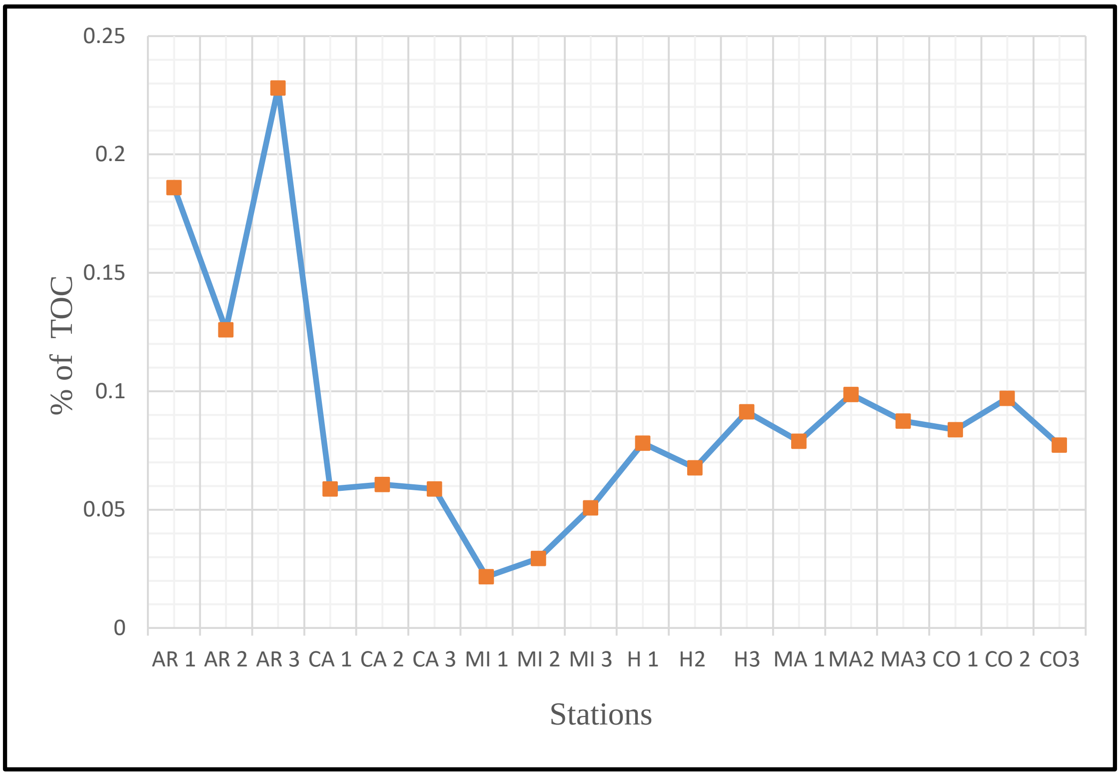
Table 4.1TOC% in surface beach sediment

Stations	TOC%
AR 1	0.18
AR 2	0.126
AR 3	0.2280.
CA 1	0.0059
CA 2	0.061
CA 3	0.059
MI 1	0.022
MI 2	0.029
MI 3	0.051
H 1	0.078
H 2	0.068
H 3	0.091
MA 1	0.0789
MA 2	0.098
MA 3	0.087
CO 1	0.083
CO 2	0.096
CO 3	0.077

The TOC % varies across different stations, ranging from 0.0059% to 0.228%. Stations AR1, AR2, and AR3 have relatively higher TOC % (0.186%, 0.126%, and 0.228%, respectively). This could be attributed to factors such as organic matter input from terrestrial sources and deposition of organic-rich materials. Stations CA1, CA2, and CA3 have lower TOC % (ranging from 0.0059% to 0.061%). This may indicate lower input of organic matter or higher decomposition rates at these locations. Stations MI1, MI2, and MI3 show varying TOC % (ranging from 0.022% to 0.051%), possibly reflecting differences in organic matter sources and environmental conditions. Stations H1, H2, and H3 exhibit relatively higher TOC percentages (ranging from 0.068% to 0.091%), suggesting significant organic carbon input, potentially influenced by factors such as nearby vegetation, urban runoff, or anthropogenic activities. Stations MA1, MA2, and MA3 have TOC percentages ranging from 0.0789% to 0.098%, indicating moderate to high levels of organic carbon content, which could be associated with factors like organic debris deposition or nearby coastal vegetation. Stations CO1, CO2, and CO3 show relatively consistent TOC percentages (ranging from 0.077% to 0.096%), possibly reflecting similar organic carbon inputs or environmental conditions across these locations.

The low percentage of TOC observed in Calangute could be attributed to its urbanized and tourism-influenced environment. Urbanization and tourism activities often result in increased sewage discharge and runoff from recreational activities, which can lead to the deposition of inorganic materials and pollutants in the sediments. Additionally, the presence of impervious surfaces such as concrete and asphalt in urban areas can limit the infiltration of organic matter into the soil, further reducing the organic carbon content in sediments. Moreover, anthropogenic disturbances associated with tourism, such as beach grooming and construction, may disrupt natural processes that contribute to the accumulation of organic matter in coastal sediments. As a result, the combined effects of urbanization, tourism, and anthropogenic disturbances may contribute to the observed lower TOC % in the sediments of Calangute beach.

Fig. 4.1TOC% in surface beach sediment



TOC % varies across stations, with higher levels at AR1, AR2, and AR3 (0.186%, 0.126%, and 0.228% respectively) due to organic matter input. Lower TOC % at CA1, CA2, and CA3 (0.0059% to 0.061%) suggests less organic matter or faster decomposition. MI1, MI2, and MI3 show varying TOC % (0.022% to 0.051%), possibly due to different organic matter sources. H1, H2, and H3 exhibit relatively higher TOC % (0.068% to 0.091%), indicating significant organic carbon input, potentially from nearby vegetation or urban runoff. MA1, MA2, and MA3 have TOC % from 0.0789% to 0.098%, suggesting moderate to high organic carbon content. CO1, CO2, and CO3 show consistent TOC % (0.077% to 0.096%), possibly due to similar organic carbon inputs. In Calangute, low TOC % may result from urbanization and tourism, leading to increased sewage discharge, runoff from recreational activities, and disruption of natural processes contributing to organic matter accumulation.

4.2 Geochemical Analysis

4.2.1Total metals

The concentration of total metals (Ni, Co, Cu, Zn, Mn and Fe) from surface beach sediments of sampled North Goa (Arambol, Calangute and Miramar) and South Goa beaches (Harbour, Majorda, Colva) are presented in the Table 4.2.1. The range of total metal content analysed for the sediment samples is as follows. The concentration of Ni exhibited a range of (1.925 - 271.875ppm), whereas Co ranged from (6.2-18.9ppm). Metal such as Cu, Zn, Mn and Fe displayed varying concentration ranges viz. Cu ranged from (15.15 - 163.575ppm), Zn from (53.8 - 193.775ppm), Mn from (88.4 - 2766 ppm), and Fe from (12020 - 20435ppm).

Table 4.2.1 Range and average of total metals in beach sediment.

ND = Not detected as the concentration was below the detection limit.

Stations	Ni (ppm)	Co (ppm)	Cu (ppm)	Zn (ppm)	Mn (ppm)	Fe (ppm)
AR 1	81.1	18.9	72.525	123.1	756.225	106250
AR 2	145.975	10.277	40.6	86.45	545.75	97845
AR 3	76.325	16.775	50.3	118.375	891.7	120845
CA 1	ND	ND	15.15	118.375	84.175	14445
CA 2	1.925	ND	21.35	193.775	148.175	20080
CA 3	43.475	ND	18.325	155.125	110.25	18060
MI 1	65.225	ND	21.525	75.75	880.9	70530
MI 2	271.875	13.25	23.1	93.1	2766	89770
MI 3	25.475	6.2	25.5	65.6	818.9	51620
H 1	7.325	ND	85.3	53.8	97.025	14910
H 2	15.95	ND	137.6	73.2	259.275	12020
H 3	8.75	ND	150.8	78.275	141.025	14115
MA 1	9.25	ND	41.325	55.925	99.8	14385
MA 2	13.4	ND	45.275	70.625	100.875	14195
MA 3	69.575	ND	20.575	55.925	130.275	20435
CO 1	9.35	ND	163.575	63.15	88.4	13475
CO 2	22.05	ND	124.1	82.075	100.725	14965
CO 3	14.325	ND	21.525	58.7	91.85	16970
Range	1.925 - 271.875	6.2 - 16.775	15.15 - 163.575	53.8 - 193.775	88.4 - 2766	12020 - 97845
Average	51.84	13.08	59.91	88.5	450.62	40273.05
Average Shale Value (Turekian and Wedepohl 1961)	68	19	45	95	850	47200

The range and the average concentration of total metals in beach sediments across different stations of North and south Goa is presented in the Table 4.2.1. The concentration of Fe in the beach sediments is extremely high, followed by Mn, compared to Ni, Co, Cu, and Zn. The concentration of Ni was highest (271.875ppm) in MI 2 and lowest (1.925 ppm) in CA 2. The concentration of Co in the sediments was lowest as compared to the other metals viz, Ni, Cu, Zn, Mn and Fe, showing values below the detection limit in most of the stations showing elevated levels (16.775) in AR 3 and reduced levels in MI 3. The Cu was highest (163.575ppm) in CO 1 and lowest (15.15ppm) in CA 1. The concentration of Zn is observed highest (193.775ppm) in CA 2 and least (5.8ppm) in H1. The Mn was highest (27.66ppm) in MI 2 and lowest (88.4ppm) in CO 1 while the Fe showed elevated levels (97845ppm) in AR 2 and decreased levels (12020ppm) in H2. The Fe concentration in the beach sediments of both North and South Goa exceeded 12020ppm, whereas the concentration of Mn was higher than 88.4ppm. Both these metals were observed to be greater than the upper crustal average value and were highly enriched in the sampled sediments of the North Goa and South Goa beaches. The enrichment of these metals in the sediments indicate anthropogenic influence in the beach sediments. However, Fe and Mn, are naturally abundant in the lithosphere; however, these metals in addition to Zn, Cu, and Co are introduced at an enhanced rate in the marine environment through iron-ore mining, industries, agricultural waste, and household sewage **(Bhutia et al. 2023)**. Several studies have indicated the open-cast iron ore mining operations of Goa as the predominant factor contributing to the enrichment of Fe and Mn in the sediments carrying these metals from the mining areas into the river's catchment area and eventually depositing them along the beach sediments during heavy riverine run off, thereby resulting in accumulation of sediments enriched with Fe and Mn **(Loveson et al. 2014).** The transportation of mining ore in an open system causes the spillage of ore into the rivers and estuaries, eventually reaching the coastal region and becoming a significant source of metallic waste. The barge maintenance units located along the river banks of Zuari and Mandovi serve as potential sources of metallic waste entering the aquatic system. Over time, these metallic particles can be transported by river currents and tidal movements, eventually reaching the coastal region and depositing into beach sediments. Once deposited, these metals can accumulate in the sediment over time, leading to elevated concentrations of metals such as Fe, Mn, Cu and Zn in beach sediments. In addition, the activities associated with barge maintenance units, such as painting, welding, and equipment repairs, involve the use of metal-containing materials and chemicals. . The levels of Zn is high in AR 1, AR 3, CA 2, CA 3 (North Goa) compared to beaches in the south. The Zn is one of the important components in many types of paint which is used to coat fishing trawlers and recreational boats and contribute to metal contamination in beach sediments and marine environments. Over time, as the painted surfaces degrade due to wear and tear, or during maintenance activities such as scraping and repainting, zinc particles may be released into the surrounding water. Thus, zinc input into these sediments could originate from fishing activities and recreational activities occurring in Arambol and Calangute **(Bhutia et al. 2023).** Moreover, anthropogenic sources such as urbanisation, industrial and agricultural, fishing and recreational activities, discharge of sewage waste contribute to the enrichment of these metals in the beach sediments. The rate of release of metals via anthropogenic activities is higher than the natural processes often resulting in the enrichment of metals in sediments subsequently leading to metal contamination.

Fig. 4.2.1 Concentration of Ni in Beach Sediments

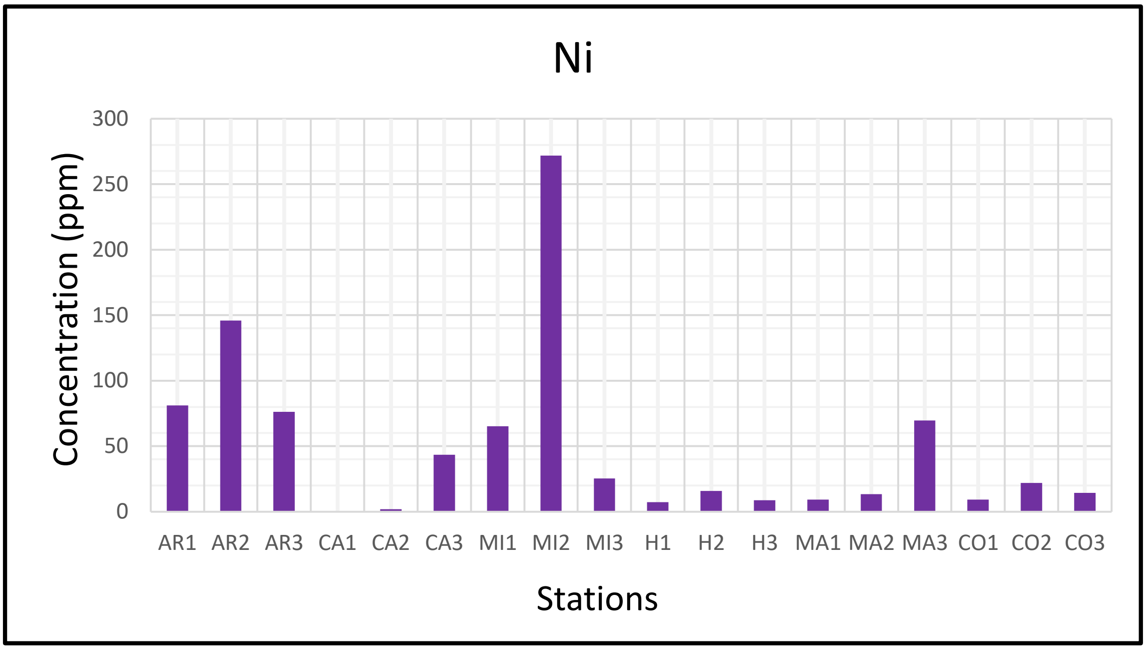


Fig. 4.2.2 Concentration of Co in Beach Sediments

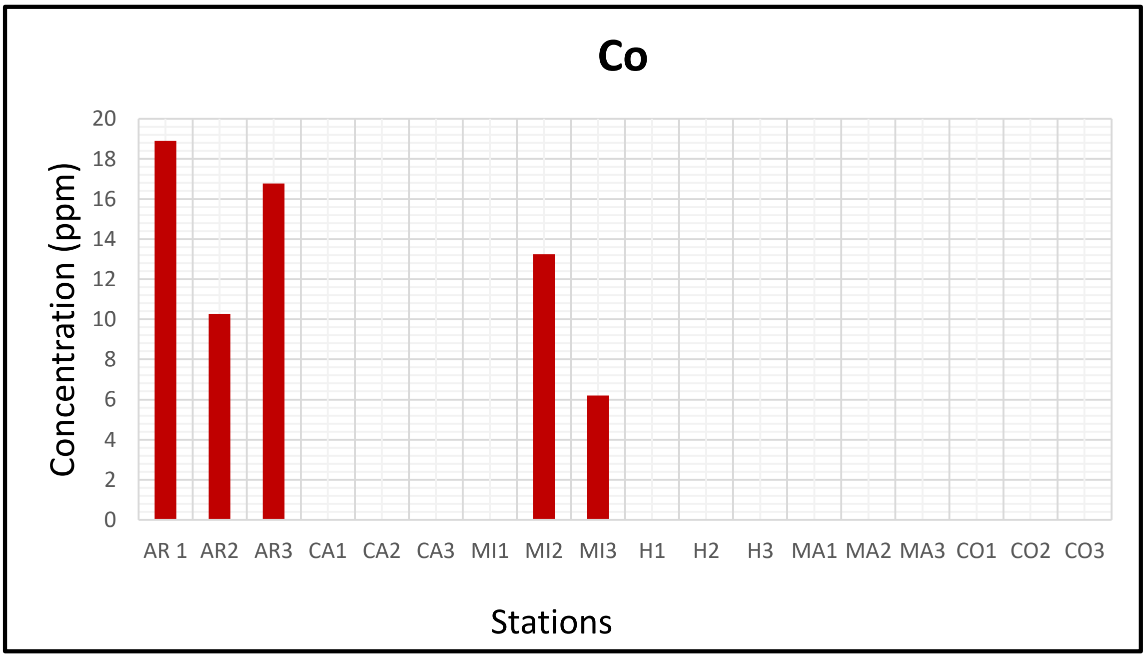


Fig. 4.2.3 Concentration of Cu in Beach Sediments

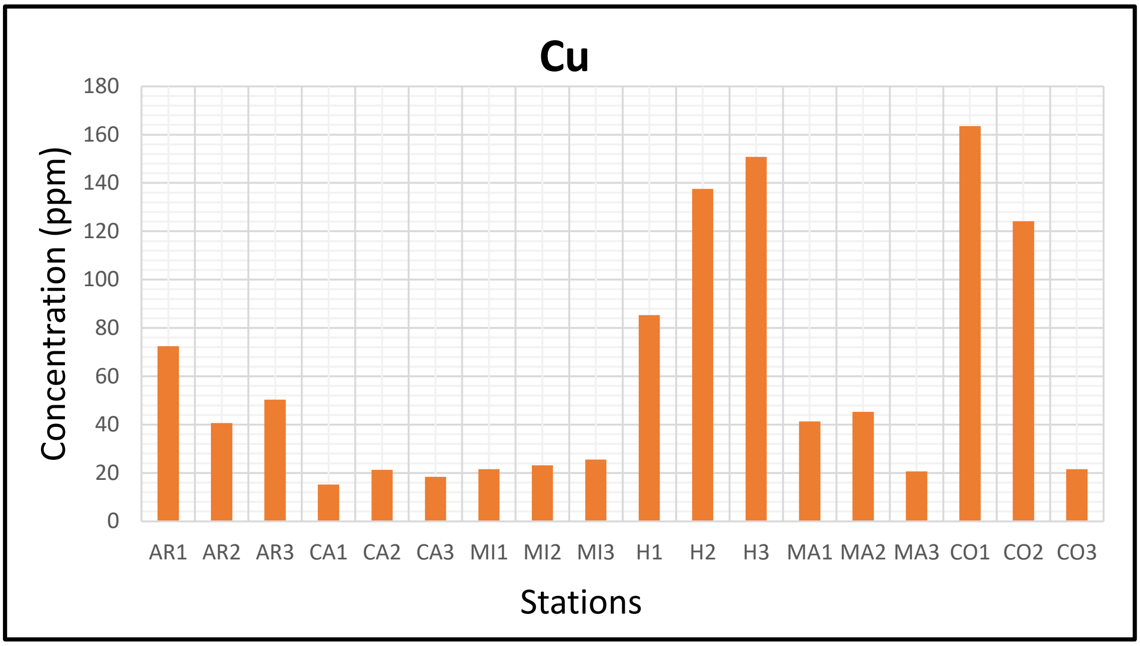


Fig.4.2.4 Concentration of Zn in Beach Sediments

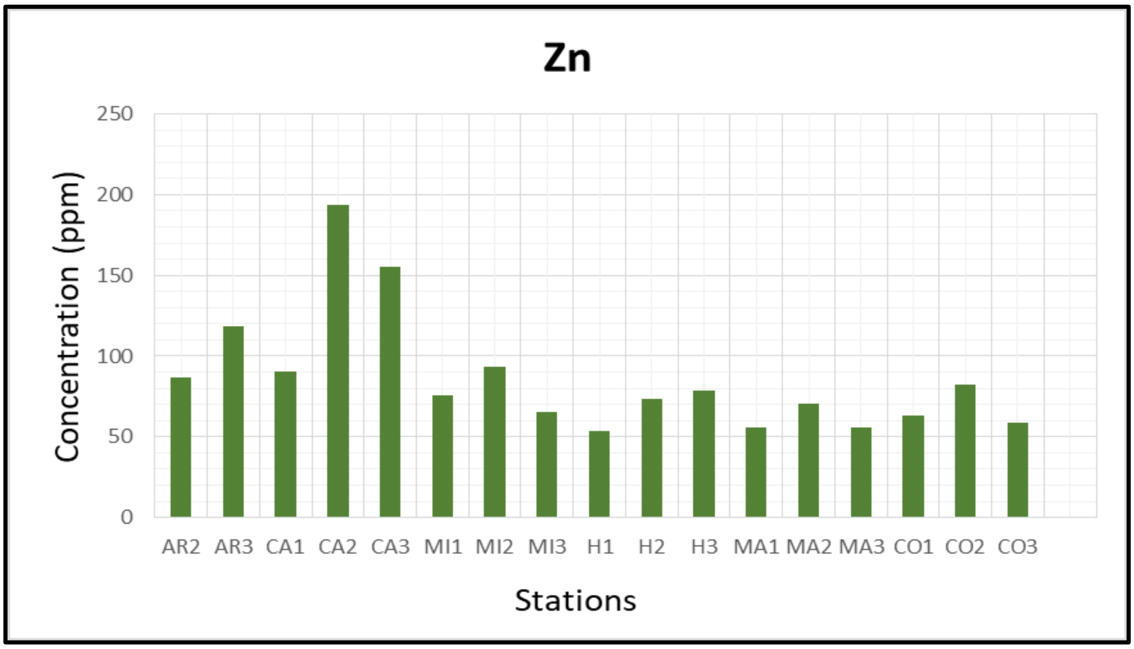


Fig.4.2.5 Concentration of Mn in Beach Sediments

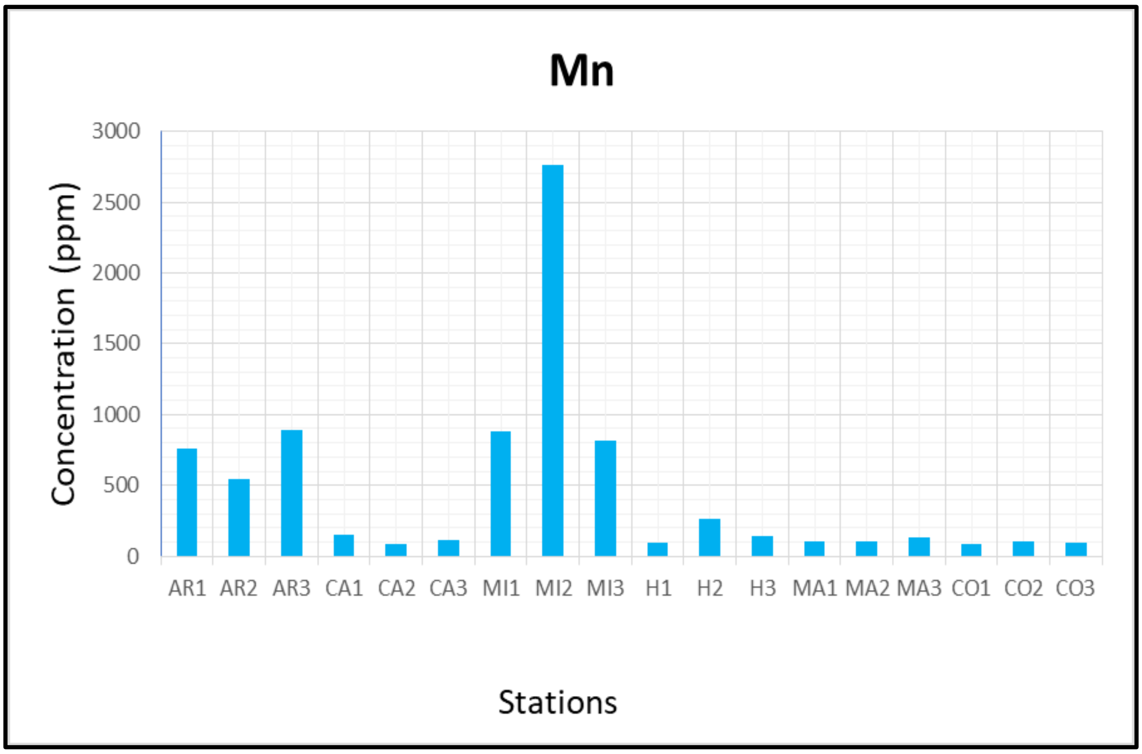
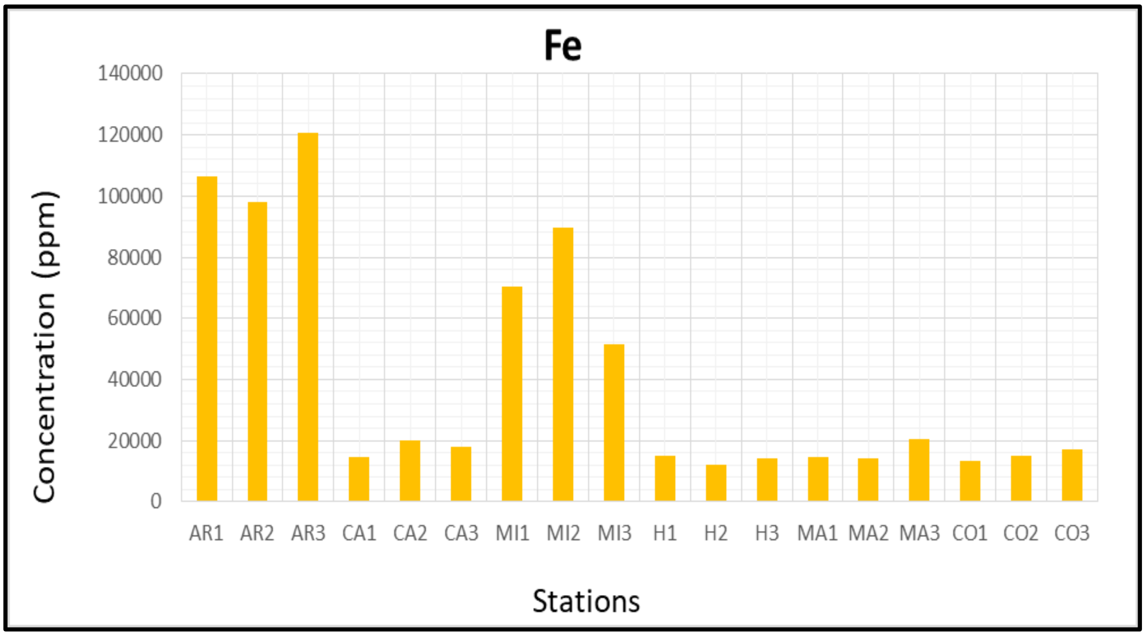


Fig.4.2.6 Concentration of Fe in Beach Sediments



Fe and Mn concentrations are notably high compared to Ni, Co, Cu, and Zn. For instance, Ni levels range from 1.925 ppm in CA 2 to 271.875 ppm in MI 2, while Co concentrations remain below detection limits in most stations, with exceptions like AR 3 (16.775 ppm) and reduced levels in MI 3. Cu levels vary from 15.15 ppm in CA 1 to 163.575 ppm in CO 1, while Zn concentrations range from 5.8 ppm in H1 to 193.775 ppm in CA 2. Mn concentrations peak at 27.66 ppm in MI 2 and reach a low of 88.4 ppm in CO 1, while Fe levels range from 12020 ppm in H2 to 97845 ppm in AR 2, surpassing the upper crustal average. These metals show enrichment in beach sediments, attributed to anthropogenic activities such as iron-ore mining, industrial discharge, agricultural waste, and sewage. Open-cast iron ore mining operations in Goa are identified as a primary contributor to Fe and Mn enrichment in sediments, carried by rivers and deposited along beaches during heavy runoff. Zinc levels are notably high in certain North Goa stations, likely influenced by fishing and recreational activities involving zinc-based paint on boats. Urbanization, industrialization, agriculture, fishing, and recreational activities further contribute to metal contamination in beach sediments, surpassing natural processes. The total metal analysis reveals significant variations in metal concentrations across different stations, with Fe and Mn levels notably higher compared to Ni, Co, Cu, and Zn. These elevated concentrations are attributed to anthropogenic activities such as iron-ore mining, industrial discharge, agricultural waste, and sewage. Open-cast iron ore mining operations are identified as major contributors to Fe and Mn enrichment, transported by rivers and deposited along beaches during runoff.

4.3 Metal Pollution indices

The Igeo was determined to understand the pollution status of metals the beach sediments of North and south Goa beaches (Table 4.3.1).

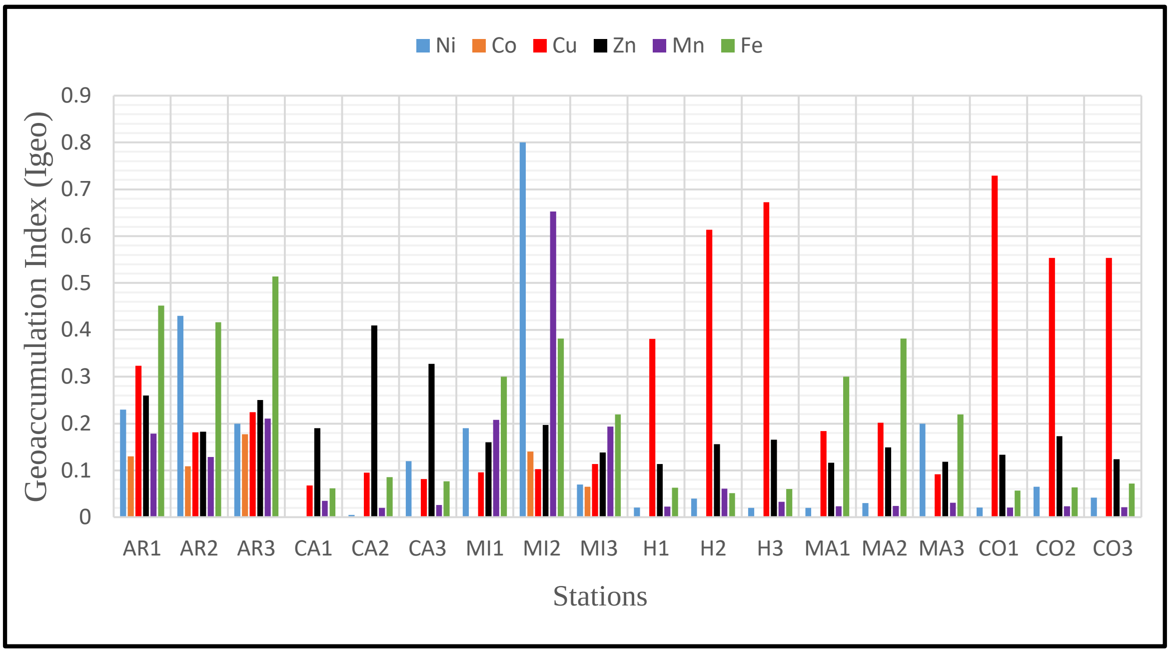
4.3.1 Geo- accumulation Index (Igeo)

Table 4.3.1Geo- accumulation Index (Igeo) considering average shale values as background concentrations.

Stations	Ni	Co	Cu	Zn	Mn	Fe
AR 1	0.23	0.13	0.3234	0.26	0.1785	0.4517
AR 2	0.43	0.1085	0.181	0.1826	0.1288	0.416
AR 3	0.2	0.1771	0.2243	0.25	0.2105	0.5138
CA 1	0	0	0.0675	0.1902	0.0349	0.0614
CA 2	0.005	0	0.0952	0.4093	0.0198	0.0853
CA 3	0.12	0	0.0817	0.3277	0.026	0.0767
MI 1	0.19	0	0.0959	0.16	0.2079	0.2998
MI 2	0.8	0.1399	0.103	0.1966	0.6528	0.3816
MI 3	0.07	0.0654	0.1137	0.1385	0.1933	0.2194
H 1	0.021	0	0.3804	0.1136	0.0229	0.0633
H 2	0.04	0	0.6136	0.1559	0.0612	0.0511
H 3	0.02	0	0.6725	0.1653	0.0332	0.06
MA 1	0.02	0	0.184	0.1166	0.0235	0.2998
MA 2	0.03	0	0.2019	0.1491	0.0238	0.3816
MA 3	0.2	0	0.0917	0.1181	0.0307	0.2194
CO 1	0.021	0	0.7294	0.1334	0.0208	0.0572
CO 2	0.065	0	0.5534	0.1733	0.0237	0.0636
CO 3	0.042	0	0.5534	0.124	0.0216	0.0721

The table (4.3.1) depicts sediment contamination levels of various metals across different stations showing polluted to moderately polluted contamination showing Igeo values below 1 and belong to Igeo class 1 as shown in Fig. 4.3.1.

Fig.4.3.1 Igeo values of metal in the surface beach sediments



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

Table 4.3.2 Contamination Factor (CF) and Pollution Load Index (PLI)

	CF						
Stations	**Ni**	**Co**	**Cu**	**Zn**	**Mn**	**Fe**	**PLI**
AR 1	1.19	0.99	1.61	1.29	0.88	2.25	0.806
AR 2	2.14	0.54	0.90	0.91	0.64	2.07	0.211
AR 3	1.12	0.88	1.11	1.24	1.04	2.56	0.617
CA 1	0	0	0.33	0.94	0.09	0.30	0.32
CA 2	0.02	0	0.47	2.03	0-17	0.42	0.22
CA 3	0.63	0	0.40	1.63	0.12	0.38	0.11
MI 1	0.95	0	0.47	0.79	1.03	1.49	0.14
MI 2	3.99	0.69	0.51	0.98	3.25	1.90	1.446
MI 3	0.10	0.32	0.56	0.69	0.96	1.09	1.05
H 1	0.23	0	1.89	0.56	0.11	0.31	0.12
H 2	0.12	0	3.05	0.77	0.30	0.25	0.11
H 3	0.12	0	3.35	0.82	0.16	0.29	0.13
MA 1	0.13	0	0.91	0.58	0.11	0.30	0.12
MA 2	0.19	0	1.00	0.74	0.11	0.30	0.03
MA 3	1.02	0	0.45	0.58	0.15	0.43	0.05
CO 1	0.13	0	3.63	0.66	0.10	0.28	0.12
CO 2	0.32	0	2.75	0.86	0.11	0.31	0.15
CO 3	0.21	0	0.47	0.61	0.10	0.35	0.16

The table depicts contamination levels of various metals across different stations. Nickel (Ni) contamination is predominantly low in most of the stations (CA 2, CA 3, MI 1, MI 3, H 1, H2, H 3, MA 1, MA 2, MA 3, CO 1, CO 2, CO 3). Arambol (AR 1, AR 2, AR3). Co contamination remains generally low across all stations, with values below 1. Cu showed low contamination in most of the stations (AR 2, CA1, CA 2, CA3, MI 1, MI2, MI 3) while moderate contamination was exhibited by Arambol (AR 1, AR 3), H 1 and CO 2 and considerable contamination was observed in Harbour (H 2, H3) and CO 1. Zn contamination is primarily low in most stations with the majority of stations having contamination factors below 1. Manganese (Mn) and Iron (Fe) levels generally indicate low contamination, with most values below 1 while moderate contamination was found in AR 2. CA 1, CA3, MI with values ranging between 1- 3. Mn showed low contamination in almost all stations, however AR 3 and M1 2 showed moderate and considerable contamination respectively. Fe contamination was low in most stations, while some stations (AR 1, AR2, AR 3, MI 1, MI 2, MI 3) from North Goa showed moderate contamination ranging between values 1 – 3.

Similarly, Pollution Load Index (PLI) was computed for metals at different stations (Table 4.3.2). The PLI values for most of the stations indicated no metal pollution in sediments showing values less than 1. However, Miramar (MI 2 and MI 3) showed values exceeding 1 indicating metal pollution in sediment.

Fig. 4.3.2 Contamination Factor (CF) of metal in the surface beach sediments

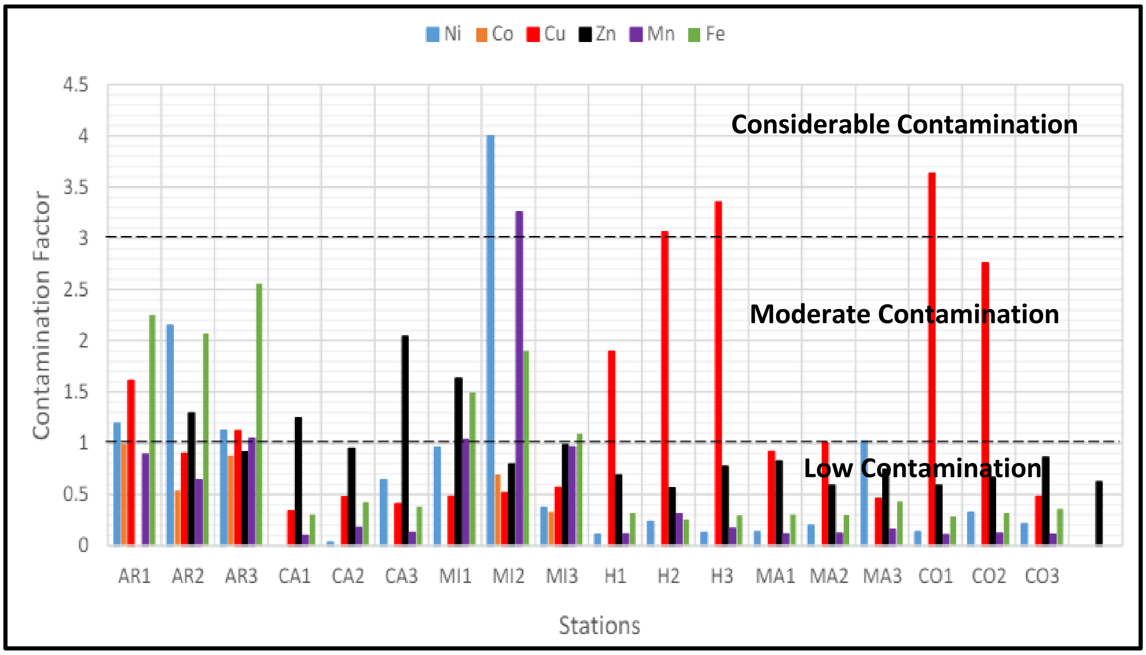
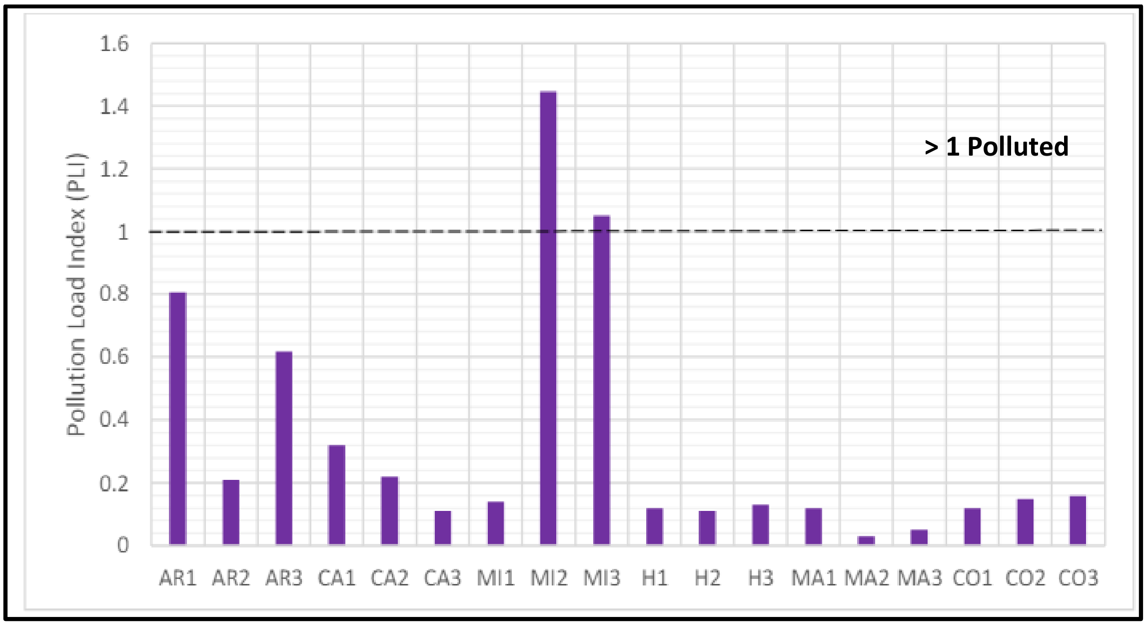


Fig. 4.3.3 Pollution Load Index (PLI) of metal in the surface beach sediments



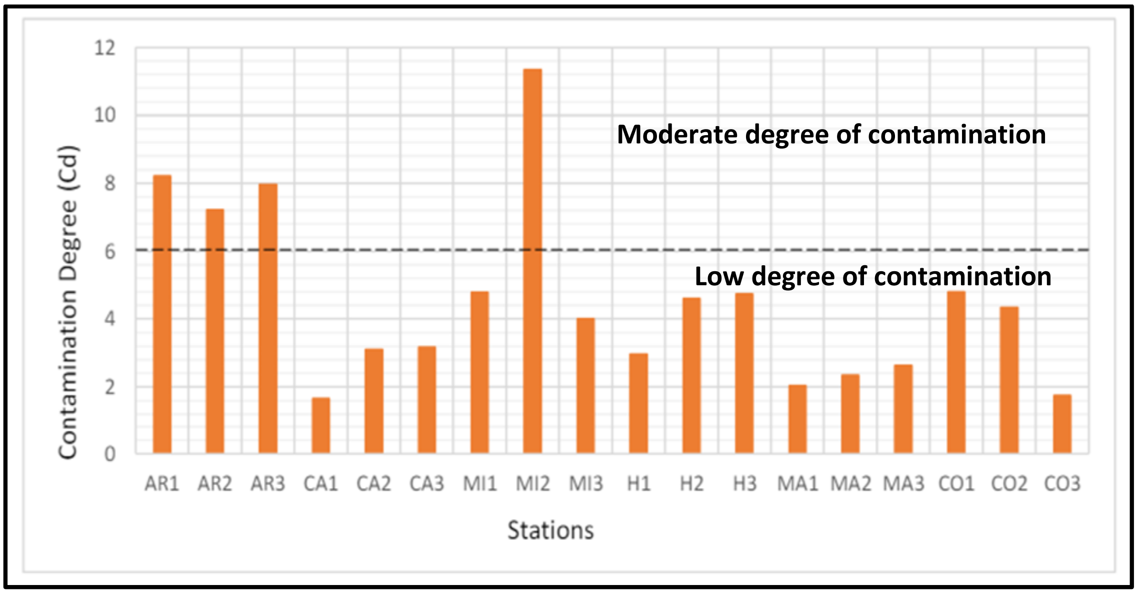
4.3.3 Contamination Degree (Cd)

Table 4.3.3 Contamination Degree (Cd)

Stations	Contamination Degree
AR 1	8.21
AR 2	7.21
AR 3	7.97
CA 1	1.66
CA 2	3.11
CA 3	3.16
MI 1	4.79
MI 2	11.34
MI 3	4.01
H 1	2.97
H 2	4.6
H 3	4.74
MA 1	2.03
MA 2	2.34
MA 3	2.63
CO 1	4.8
CO 2	4.35
CO 3	1.74

The Contamination Degree (Cd) was computed for metals at different stations (Table 4.3.3). The Cd values indicated low degree of contamination for most of the stations with Cd values ranging between 0 – 6. However, few stations like Arambol (AR 1, AR 2, AR3) Miramar (MI 1) surpassed values of 1 showing a moderate degree of contamination in these stations. (Fig.4.3.3).

Fig. 4.3.4 Cd values of metal in the surface beach sediments



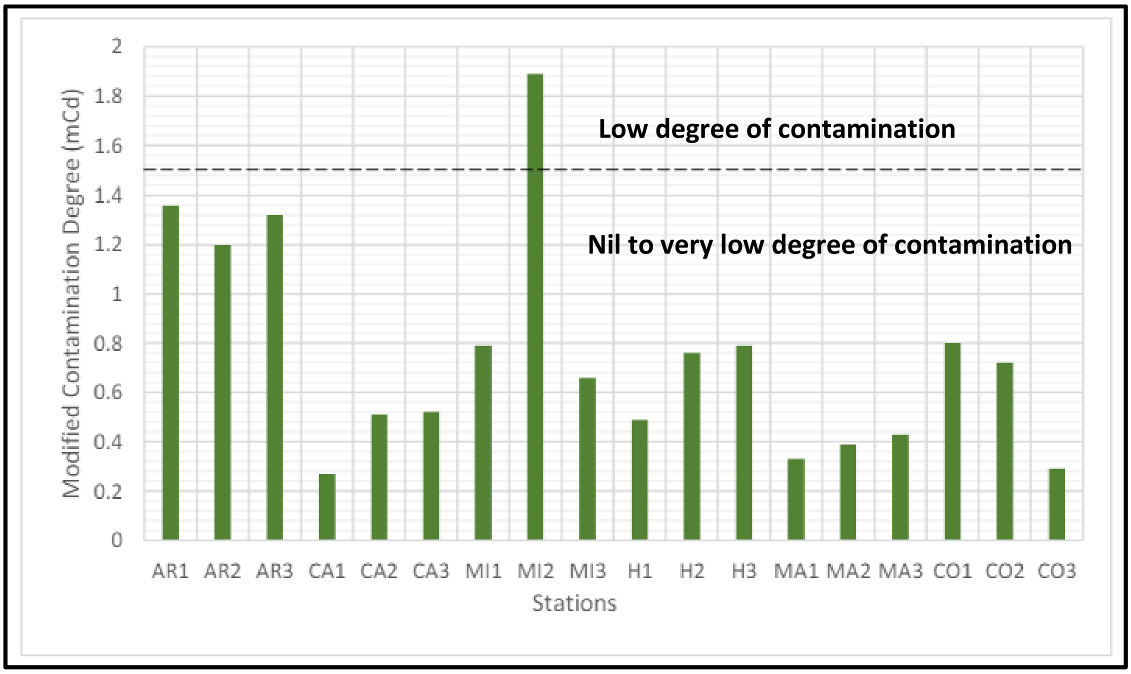
4.3.4 Modified Degree of Contamination (mCd)

Table 4.3.4 Modified Contamination Degree (mCd)

Stations	Modified Degree of Contamination
AR 1	1.36
AR 2	1.2
AR 3	1.32
CA 1	0.27
CA 2	0.51
CA 3	0.52
MI 1	0.79
MI 2	1.89
MI 3	0.66
H 1	0.49
H 2	0.76
H 3	0.79
MA 1	0.33
MA 2	0.39
MA 3	0.43
CO 1	0.8
CO 2	0.72
CO 3	0.29

The Modified Degree of Contamination (mCd) was computed for metals at different stations (Table 4.3.4). The mCd values indicated nil to a very low degree of contamination for most of the stations with mCd values ranging between 0–1.5. However, station MI 2 exceeded 1.5 indicating a moderate degree of contamination at this station. (Fig.4.3.5).

Fig. 4.3.5 Modified Degree of Contamination (mCd) in the surface beach sediments



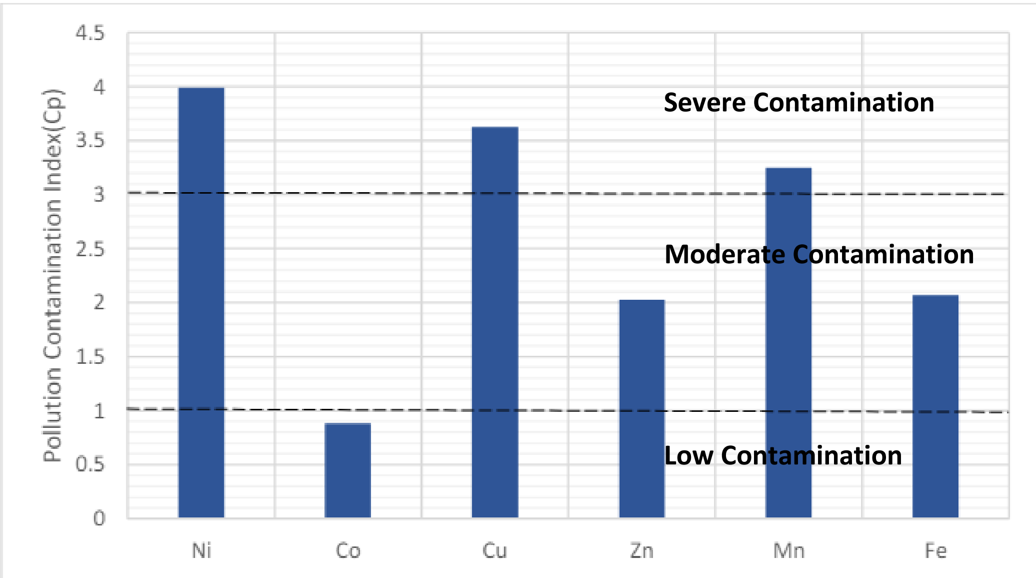
4.3.5 Pollution Contamination Index (Cp)

Table 4.3.5 Pollution Contamination Index (Cp) in the surface beach sediments.

Metals	**Contamination level**
Ni	3.99
Co	0.88
Cu	3.63
Zn	2.03
Mn	3.25
Fe	2.07

The Pollution Contamination Index (Cp) was determined for the metals (Ni, Co, Cu, Zn, Mn and Fe) exhibiting low, moderate and severe contamination. (Table 4.3.5). The Cp values indicated low contamination for Co with values below, while Zn and Fe reported moderate contamination with Cp values ranging between1–3. However, Ni, Cu and Mn exceeded 3 indicating severe or very severe contamination (Fig.4.3.6).

Fig. 4.3.6 Pollution Contamination Index (Cp) in the surface beach sediments



4.3.6 Pollution Ecological Risk

Table 4.3.6 Potential Ecological Risk Index (E^i_r) and Ecological Risk Index (Ri)

	Potential ecological risk factor (E^i_r)					Ecological risk index (Ri)
Stations	**Ni**	**Co**	**Cu**	**Zn**	**Mn**	
AR 1	5.96	4.95	8.05	1.29	0.88	21.13
AR 2	10.73	2.7	4.5	0.91	0.64	19.48
AR 3	5.61	4.4	5.55	1.24	1.04	17.84
CA 1	0	0	1.65	0.94	0.09	02.68
CA 2	0.14	0	2.35	2.03	0.17	4.69
CA 3	3.19	0	2	1.63	0.12	6.94
MI 1	4.79	0	2.35	0.79	1.03	8.96
MI 2	19.9	3.45	2.55	0.98	3.25	30.13
MI 3	1.87	1.6	2.8	0.69	0.96	7.92
H 1	0.53	0	9.45	0.56	0.11	10.65
H 2	1.17	0	15.25	0.77	0.3	17.49
H 3	0.64	0	16.75	0.82	0.16	18.37
MA 1	0.68	0	4.55	0.58	0.11	5.92
MA 2	0.98	0	5	0.74	0.11	6.83
MA 3	5.11	0	2.25	0.58	0.15	8.09
CO 1	0.68	0	18.15	0.66	0.1	19.59
CO 2	1.62	0	13.75	0.86	0.11	16.34
CO 3	1.05	0	2.35	0.61	0.1	4.11

The values of potential ecological risk factor (E^i_r) and the ecological risk index (RI) are given in Table 4.3.6. The average of (E^i_r) of Ni, Co, Cu, Zn and Mn was less than 40, and thus suggested low ecological risk in the surface beach sediments of North and South Goa beaches. . The order of the average of potential ecological risk coefficient (E^i_r) declined in the following sequence: Cu > Ni > Co > Zn > Mn. The

Risk Index (RI) ranged from 02.68 (CA 1) to 21.13 (AR 1), thereby indicating low risk level at all the stations where the RI values were below 40. It is evident from the above data that there is no significant environmental risk occurring in the beach sediments of North and South Goa beaches in the present study. Study carried out by **Goankar et al. (2021)** also showed similar results of lower risk indicating lower ecological risk indicating no significant environmental risk in the Mandovi Estuary similar to the present study.

CHAPTER 5: SUMMARY AND CONCLUSIONS

The present study was conducted with objectives to study the organic carbon content in the surface beach sediments of North and South Goa beaches, understand the distribution of total metals in the surface beach sediments of North and South Goa beaches and assess the pollution indices of beach sediments. The study area comprised of three beaches from North Goa (Arambol, Calangute and Miramar) and three beaches from South Goa (Harbour, Majorda, Colva). The sediment samples were subjected to sedimentological (Total organic carbon analysis) and geochemical analysis (total metal analysis). The pollution indices including Geoaccumulation Index (Igeo), Contamination Factor (CF), Pollution Load Index (PLI), Contamination Degree (Cd), Modified contamination degree (mCd), Pollution Contamination Index (Cp) and potential ecological risk were computed to understand the contamination and pollution of metals in sediments.

The study revealed that the sediment components and TOC that was attributed to prevailing environmental conditions at the sampling sites. Apart from Arambol, the total carbon content in the sediments of Calangute and Miramar beaches in North Goa was comparatively low, while Harbour, Majorda, and Colva beaches showed relatively consistent levels. This disparity may stem from Calangute and Miramar being urbanized areas with limited vegetation cover, resulting in lower organic carbon content. Conversely, Harbour's status as a fishing zone may lead to increased organic carbon levels due to the decomposition of marine biota. Additionally, Majorda and Colva, characterized by rural settlements with abundant vegetation cover, likely experience higher input of organic matter, contributing to more stable levels of total carbon content in their sediments. The pollution indices computed for metals at different stations indicated depicted various levels of contamination. The Geoaccumulation Index (Igeo) indicated unpolluted to moderately polluted levels, Contamination Factor (CF) showed low,moderate and considerable contamination, Pollution Load Index (PLI) showed no metal pollution for most of the sediments, while it showed metal pollution for Miramar (MI2 and MI 3), Contamination degree(Cd) indicated low degree of contamination, except Arambol exhibed moderate degree of contamination), Moderate degree of Contamination (mCd) indicated nil to very low degree of contamination for almost all stations , except MI 2 showed low degree of contamination, Pollution Contamination Index (Cp) showed low, moderate and severe or very severe contamination and potential ecological risk revealed lower risk indicating lower ecological risk indicating no significant environmental in the beach sediments of North and South Goa beaches in the present study.

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