STUDIES ON TRACE METALS IN COASTAL SURFACE SEDIMENTS OF MANDOVI AND ZUARI ESTUARIES, WEST COAST OF INDIA

A Dissertation for

Course code and Course Title: MSC 617 Discipline Specific Dissertation

Credits: 16

Submitted in partial fulfilment of Master's Degree

M.Sc. in Marine Sciences

by

DIPTESH DEELIP KOLVALKAR

Seat number: 22P0400008

ABC ID: 376864818445

P.R.No.: 201811025

Under the Supervision of

Prof. VISHNU MURTY MATTA

School of Earth, Ocean and Atmospheric Sciences

Marine Sciences

GOA UNIVERSITY

April 2024

Examined by:

Seal of the School

DECLARATION BY STUDENT

I hereby declare that the data presented in this Dissertation report entitled, "**Studies on trace metals in coastal surface sediments of Mandovi and Zuari estuaries, west coast of India**" is based on the results of investigations carried out by me in the **Marine sciences** at the **School of Earth, Ocean and Atmospheric Sciences**, Goa University under the Supervision of **Prof. Vishnu M. 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.

I hereby authorize the University authorities to upload this dissertation on the dissertation repository or anywhere else as the UGC regulations demand and make it available to any one as needed.

DIPTESH KOLVALKAR
Seat No.: 22P0400008
M.Sc. Marine Sciences
School of Earth, Ocean and Atmospheric Sciences

Date: 29/04/2024
Place: Goa University

COMPLETION CERTIFICATE

This is to certify that the dissertation report "**Studies on trace metals in coastal surface sediments of Mandovi and Zuari estuaries, west coast of India**" is a bonafide work carried out by **Mr. Diptesh Deelip Kolvalkar** under my supervision in partial fulfilment of the requirements for the award of the degree of **Master of Sciences** in the Discipline **Marine Sciences** at the **School of Earth, Ocean and Atmospheric Sciences, Goa University**.

29/04/2024

Date: 29/04/2024

Prof. Vishnu Murty Matta
Marine sciences

29/4/24

Dean
Marine Sciences
School of Earth, Ocean and Atmospheric Sciences
Date:
Place: Goa University

SEOAS, GOA UNIVERSITY TALEIGAO PLATEAU GOA

Seal of the School

AKNOWLEDGEMENT

Firstly, I would like to express my immense gratitude and would like to whole hearted thank my guide, **Prof. Dr. Vishnu Murty Matta**, School of Earth, Ocean and Atmospheric Sciences, for his valuable guidance, support and untiring effort during the course of the dissertation. He has been a great source of motivation and encouragement for me take up this topic as my study.

Also, I am grateful to **Sr. Prof. Sanjeev C. Ghadi**, Dean, School of Earth, Ocean and Atmospheric Sciences, and all the faculties of the Marine Sciences Sr. **Prof. C. U. Rivonkar**, **Prof. Dr. M. R. Nasnodkar**, **Dr. Joshua D'Souza**, **Dr. Sheryl O. Fernandes**, **Prof. Manjusha Madkaikar**, **Dr. Nikita Mangeshkar** for their willingness to help me whenever approached.

I extend my sincere thanks to **Ms. Sitam**, **Mrs. Mahima**, **Mrs. Utkarsha**, **Mr. Dipam**, **Mr. Madhukar** and **Mrs. Gayatri** and all other non-teaching and labouratory staff members.

My sincere appreciation and gratitude also extends to all my friends and classmates Gaurav, Rahul, Sumedha, Glennis, Krutika and Varsha for their support throughout the course of research work.

Lastly, I would like to express my profound gratitude to my parents for their understanding, encouragement and un wavering support during this course of my study.

Diptesh D. Kolvalkar

CHAPTER 1

INTRODUCTION

INTRODUCTION

The area where land meets a significant amount of water, such as the sea or ocean, is called a coastal zone. In addition, the coastal zone is the land surface affected by marine processes. It extends from the seaward point where waves interact significantly with the seabed to the landward limit of tides, waves and wind-blown coastal dunes. In the coastal zone, which is a dynamic region of the earth's surface, marine and atmospheric processes combine to form rocky coasts, as well as beaches, dunes, barriers, tidal inlets, and deltas. While waves, tides, water temperature and salinity are the main processes of the sea. Atmospheric processes include temperature, precipitation, and wind. Rich ecosystems such as mangroves, seagrass and salt marshes are also supported by the coast.

The word "estuary" is derived from the Latin word aestuarium meaning tidal inlet of the sea, which is itself derived from the term aestus, meaning tide. There have been many definitions proposed to describe an estuary. The most widely accepted definition is: "a semi-enclosed coastal body of water, which has a free connection with the open sea, and within which seawater is measurably diluted with freshwater derived from land drainage" **(Pritchard, 1967)**. However, this definition excludes a number of coastal water bodies such as coastal lagoons and brackish seas.

Estuaries form a transition zone between fluvial and marine environments and are an example of an ecotone. Estuaries are subject to both oceanic influences, such as tides, waves, and saltwater input, and fluvial influences, such as freshwater and sediment flow. The mixing of seawater and freshwater ensures high nutrient levels in both the water column and sediments, making estuaries some of the most productive natural habitats in the world **(Wolanski, 2007)**.

The estuary is a dynamic ecosystem, connected to the open sea and penetrated by sea water according to the tidal rhythm. Tidal influences in estuaries can have a non-linear impact on water movement and have significant impacts on ecosystems and water flows. Sea water entering the estuary is diluted by fresh water from rivers and streams. Dilution patterns vary between estuaries and depend on the amount of freshwater, tidal differences, and the degree of evaporation of estuarine water **(Wolanski, 2007)**. Estuaries are often classified based on topographic features and water circulation patterns. These waters have a variety of names, including bays, harbours, lagoons, embayment’s or straits, but some of these waters do not necessarily meet the definition of an estuary above and may be completely salty.

Fairbridge, (1980) defined an estuary as an inlet of the sea reaching into the river valley as far as the upper limit of tidal rise, usually being divided into three sectors:

1) A sub-marine or estuary that has unrestricted access to the open sea.
2) A middle estuary, subjected to strong salt water and fresh water mixing.
3) An upper or fluvial estuary characterized by fresh water but subjected to daily tidal action.

An estuary can be classified based on its geomorphology, circulation pattern (salinity distribution), and tidal range. According to geomorphology, estuaries are divided into drowned river valleys, estuaries, dune-built estuaries, fjords and tectonic estuaries. Based on salinity estuaries can be divided into:

a) Salt-wedge estuaries, where freshwater flow is greater than tidal flood flow,

b) Partially mixed estuaries, where upwelling occurs.

Typically, estuaries form a transition zone between river and marine environments. All estuaries have free connectivity, either continuous or intermittent **(Gazette, 2006)**. There are two different types of estuaries namely river type and basin type in Sri Lanka as well as in other countries. Estuaries are places where rivers and streams flow directly into the sea through relatively narrow channels, and estuaries are in basins where rivers and streams first flow into a relatively shallow basin before emptying into the sea. The geological time scale indicates that estuaries are inactive, resulting in life expectancy of only a few thousand years and no more than tens of thousands of years. Weather events, such as storms and floods, can accelerate the development of an estuary and significantly shorten its lifespan **(Schubel & Hirschberg, 1978).**

The environmental conditions of estuarine habitats are influenced by,

1) Short-term fluctuations caused by tides and waves

2) Seasonal variations caused by the monsoonal cycle.

These estuarine waters are among the most productive in the world, not only in terms of phytoplankton primary production, but also in their importance as reproductive and nursery grounds for a range of fish species **(List, 1967; Burton, 1976)**.

The investigation of estuarine waters, sediments and biota for trace metals is typically carried out for various reasons:

1) To consider the general level of trace metals in an estuary.

2) To monitor water quality with time,

3) To study the primary processes in estuaries which organize trace metal behaviour and,

4) To study the pollution due to increase in the levels of trace metals **(Riley and Chester, 1981)**.

Both natural and man-made sources, including mining, urbanization, treated or untreated industrial waste, and municipal sewage effluents, can introduce trace metals into the estuarine ecosystem **(Chakraborty and Babu, 2015)**. Natural processes, including rock weathering, erosion, and the dissolution of salts that dissolve in water, are some of the ways that metals have always found their way into the estuarine ecosystem **(Jordao et al., 2002)**. However, the advancement of human civilization has also sparked expansion in a variety of other sectors, such as mining, industry, tourism, and agriculture.

Metals released into the atmosphere as a result of mining, industrial processes, agricultural practices, tourism, and other human activities are carried to estuaries and finally settle in sediments due to the processes of flocculation and sedimentation **(Fernandes and Nayak, 2011)**.

Estuaries and nearby oceans primarily receive sediment from rivers **(Rao, 2016; Lee et al., 2017)**. In addition to natural processes, human activities like mining, the disposal of industrial, agricultural, and domestic waste, and waste management practices release metals into the aquatic system **(Rezaei and Sayadi, 2015)**. Metals of various speciation and oxidation states are naturally found in the earth's crust **(Hill MK, 2010)**. Metal concentrations in sediments, soils and water vary based on rock type, geophysical condition, and geographical location **(Martin and Whitfield, 1983, p. 265–96)**. Metals are transported to estuaries in the form of suspended particles or dissolved ions, which are then removed from the water, absorbed, and eventually incorporated into the sediment. As a result, estuarine sediments serve as important metal reservoirs, and their concentrations are influenced by a number of physical and chemical factors, such as the mineralogical and chemical composition of suspended matter, anthropogenic activities, biological enrichment, and physico-chemical processes **(Singh et al., 2005; Jain et al., 2007)**. Furthermore, sediments play an important role in the transportation of contaminants as suspended particles in the water column that are attached to fine-grained organic and inorganic materials **(Birch, 2017)**.

Sediments not only have a high ability to absorb metals and organic pollutants from the surrounding water column **(Tam and Wong, 2000)**, but they can also act as a source of contaminants in aquatic systems **(Singh et al., 2005)**. Many researchers have confirmed that sediment re-suspension results in the release of metal into aquatic systems **(Saulnier and Mucci, 2000; Kalnejais et al., 2010).** Nevertheless, sediments are called 'trace element traps' since they eventually absorb almost all heavy metals that enter the aquatic environment **(Eugenia et al., 2004; Karthikeyan et al., 2007)**. This ability of sediments to trap heavy metals has both positive and negative consequences for aquatic ecosystems. On the one hand, sediment can help to prevent contaminants from spreading rapidly throughout the water column, lowering the risk of harm to aquatic organisms. However, if disturbed or re-suspended, these trapped metals can be released back into the water column, posing a threat to the ecosystem. Altogether, recent investigations have indicated that toxic metals are increasingly polluting sediments in estuaries and coastal areas due to rapid industrialization and urbanization **(Manta et al., 2002; Feng et al., 2004; Liu et al., 2007)** and this requires monitoring of pollutants in a coastal environment.

Coastal areas have seen a significant increase in anthropogenic metal input due to urbanization and industrialization in the 20th century, accounting for approximately 80% of human-caused pollution **(Feng et al., 2008)**. The coastal environment is a complex system with physical, chemical, and biological

activities that influence the metal biogeochemical cycle. Metal pollution in coastal areas is a result of thehuman activity. Sources include mining, metal product fabrication, solid waste disposal, fossil fuel burning, and municipal and industrial waste discharge **(Salmons, 1995)**. Acid rain has the ability to leach these metals and accelerate the release of hazardous metals into the environment from sources of pollution **(Müller et al., 2000)**.

Once toxic metals enter coastal environments, they tend to accumulate in sediments due to particle scavenging and settling. Therefore, high concentrations of toxic metals are often detected in sediments. Trace amounts of metals are necessary micronutrients for growth and metabolism in many organisms. But excessive metals can harm organisms and ecosystems **(Underwood, 2012)**. In general, fine-grained sediments have a higher specific surface area, making them one of the main carriers of toxic metals. Many studies have shown that coastal sediments serve as a repository for metal pollutants and record pollution history over time **(Feng et al., 2004; RF and HJ, 1989; Qian et al., 2011)**. Overall, toxic metals in coastal sediments can harm both the marine ecosystem and human health; therefore, monitoring and regulating harmful metal levels in coastal sediments is critical for sustaining the health and sustainability of coastal habitats, particularly in Goa **(NIO, 1979)**.

The current investigation will be conducted in the Mandovi and Zuari estuaries, which are located on India's west coast. These two important rivers in Goa are under threat from mining activity along their shores **(Singh et al., 2009)**, because both Mandovi and Zuari estuaries have been used for the transportation of iron and ferromanganese ores to Marmugao harbor for the past six decades **(Manoj et al., 2009; Alagarsamy, 2006)**. The transportation of ores to Marmugao harbor might have led to increased sedimentation and pollution in the estuaries, which may affect marine life and biodiversity. Industries located near the mouths of the rivers also contribute to the pollution of the Arabian Sea **(NIO, 1979)**, further threatening the fragile ecosystem of the estuaries. Despite these challenges, the Mandovi and Zuari estuaries remain crucial for fishing and tourism activities.

But in recent years, due to a halt in mining activities in Goa, which were the primary sources of metals for the Mandovi and Zuari rivers, an attempt has been made to examine the distribution and evaluation of pollution levels in the Mandovi and Zuari estuarine coastal surface sediments. This study will also fill a gap in the literature by analysing current levels of metal pollution in the sediments of the Mandovi and Zuari estuaries

1.1 REVIEW OF LITERATURE

Several researchers have studied the distribution of metals in sediments, water, and suspended material in numerous estuaries and rivers in India and across the world. Among the studies are the following:

Algarsamy, (2006) investigated the distribution and seasonal change of trace metals in sediments from the Mandovi Estuary. The concentration of sedimentary iron has been found to be significantly greater than that shown in the rest of India's estuarine areas, which may have resulted from excessive discharges during the transport of iron. Elevated Igeo values indicate that surface sediments are moderately or strongly distinguishing between natural and anthropogenic activity.

Singh et al., (2008) studied the seasonal variation of trace metals in the Mandovi Estuary. They discovered that trace metal concentrations were highest before the rainy season, then during the monsoon season, and finally after the monsoon season. Furthermore, they found that water concentrations are higher than those seen in the Indian Ocean and its average seawater composition. These elevated levels may be linked to the intensified mining activities that are occurring during this period.

Singh et al., (2010) investigated the seasonal change of trace metals in the Zuari Estuary. They observed an increase in trace metal concentrations (Zn, Fe, Cd, Co, and Cr) during the pre-monsoon, monsoon and post-monsoon periods. This might be due to land runoff, which is responsible for the distribution of these metals.

Magesh et al., (2011) After measuring the level of trace element pollution in the estuarine sediments, the effect of industrial effluents on the Tamiraparani Estuary was examined. 30 sites throughout the estuary were used to collect surface samples. For the purpose of determining the degree of contamination in the study region, variations in grain size and trace elements (Ni, Pb, Co, Cu, Zn, Cd, Mn, Fe and Al) enrichment factors (EF) as well as geo-accumulation indices (Igeo) were examined. According to Igeo values, the estuary has been severely polluted with Cd and only moderately contaminated with Zn and Pb. These metals come from neighboring chemical plants and harbor activities, which are their sources.

In coastal waters off the south-west coast of India, **Udayakumar et al., (2011)** investigated changes in dissolved metal concentrations of Cu, Pb, Cr, Ni, Zn, Cd and Hg. They found that there was an increase in Cu, Ni, Zn and Hg due to anthropogenic influence. Metal levels fluctuated in both their temporal and spatial distribution.

Shynu et al., (2012) studied the temporal and spatial variability of trace and major metals in suspended matter from the Mandovi estuary on India's central west coast. The collected samples were examined for

major (Al, Fe and Mn) and trace (Cu, Ni, Zn, Cr, Pb and Co) metals. Suspended particulate matter levels rise during the monsoon and pre-monsoon seasons, but major and trace metal concentrations fall from upstream to downstream locations along the estuary. However, suspended particulate levels remain consistently low during the post-monsoon. Cr, Cu and Pb concentrations are high during the post-monsoon. Enrichment factor and geo-accumulation index values of Mn indicate considerable to strong pollution in all seasons, while Cr, Ni and Zn during the monsoon and Cr during the post-monsoon exhibit moderate pollution. However, the settling of pollutant-borne particulates close to the discharge site allows a wide portion of the estuary to be free of significant contamination.

Manan et al., (2014) assessed the environmental and ecological risks of heavy metals in the sediments of Nador Lagoon in Morocco. They found higher concentrations of Cd, Cr, Cu, Ni, Pb and Zn in the sediment samples, along with the highest values of contamination factor, pollution load index, potential contamination index, contamination degree, modified degree of contamination and enrichment factor near the river discharges in Nador city due to the discharge of sewage and industrial waste without any pre-treatment. However, except for Nador City, the metal contamination in the sediments of the rest of the sampling stations was uncontaminated.

In the Mandovi estuary along the west coast of India, **Veerasingam et al., (2016)** analyzed concentrations of trace elements like Fe, Mn, Cu, Cr, Co, Pb and Zn from three sediment cores to assess the depositional trends of metals and their respective contamination levels. The enrichment of the trace metals indicated a higher than normal anthropogenic load due to mining activities.

Devanesan et al., (2017) assessed heavy metal levels and potential ecological risks in sediments collected from Poombuhar to the Karaikal shore on Tamil Nadu's south-east coast. Sediment samples from 20 locations were collected and examined for heavy metals (Ca, Ti, K, Al, Fe, Mg, Zn, Ni, Cr, V, Mn and Co). Calcium is the most abundant metal in sediments. Pollution indices revealed that sediments are moderately polluted by Ca, Fe, Co and Zn, whereas they are severely polluted by Ti, V, Cr, Mn, Ca and Pb as a result of human activities. However, the potential ecological risk index provided satisfactory results.

Iwegbue et al., (2018) investigated the distribution, sources and ecological risk of metals in the surficial sediments of the Forcados River and estuary in Nigeria's Niger Delta. Samples from nine locations were collected monthly for six months, including both rainy and dry seasons, and examined for eleven elements (Cd, Pb, Cr, Ni, Cu, Co, Ba, Mn, Zn, Fe and Al). Except for Cd, metal concentrations in Forcados river sediments were found to be below the regulatory control limits. In addition, the enrichment factor, geo-accumulation index, contamination, or pollution indices show that exposure to these metal concentrations has a low ecological risk, with the exception of Cd.

Rane and Matta, (2019) examine metal contamination in sediment cores from the Zuari and Kushavati rivers on India's west coast, with a focus on post-mining. The results showed that the Zuari river sediment core is moderately polluted with Mn, whereas the Kushavati river core is significantly polluted with Mn and moderately polluted with Fe and Cr with respect to Cu, Zn, Pb, Cr, and Co. When compared to the Zuari River, the Kushavati River is enriched with Fe, Mn, Al, and Cr. The study found that previous iron-ore mining activities had a significant environmental impact on both rivers.

Gaonkar and Matta, (2019) studied the effect of mining on metal concentration in the waters of India's Zuari Estuary. Metals such as Zn, Cr and Cu were found in very high levels near the river mouth, whereas Fe, Mn and Pb were found in relatively high concentrations near the river head. Except for Pb, seasonal fluctuations in trace metal concentrations revealed high concentrations during non-monsoonal months. Contamination factor studies found low Mn and Fe concentrations, intermediate Zn and Cu values, significant Cr values, and high Pb values. The investigation confirmed that mining has an impact on metal concentrations in the Zuari estuary.

Ren et al., (2020) investigated the concentrations, spatial distribution and pollution assessment of heavy metals in surficial sediments from upstream of the Yellow River in China. Surface sediment samples were taken from 122 sites to determine the spatial distribution of Fe, Mn, Cu, Ni, Zn, Cr, Pb and Cd. The mean concentrations of Cu, Ni, Cr and Cd were higher than the threshold effect levels (TEL), but Zn and Pb were lower. According to the probable effect level quotient, the combination of Cu, Ni, Zn, Cr, Pb and Cd has a 21% chance of being harmful upstream of the Yellow River. Higher amounts of all heavy metals occurred in the Qinghai and Gansu portions, but lower quantities of Cu, Ni and Zn were found in the Qinghai section.

Kumar et al., (2020) examined the distribution of heavy metals in seawater on India's south-east coast and assessed their ecological health risk. Eight water samples (surface and bottom) were taken along India's south-east coast and examined for heavy metals, including Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb, Cd and U. Except for U, all of the dissolved metals tested had somewhat higher amounts in bottom water than in surface water. According to the ecological risk assessment, the seawater at station 2 of the examined coast poses the highest ecological danger in terms of heavy metal levels. The risk assessment index value suggested that the coastal water provides no potential ecological or health concern in relation to the investigated heavy metal concentration.

Vineethkumar et al., (2020) used trace element concentrations in **c**oastal sediments in Kerala, India's southwest coast, to estimate pollution indices and evaluate hazards. At nearly all locations, Fe concentrations were higher than those of As, Cd, Cr, Zn, Ni, Pb and Ti. The enrichment factor for As is the highest when compared to the other elements in the sediment sample, and the contamination factor

values indicate that the research area is low in contamination. Furthermore, the geo-accumulation, pollution load index and modified degree of contamination all revealed that the research area is either unpolluted or has a low contamination level. As a result, pollution indices clearly show that the sediment samples in Kerala's coastal environment are not very harmful.

Ajani et al., (2020) assessed the pollution levels of Lagos coastal waters and sediments in the south-western region of Nigeria. The samples were collected from five locations over the period of the wet season (May to October 2016) and evaluated for six heavy metals (Fe, Pb, Cr, Cu, Zn, and Cd). Pb, Cd, and Cr concentrations were higher in water samples than the other heavy metals. The contamination factor revealed that Cd has extremely high contamination compared to the other heavy metals, which have low to moderate contamination. The potential ecological risk index also revealed that cadmium (Cd) poses a very high ecological danger to the marine ecosystem. The investigation revealed substantial pollution of cadmium and moderate pollution of lead (Pb) in the water and sediments across the study area.

Arunkumar, (2020) investigated heavy metal accumulation in the sediments of a tropical estuary off the southwest coast of India. Surface sediment samples were collected from eight stations along the Akkulam-Veli estuary and examined for heavy metals, including Fe, Mn, Zn, Pb, Cu and Cr. The estuary is polluted with heavy metals, with particularly high results for Pb and Cu, indicating a large concentration of these metals in the sediment. The pollution load index value indicated that lake sediments were contaminated. The geo-accumulation index result demonstrated that the estuarine sediment is free of all examined elements except Pb. However, contamination factor values revealed that the sediments of the Akkulam-Veli estuary are contaminated with heavy metals.

Gaonkar and Matta, (2020) evaluated metal pollution (Fe, Mn, Zn, Cr, Cu and Pb) in the surface sediments of a tropical estuary on India's west coast. The upper region of the Zuari estuary was dominated by sand, whereas the lower region was characterized by silt or clay with a higher concentration of organic carbon, resulting in increased productivity in the overline water column. Except for Pb and Zn during the non-monsoon and monsoon seasons, no noticeable seasonal variation was observed for the other metals. The Igeo and contamination factor values suggested that Pb and Cr were moderately polluted, while the remaining metal concentrations were low. Overall concentration Fe and Mn was lower than before the mining ban.

Gayathri et al., (2021) used multivariate methods and environmental indices to assess heavy metal contamination in the Netravati river basin. Ca^{2+} and Mg^{2+} were discovered to be the dominant cations in river water, while phosphate, nitrate, nitrite and silicate are within acceptable limits. The examination of total heavy metal concentrations and distribution revealed that the sediments of the Netravati river basin

are somewhat contaminated. The contamination factor, pollution load index, enrichment factor, and geo-accumulation index all suggested that sediments ranged from unpolluted to very polluted with heavy metals due to increased urbanization and agricultural practices that impact river hydrological regimes.

Gaonkar et al., (2021) measured metal enrichment and pollution levels in the Mandovi estuary. The metal distribution in the Mandovi estuary revealed that mining, fishing, and farming all contributed to the metal influx. Significant rainfall during the monsoon season led to increased river discharge, which in turn affected the distribution of Mn, Zn and Pb. Fe-Mn oxides, organic content, and sediment particle size all had an impact on the metal distribution in the surface sediment. According to the geo-accumulation index, contamination factor and potential contamination factor, the surface sediments of the Mandovi estuary were contaminated with Cr and Pb.

Trifuoggi et al., (2021) investigated the spatial distribution of trace elements in the Hoogly (Ganges) river estuary in west Bengal, India. From November 2014 to May 2017, surface sediment samples were collected from eight different locations seasonally and analyzed for 13 trace elements (Fe, Al, Mn, Ni, Hg, Cd, U, As, Co, Cu, Pb and Cr). These elements' distribution and transportation in sediments are not uniform. The contamination factor index demonstrated that both Ni and Cd have very high contamination, but the contamination degree and pollution load index suggested that sediments were severely contaminated with trace metals. According to the potential ecological risk index, As, Cd and Ni are at a moderate risk level, which is most likely due to anthropogenic input.

Nishitha et al., (2022) investigated trace metal pollution and ecological risk assessment in sediments from Sita Swarna, a tropical river estuary in south-western India. Two sediment cores were collected in the Sita Swarna estuary, one upstream (near the mangrove vegetation) and one downstream (near the mudflat), and analyzed for trace metals (Zn, Pb, As, Co, Cr, Ni, Fe, Cd, Cu and Mn). Core A (near mangroves) had a higher metal concentration than Core B. The geo-accumulation index and enrichment factor revealed reduced contamination for all metals studied; however, Pb and Zn had somewhat greater levels in both cores, indicating moderate pollution. On the other hand, the potential ecological risk and toxicity response index suggested no risk to aquatic life in the catchment area.

Alzahrani et al., (2023) investigated the contamination and risk assessment of potentially harmful elements in coastal sediments between Al-Jubail and Al-Khafji, Arabian Gulf, Saudi Arabia. 32 sediment samples were collected from 32 sampling sites in the intertidal zone and evaluated for elements such as Ni, Cu, Cr, As, Zn, Pb and Hg. Elements such as As and Hg were found to be enriched in coastal sediments, while other elements showed minimal or slight enrichment and low contamination. Hg enrichment is primarily attributable to anthropogenic sources, whereas As enrichment is a combination of geonic and anthropogenic origins.

The literature study above shows that some information on the distribution and pollution of metals in the estuarine ecosystem exists. However, due to a recent halt in mining activities, which were the primary sources of metals for the Mandovi and Zuari rivers, an attempt is being made to examine the distribution and evaluation of pollution levels in the Mandovi and Zuari estuarine coastal surface sediments. This study seeks to fill a gap in the literature by analyzing current levels of metal pollution in the sediments of the Mandovi and Zuari estuaries with the following objectives:

1.2 OBJECTIVES

1) To study the distribution pattern of trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of Mandovi and Zuari Estuaries,

2) To study the spatial and seasonal variation of trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of Mandovi and Zuari Estuaries, and

3) To assess the metal enrichment and contamination in coastal surface sediments of Mandovi and Zuari Estuaries using different pollution indices.

CHAPTER 2

PHYSIOGRAPHY OF THE STUDY AREA AND SAMPLING TECHNIQUES

2.1 THE STATE OF GOA

Goa is a tiny emerald island on India's west coast, with coasts stretching along the Arabian Sea, and it is one of India's biggest mineral-producing states. It covers 3700 km2 and has a population of over one million **(Pradhan and Shirodkar, 2011)**. The coastline is approximately 100 km long, and it has more than 40 estuary islands, 8 sea islands, and about 90 river islands. The economy of Goa is mainly dependent on iron and manganese ore mining and its exports **(Parvez Al-Usmani, 2018)**. The Fe-Mn ore deposits are considered the natural wealth of Goa and are crisscrossed by seven rivers: The Mandovi, Zuari, Terekhol, Chapora, Galgibag, Cumbharjua Canal, Talpona and Sal **(Hiremath, K. G., 2003)**, of which the Mandovi and the Zuari are major drainages. The Cumbharjua Canal separates Zuari and Mandovi, forming a large estuary complex. These rivers are fed by southwest monsoon rains, and their basins cover 69% of the state's geographical area. These rivers are some of the busiest rivers in India. Goa is also known for its tourism industry, which attracts millions of domestic and international tourists each year. The state is famous for its beautiful beaches, vibrant nightlife, and rich cultural heritage **(Kumar and Desai, 2016)**.

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

2.1.2 MANDOVI RIVER

The Mandovi River in Goa, India's central west coast, rises in the Western Ghats (mountain ranges), flows across the narrow coastal plains, and empties into the Arabian Sea via a broad bay (Aguada Bay). The river basin's rainfall is highly seasonal. The yearly rainfall during the southwest monsoon (June–September) ranges from 286 cm at Panaji on the coast to 661 cm at Gavali on the mountain slopes **(Shetye et al., 2007)**. During the dry season, which lasts 8 months (October to May), rainfall is minimal. The annual run-off measured in the Mandovi basin at Ganjem, 50 kilometers from the mouth, is 3400 Mm^3 (million cubic meters), with a standard deviation about the mean being 648 Mm^3 **(Shetye et al., 2007)**.

The Mandovi estuary has a mesotidal environment. During spring and neap tides, the tidal ranges are 2.3 m and 1.5 m, respectively **(Manoj and Unnikrishnan, 2009)**. The estuary's currents are tide-dominated, and saline waters can be found many kilometers upstream from the river mouth during the dry season **(Shetye et al., 1995)**. During the dry season, the water within the estuary's channels shifts from primarily freshwater river flow during the monsoon to extremely saline water from marine sources for many kilometers from the mouth. During the monsoon, all motorized fishing boats are stationed at the lower estuary.

The Mandovi basin is home to around two-thirds of Goa's mining activities for Fe-Mn ores **(Pathak et al., 1988)**. Several sites along the estuary channel are where Fe-Mn ore deposits from local mines are crushed and stored on the coast before being loaded onto ships. From October to May, the river is used for the export of Fe-Mn ore. A ship-building operation on the lower estuary's shore could contribute metals. Panaji, the municipal city, is located on the lower estuary. Every year, Mandovi receives 5.21 x 106 m^3 of sewage and effluents **(Qasim and Sengupta, 1981)**. Sand mining is a significant activity in the estuary's upstream channel.

2.1.3 ZUARI RIVER

The Zuari River is the largest river in Goa, India. It originates at Hemad-Barshem in the Western Ghats. Zuari River is also called landlocked Aghanashni. It flows southwest through the Taluka of Tiswadi, Ponda, Mormugao, Salcete, Sanguem and Quepem. Zuari is 92 km long; however, its length and width vary with tides and other seasonal floods **(Dehadrai, 1970)**. It has a catchment area of around 550 km2 that drains through the rocks of the Dharwar supergroup of the Archean Protozoic age. The Dharwarian rocks are represented by igneous acidic and metamorphic basic rocks **(Gokulam, 1972)**. The Sanvordem Formations occupy a massive area downstream of the Zuari River basin **(Mascarenhas and Kalavampara, 2009)**, and the drainage basin is covered by ferruginous laterites. Sanvordem Formations include metagraywacke, conglomerate and argillite's **(Gokul et al., 1985)**. The Zuari River is connected to the Mandovi River (62 km long) through the Cumbharjua Canal (15 km) **(Anant, 2012)**.

The Zuari and Mandovi Rivers form an estuarine system; they are the backbone of Goa's agricultural industry **(Shetye et al., 1995)**. The Zuari river flows in a south-western direction through the Quepem, Salcete, Ponda, Mormugao and Tiswadi talukas and finally evacuates into the Arabian Sea around the Mormugao harbor. Later, it merges with the Talaulim stream at the town of Sanguem, and it is in this town that the river widens and accepts waters from its tributary, Kushavati. The mouth of the Zuari River is about 5.5 km wide, narrowing to less than 0.5 km in the upper reaches. Cross-sectional area decreases from mouth to head, and tides occur in the two estuaries up to a distance of about 50 km **(Shetye et al., 1995)**. The increase in elevation of the estuarine channels prevents tides from propagating beyond this distance.

The Zuari River is fed by monsoon precipitation and also receives discharge from a catchment area of 550 km^2. The flow in the estuarine channels is primarily tidal after the withdrawal of the monsoon and continues to be so until the onset of the next monsoon **(Sundar and Shetye, 2008)**. Its basin constitutes about 27% of the total land area of Goa. It carries drainage from 309 km^2 of forest land. There are a total of 127 industries in its basin, which discharge about 4.4 x 106 m^3 of effluents per year into the river and

its tributaries. There are 10 large mines in its basin, which generate 1000–4000 tons of rejects per day per mine, of which a good portion can be expected to reach the river **(NIO, 1979)**. On the southern bank of the Zuari estuary, near the mouth, Mormugao harbor is situated, which facilitates the export of more than 10 million metric tons of iron ore annually. Also, barge building and repair activities, coastal construction and dumping of water take place **(Dessai and Nayak, 2009)**.

2.1.4 STATION LOCATION

The station locations for the study region are given in Fig. 2. The area of investigation covers the Mandovi and Zuari estuarine systems. It comprises 11 sampling stations, which cover the entire course of both estuaries (from head to mouth). For both estuaries, stations were named 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11.The coastal surface sediment samples for Mandovi and Zuari estuaries were collected during three different seasons: monsoon (June–July and August–September (for Zuari estuary) 2022), pre-monsoon (April–May 2023), and post-monsoon (November–December 2022).

The collection of sediment samples during different seasons enables a thorough understanding of estuarine systems and their dynamics throughout the year. Collecting samples at each site along the estuarine course helps to determine any spatial changes in sediment characteristics. The inclusion of many seasons allows for better detection of seasonal patterns as well as variations in sediment composition and distribution within the Mandovi and Zuari estuaries. This information will help to provide a more comprehensive assessment of the environmental health and functionality of these estuarine systems.

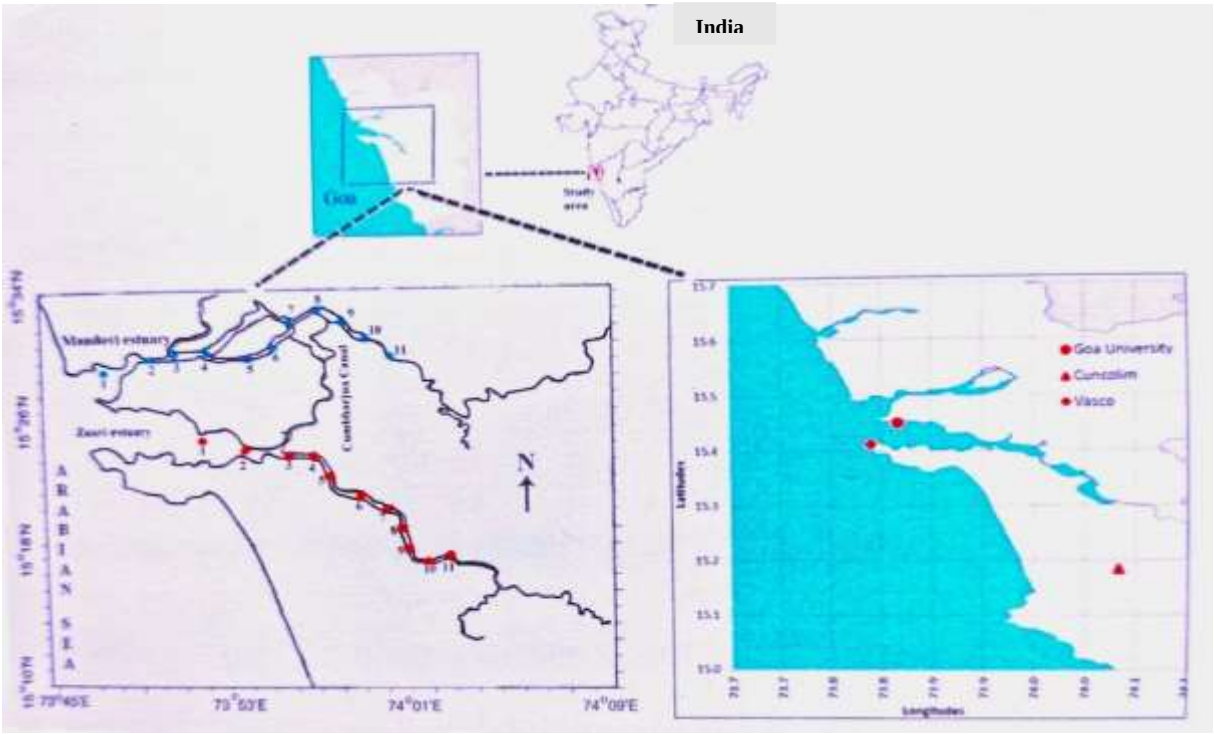

Fig. 1 – Station location map (Mandovi and Zuari estuary)

2.2 SAMPLING TECHNIQUE

2.2.1 COLLECTION OF SEDIMENT SAMPLES

The surface sediment samples were collected using Van-Veen Grab during the monsoon, post-monsoon, and pre-monsoon periods. The collected samples were then transferred to clean polythene zip-loc bags and kept in an ice box during transport. Later, samples were stored in a deep freezer.

2.2.2 DIGESTION OF SEDIMENT SAMPLES

Accurately weighed (0.2 g) of finely powdered sample is transferred to a Teflon beaker and treated with an acid mixture of HF, HNO_3, and $HClO_4$ in the ratio 7:3:1, respectively, and completely dried on a hot plate. After complete drying, another 5 ml of the above acid mixture is added and dried for 1 hour. Later, 2 ml of concentrated HCl is added to the Teflon beaker and dried completely on a hot plate. After complete drying, the residue in the Teflon beaker is back extracted by adding 10 ml of 1:1 HNO_3 and warmed for a few minutes. Then the residue is filtered and diluted to 50 ml with Milli-Q water **(Jarvis and Jarvis, 1985)**.

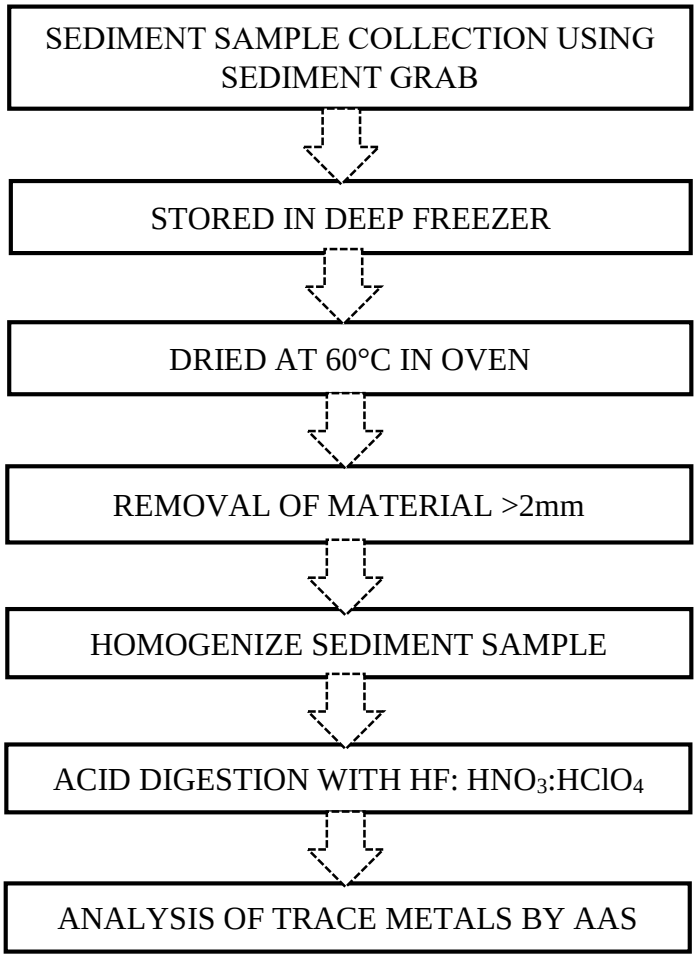

Fig. 2 – Analytical procedure for estimation of trace metals from sediments.

CHAPTER 3

ANALYTICAL METHODS

3.0 ANALYTICAL TECHNIQUES

All the measurements were carried out using an atomic absorption spectrophotometer (AAS) with an air-acetylene fuel mixture for the determination of trace metals. The chemicals used in the analysis are analytical-grade reagents. Milli-Q was used throughout the analysis.

3.1 TRACE METALS

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

Table 1 – Optical instrumental conditions for Elemental analysis by AAS.

SR. NO.	ELEMENTS	WAVELENGTH	FUEL MIXTURE	FLAME TYPE	RANGE OF STANDARDS (µg/l)
1.	Mn	279.5	Air-acetylene	Ox-lean blue	1 – 3.6
2.	Fe	248.3	Air-acetylene	Ox-lean blue	2 – 9
3.	Zn	213.9	Air-acetylene	Ox-lean blue	0.4 – 1.5
4.	Cu	324.7	Air-acetylene	Ox-lean blue	1 – 5
5.	Co	240.7	Air-acetylene	Ox-lean blue	2.5 – 9

*Ox – Oxidising flame

The concentration of trace metal in sediment sample was computed using following equation,

C=A × D

Where,
A = AAS reading
D = Dilution factor

Dilution factor is calculated by using following formula,
D = V / Amount of sediment sample weighed
Where,
V = Volume of the volumetric flask used for dilution after digestion.

3.2 ACCURACY AND PRECISION

Accuracy is the degree to which a measured or calculated quantity is close to its real (true) value. Precision, also known as reproducibility or repeatability — the degree to which subsequent measurements or calculations yield the same or comparable results — is closely connected to accuracy. The analytical procedure's precision and accuracy are adopted and evaluated using replicate analysis and a standard solution of known concentration.

Standard deviation (σ) = $\sqrt{\Sigma (X_i - \bar{X})^2 / n - 1}$

Where,

X_i = The determined value
$\bar{X}$ = The arithmetic mean
n = Number of determinations

Coefficient of variation (%) = $\sigma \times 100 / \bar{X}$

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

Table 2 – Statistical data for trace metals.

ELEMENTS	QUANTITY TAKEN FOR ANALYSIS	FOUND	STANDARD DEVIATION (Σ)	COEFFICIENT OF VARIATION
Mn	3.6 ppm	3.5	0.03	1.86
Fe	9 ppm	9.01	0.17	1.91
Zn	1.5 ppm	1.51	0.02	1.43
Cu	4 ppm	4.002	0.11	2.95
Co	9	9.18	0.18	1.28

3.3 POLLUTION INDICES

Sediments are metal history archives that indicate the extent of metal contamination. This study will utilize various pollution indices to examine contamination in the coastal sediments of the Mandovi and Zuari estuaries, both spatially and seasonally. These indices include the geo-accumulation index (Igeo), contamination factor (CF), pollution load index (PLI), contamination degree (Cd), modified degree of contamination (mCd), potential contamination index (Cp), and potential ecological risk. **Turekian and Wedepohl, (1961)** suggested the average shale value, which will be utilized as the geochemical background value in the current analysis of surface sediments.

- **Geo-accumulation index (Igeo) -**

Muller, (1979) proposed the geo-accumulation index, which estimates the concentration of metal accumulation in sediment over the baseline concentration. It is a quantitative assessment of the degree of contamination in aquatic sediments that is classified into seven types. The seven groups range from unpolluted to highly contaminated **(Rubio et al., 2000; Praveena et al., 2008)**.

$$\mathbf{Igeo = \log_2 (Cn / 1.5 * Bn)}$$

Where 'Cn' is the measured concentration of the analyzed metal and 'Bn' is the metal concentration in average shale **(Turekian and Wedepohl, 1961)**, and '1.5' is the background concentration factor due to lithogenic variability **(Haris et al., 2017)**. The classification of the geo-accumulation index is given in **Table 3**.

Table 3 – Classification of geo-accumulation index (Igeo)

Geo-accumulation index	Igeo class	Pollution intensity
> 5	6	Very strongly polluted
> 4 – 5	5	Strong to very strongly polluted
> 3 – 4	4	Strongly polluted
> 2 – 3	3	Moderately to strongly polluted
> 1 – 2	2	Moderately polluted
> 0 – 1	1	Unpolluted to moderately polluted
> 0	0	Unpolluted

Muller, (1979)

- **Contamination factor (CF) –**

The contamination factor is defined as the ratio of observed concentrations of various metals in sediment to background geochemical concentrations in the average shale value **(Turekian and Wedepohl, 1961)** and is determined by the formula:

$$\mathbf{CF = C_m / B_c}$$

Where 'C_m' is the measured concentration of a sediment sample and 'B_c' is the background concentration (average shale value), the background value of metal is the average shale value given by **Turekian and Wedepohl, (1961)**. **Table 4** shows the classification of contamination factors.

Table 4 – Classification of contamination factor (CF)

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

Håkanson, (1980)

- **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:

$$\mathbf{PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots\ldots \times CF_n)^{1/n}}$$

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. **Table 5** shows the classification of the pollutant load index.

Table 5 – Classification of pollution load index (PLI)

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

Tomlinson et al., (1980); Bramha et al., (2014)

- **Contamination degree (Cd) –**

Håkanson, (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.

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

where 'CF_i' is the contamination factor of the individual metal "i". The contamination degree is classified in **Table 6**.

Table 6 – 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

Håkanson, (1980)

- **Modified degree of contamination (mCd) –**

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

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

where ‘n’ denotes the number of investigating elements, ‘i’ denotes the ith element, and ‘CF’ denotes the contamination factor. **Table 7** shows the classification of the modified degree of contamination.

Table 7 – 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

Abrahim and Parker, (2008); Bramha et al., (2014); Sivakumar et al., (2016)

- **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 $Metal_{(Samplemax)}$ 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 **Table 8**.

Table 8 – 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

Davaulter and Rognerud, (2001)

- **Potential ecological risk –**

Håkanson, (1980,1988) proposed a potential ecological risk index approach from a sedimentological perspective to examine the features and environmental behavior 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.

$$E_r^i = T_r^i \, CF$$

$$\text{Risk Index (RI)} = \sum E_r^i$$

'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 E_r^i, the contamination factor is 'CF', and the toxicity response factor is T_r^i (Mn, Zn = 1 ; Cr = 2 ; Cu, Co, Pb = 5 ; Cd = 30). **Håkanson, (1980)** introduced the classification that is used to characterize the risk parameters E_r^i and RI. The classification of risk index and potential ecological risk is shown in **Table 9**.

Table 9 – Classification of risk index and potential ecological risk

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

Håkanson, (1980)

Risk index	Ecological risk level
$R_i < 95$	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 ecological risk

Håkanson, (1980)

CHAPTER 4

RESULTS AND DISCUSSION

4.1 PROCESSED DATA FOR THE MANDOVI ESTUARY

Table 10 – Data on the variation of trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Mandovi estuary, Goa, during the monsoon season.

STATION NUMBER	Mn (%)	Fe (%)	Zn (ppm)	Cu (ppm)	Co (ppm)
ME- 1	0.3115	4.5916	64.15	16.2125	10.9
ME- 2	0.9282	15.3156	105.1	34.3375	27.5375
ME- 3	0.4651	9.9478	92.5375	32.6375	25.825
ME- 4	0.4900	10.3740	86.125	27	20.4875
ME- 5	0.5988	17.3806	98.925	34.6625	28.8875
ME- 6	0.4006	22.8328	99.675	38.6375	30.3875
ME- 7	0.4499	10.4071	83.325	24.7125	18.7625
ME- 8	0.3024	8.8314	63.7125	20.4125	13.4375
ME- 9	0.2875	10.9049	66.7875	27.375	17.925
ME- 10	0.4985	12.1984	81.375	22.65	20.3875
ME- 11	0.1919	8.6860	61.0125	22.7	15.8875
AVERAGE CONCENTRATION	0.4477 %	11.9518 %	82.0659 ppm	27.3943 ppm	20.9477 ppm
MINIMUM CONCENTRATION	0.1919 %	4.5916 %	61.0125 ppm	16.2125 ppm	10.9 ppm
MAXIMUM CONCENTRATION	0.9282 %	22.8328 %	105.1 ppm	38.6375 ppm	30.3875 ppm
STANDARD DEVIATION	0.1977 %	4.9377 %	16.0859 ppm	6.9326 ppm	6.4557 ppm

***ME-** Mandovi Estuary

Table 11 – Data on the variation of trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Mandovi estuary, Goa, during the post-monsoon season.

STATION NUMBER	Mn (%)	Fe (%)	Zn (ppm)	Cu (ppm)	Co (ppm)
ME- 1	0.6871	7.8119	63.7375	19.7625	13.475
ME- 2	0.7551	17.7624	105.6375	51.9125	35.625
ME- 3	0.8169	12.1146	80.525	32.7375	28.275
ME- 4	0.4870	8.7094	72.225	25.75	18.4625
ME- 5	0.6981	15.4431	87.375	34.4875	27.7625
ME- 6	0.4559	10.4112	74.275	28	21.8
ME- 7	0.5116	11.3276	68.275	26.375	19.175
ME- 8	0.5109	13.5122	79.4	31.6875	24.325
ME- 9	0.3028	14.0096	140.1375	28.2125	20.6375
ME- 10	0.6146	24.1322	97.425	49.7375	28.8625
ME- 11	1.2105	26.3386	89.025	50.875	35
AVERAGE CONCENTRATION	0.6410 %	14.6884 %	87.0943 ppm	34.5034 ppm	24.8545 ppm
MINIMUM CONCENTRATION	0.3028 %	7.8119 %	63.7375 ppm	19.7625 ppm	13.4750 ppm
MAXIMUM CONCENTRATION	1.2105 %	26.3386 %	140.1375 ppm	51.9125 ppm	35.6250 ppm
STANDARD DEVIATION	0.2408 %	5.9668 %	21.5765 ppm	11.2075 ppm	6.9653 ppm

***ME-** Mandovi Estuary

Table 12 – Data on the variation of trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Mandovi estuary, Goa, during the pre-monsoon season.

STATION NUMBER	Mn (%)	Fe (%)	Zn (ppm)	Cu (ppm)	Co (ppm)
ME- 1	0.3158	4.5282	68.9625	17.45	12
ME- 2	0.9399	21.0337	113.0125	56.05	32.3625
ME- 3	0.7056	13.6851	108.7	43.05	26.7375
ME- 4	0.5358	9.0415	85.775	27.7625	20.05
ME- 5	0.6048	16.9684	103.15	40.1	26.2125
ME- 6	0.4870	14.1225	99.4	32.3875	24.025
ME- 7	0.3062	9.1952	79.1	29.5375	17.7625
ME- 8	0.5398	17.8419	107.4375	48.7875	28.6125
ME- 9	0.3832	14.2519	83.3375	33.35	21.525
ME- 10	0.4521	17.6881	86.15	34.975	23.55
ME- 11	1.1484	16.8830	115.025	53.5	30.5625
AVERAGE CONCENTRATION	0.5835 %	14.1127 %	95.4591 ppm	37.9045 ppm	23.9455 ppm
MINIMUM CONCENTRATION	0.3062 %	4.5282 %	68.9625 ppm	17.45 ppm	12 ppm
MAXIMUM CONCENTRATION	1.1484 %	21.0337 %	115.025 ppm	56.05 ppm	32.3625 ppm
STANDARD DEVIATION	0.2608 %-	4.8206 %	15.4321 ppm	11.7139 ppm	5.9285 ppm

***ME-** Mandovi Estuary

4.1.1 Manganese (Mn)

Manganese, the 12th most abundant element in the universe, constitutes approximately 0.1% of the Earth's crust. Pyrolusite (manganese dioxide), rhodochrosite (manganese carbonate), and rhodonite (manganese silicate) are the most common minerals of manganese and are widely distributed. Manganese is typically found in small quantities within iron ores. Manganese naturally exists in rivers, lakes, and certain underground water sources. Manganese is transported as a weathered mineral and as discrete particles of hydrous manganese oxide.

Human activities, such as using inorganic fertilizers in agriculture, industrial processes and burning fossil fuels, can introduce manganese into the environment **(Mohaihsh et al., 2004)**. Manganese plays a vital role in the production of iron and steel. Currently, manganese is predominantly demanded for steel production, accounting for 85% to 90% of the total demand. Manganese is a crucial component in cost-effective stainless steel formulations and is extensively utilized in the production of aluminum alloys. Manganese oxide serves as a catalyst in glassmaking processes, aiding in the decolorization and production of violet-colored glass. $KMnO_4$, a strong oxidizer, is utilized as a disinfectant. Additionally, compounds like MnO_2 and manganese carbonate find applications in fertilizers and ceramics **(Emelina, 2011)**.

In the current study, the concentration of manganese (Mn) in the coastal surface sediment of the Mandovi estuary varied from 0.1919% to 0.9282% during the monsoon season **(Table 10)**, from 0.3028% to 1.2105% during the post-monsoon season **(Table 11)** and from 0.3062% to 1.1484% during the pre-monsoon season **(Table 12)**. Furthermore, the present study discovered that the range and average manganese concentrations in the Mandovi estuarine coastal surface sediments were higher than those previously reported by **Gaonkar et al., (2021)**.

During both the post-monsoon and pre-monsoon seasons, station 11 had the highest manganese concentration, while stations 9 and 7 had the lowest concentrations, as depicted in the plotted graph **(Fig. 3)**. Conversely, station 2 exhibited the highest manganese concentration during the monsoon season, while station 11 had the lowest concentration. The relatively high concentration of Mn between stations 2 and 5 during the pre-monsoon and post-monsoon seasons might be due to the precipitation of Mn in high saline conditions in the lower estuarine region. Flushing of ores from these points during the monsoon caused an increase in Mn concentration in some stations. Stations 10 and 11 are located in the vicinity of ore deposits, hence the higher concentrations recorded. In the lower estuarine region, relatively higher values of Mn were reported, which might be due to several processes such as the effects of salinity and ionic strength, sorption phenomena between particles and sediments, and flocculation and coagulation processes that increase Mn concentration in the lower estuary. In general, the behavior of

Mn is different from the rest of the metals in estuaries. For instance, at low (10 ppt) salinity, Mn is available in dissolved form **(Kerdijk and Salomons, 1981)**, while Mn flocculates and eventually precipitates under high salinity conditions **(Balachandran et al., 2006)**.

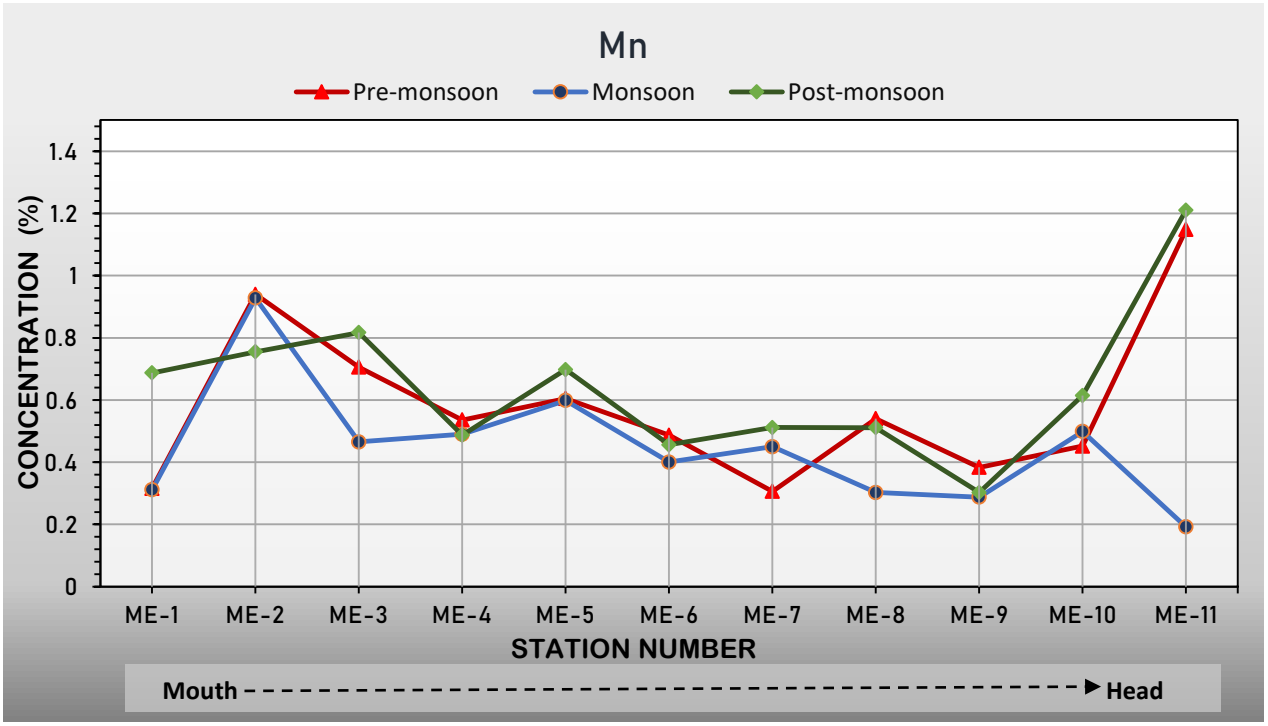

Fig. 3 – Shows the spatial variation of Manganese (Mn) in the coastal surface sediments of the Mandovi Estuary during the pre-monsoon, monsoon and post-monsoon seasons.

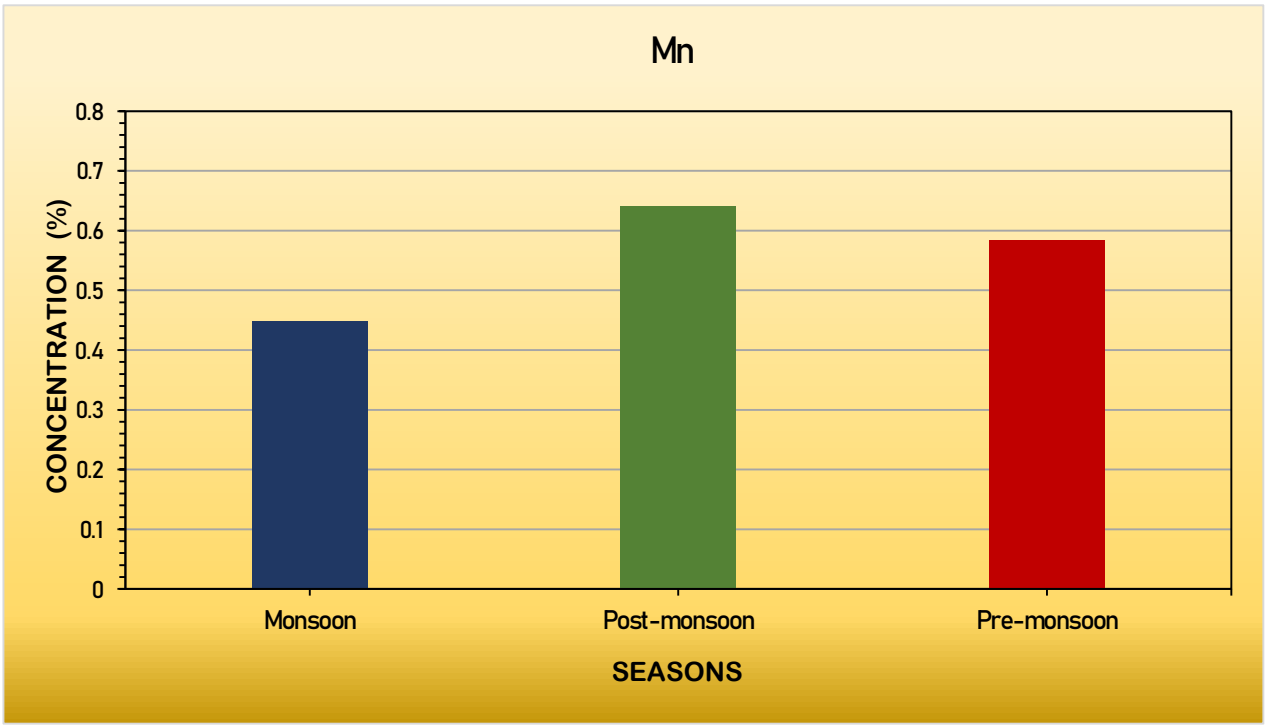

Fig. 4 – Depicts the seasonal variation of Manganese (Mn) in the coastal surface sediments of the Mandovi Estuary during the monsoon, post-monsoon and pre-monsoon seasons.

The seasonal variation of manganese concentration **(Fig. 4)** in coastal surface sediments from the Mandovi estuary showed higher concentrations during the post-monsoon season. This was followed by the pre-monsoon and monsoon seasons. The higher concentrations of manganese during the post-monsoon and pre-monsoon seasons could be attributed to the precipitation of manganese in highly saline conditions. Furthermore, in the post-monsoon season, the entry of saline water and organic matter significantly contributes to the deposition of manganese in the estuarine sediments **(Dessai and Nayak, 2009)**.

4.1.2 Iron (Fe)

Iron (Fe) is abundant in the Earth's crust and can be found in natural waters in varying amounts, influenced by the local geology and water composition **(USEPA, 1986)**. Iron in water is commonly found in the ferrous (Fe^{2+}) and ferric (Fe^{3+}) states, with the possibility of other forms in organic and inorganic wastewater streams. Iron is typically in the ferric state in surface waters, while the ferrous form can persist in reducing waters. When oxygen is present, iron is commonly seen as colloidal suspensions of ferric hydroxide, which can either stay suspended in water or settle and solidify **(CCREM, 1987)**.

Iron (Fe) can be found in various phases in marine and freshwater sediments. Reactive Fe minerals like oxides, sulfides, phosphates and carbonates participate in sediment reactions, influencing the cycling of carbon and nutrients **(Berner, 1970; Slomp et al., 1996a, b; Lovley et al., 2004; Jilbert and Slomp, 2013; Kraal et al., 2015; Robertson et al., 2016)**. Recent studies have demonstrated that iron stabilizes organic carbon in sediments, facilitating carbon burial **(Lalonde et al., 2012; Shields et al., 2016)**.

In the present study, the concentration of Iron (Fe) in the coastal surface sediment of the Mandovi estuary ranges from 4.5916 % to 22.8328 % **(Table 10)**, 7.8119 % to 26.3386 % **(Table 11)** and 4.5282 % to 21.0337 % **(Table 12)** during the monsoon, post-monsoon and pre-monsoon seasons, respectively. Similarly, like manganese, the iron concentrations in the coastal surface sediments of the Mandovi estuary were found to be higher in this study as compared to the findings of **Gaonkar et al., (2021)**.

During the post-monsoon and pre-monsoon seasons, stations 11 and 2 had the highest iron (Fe) concentrations, respectively, while station 1 had the lowest Fe concentrations in both seasons; this is depicted by the plotted graph **(Fig. 5)**. During the monsoon season, station 6 exhibited the highest iron (Fe) concentration, while station 1 had the lowest levels. The iron levels varied irregularly from the estuary's mouth to its upper region. The slightly elevated iron levels in the upper estuarine region may

be attributed to historical mining activities, which previously introduced additional iron into the estuarine system. The higher iron concentrations at specific stations may be linked to materials from an iron ore processing plant or accidental ore spills at loading points prior to the mining prohibition. The increased Fe levels in the pre-monsoon season could be due to iron adsorption onto the sediments because of low water volume, high evaporation rates **(Obasohan, 2008)**, organic carbon (OC) content and fine-grained sediments. The peaks in Fe concentrations at stations in the lower estuarine region may be due to sediment size, the amount of organic carbon (OC) **(Gopal et al., 2017)** and sediment resuspension at increased salinities. The increased Fe concentration at station 6 in the monsoon season is likely due to reduced water movement, which allows finer sediment to settle in this area.

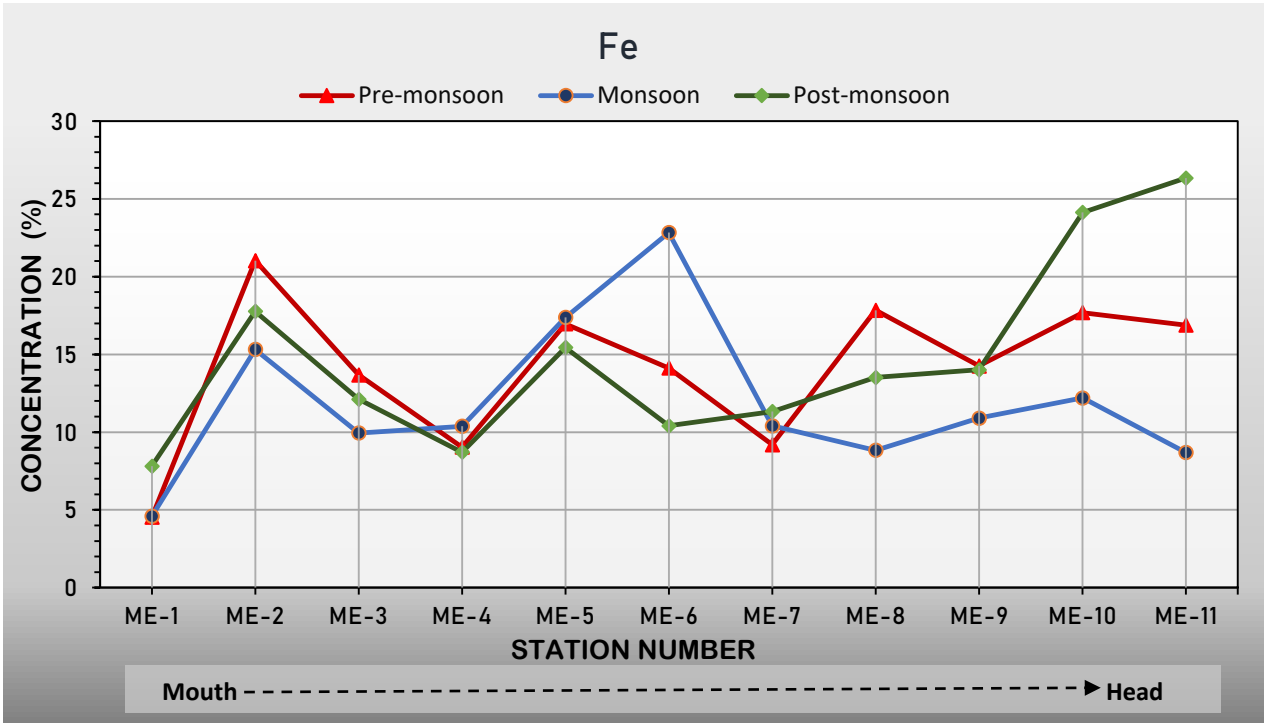

Fig. 5 – Shows the spatial variation of Iron (Fe) in the coastal surface sediments of the Mandovi Estuary during the pre-monsoon, monsoon and post-monsoon seasons.

Higher concentrations of iron (Fe) were observed in coastal surface sediments from the Mandovi estuary during the post-monsoon season **(Fig. 6)**. Similarly, the seasonal variation of Mn in the Madovi Estuary followed a pattern similar to that of Fe, with the pre-monsoon and monsoon seasons showing lower concentrations. The elevated Fe concentration during the post-monsoon season is likely due to the mobilization of metal-rich sediment caused by the excessive inflow of metal-rich wastewater into the estuary. Further, during the pre-monsoon season, a higher concentration of Fe might be due to the lower volume of water associated with a high rate of evaporation **(Obasohan, 2008)**.

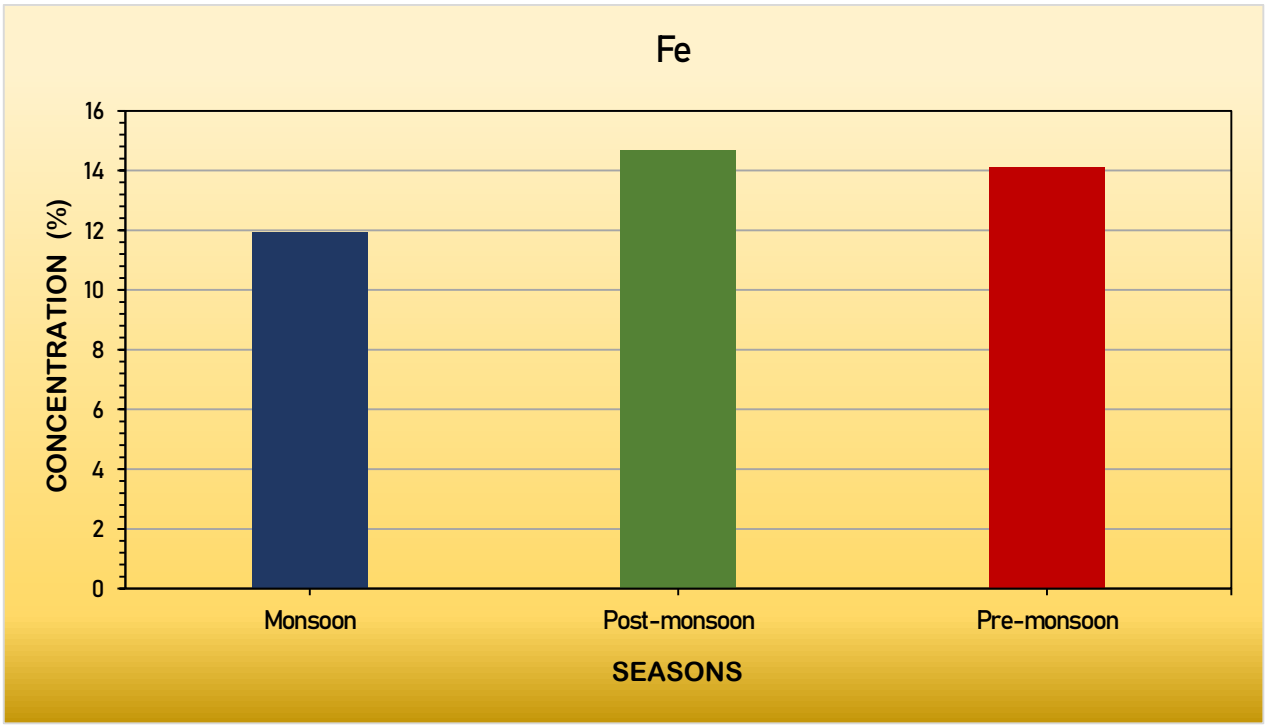

Fig. 6 – Depicts the seasonal variation of Iron (Fe) in the coastal surface sediments of the Mandovi Estuary during the monsoon, post-monsoon and pre-monsoon seasons.

4.1.3 Zinc (Zn)

Zinc is a commonly found element in the environment. Because of its abundance in the earth's crust and the numerous purposes it serves in many aspects of human life, significant amounts of zinc can be found in sediment, surface waters and living organisms. Anthropogenic emissions of this element are created by a range of human activities, including the extraction and processing of zinc ores, fuel burning and the discharge of urban and industrial sewage into the environment. Intensive fish breeding, which involves the ingestion of huge amounts of commercial fodder or medicines, contributes significantly to water contamination by trace metals such as zinc **(Dean et al., 2007)**.

Zinc exists in water in three forms: dissolved, colloidal and suspended. These cations can also produce hydrated ions, ion pairs and complex molecules in water. Zinc is an essential element for living organisms and participates in many physiological processes, including controlling ligand exchange processes, contributing to nucleic acid metabolism and gene expression, exhibiting antioxidant activity, influencing an organism's immunological processes and controlling the ionic regulation of elements such as copper, selenium, manganese and magnesium. A deficiency of zinc can lead to inhibition of growth, delay maturity, impair immunity and cause neurosensory problems. On the other hand, excessive zinc intake produces anemia. In fish, excess zinc can cause both mortality and embryonic deformation. Excess zinc also causes digestive tract problems, such as gastrointestinal issues **(Niemiec, 2016)**.

In this study, the zinc (Zn) concentration in the coastal surface sediment of the Mandovi estuary ranges from 61.0125 to 105.1 ppm during the monsoon season **(Table 10)**. During the post-monsoon season, the range of zinc concentration is 63.7375 to 140.1375 ppm **(Table 11)**, while in the pre-monsoon season, it varies from 68.9625 to 115.025 ppm **(Table 12)**. The zinc concentrations in the coastal surface sediments of the Mandovi estuary during the study were compared to the findings of Gaonkar et al. (2021). In the current study, zinc showed slightly higher values during the post-monsoon season, lower values during the monsoon season, and similar concentrations during the pre-monsoon season than the range reported by **Gaonkar et al., (2021)**.

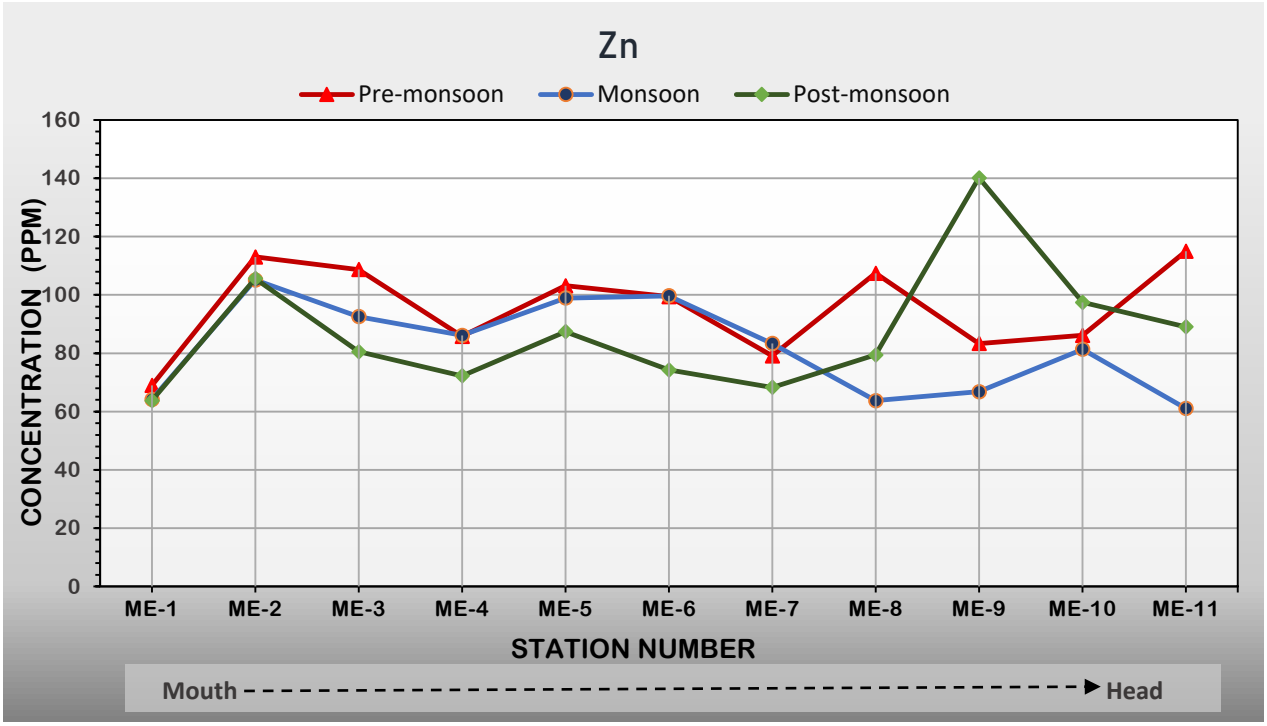

Fig. 7 – Shows the spatial variation of Zinc (Zn) in the coastal surface sediments of the Mandovi Estuary during the pre-monsoon, monsoon and post-monsoon seasons.

In spatial variation of zinc, stations 9 and 11 had the highest (Zn) concentrations during the post-monsoon and pre-monsoon seasons, respectively, while station 1 had the lowest zinc concentrations in both seasons. This information is depicted in the graph **(Fig. 7)**. During the monsoon season, station 2 exhibited the highest zinc (Zn) concentration, while station 11 had the lowest levels. Zinc can enter into the waterbody from various sources, such as industries, sewage, roads, vehicles, pesticides and runoff with organic waste **(Boxall et al., 2000; Silambarasan et al., 2012)**. Overall, there was an relative variation in zinc concentrations in Mandovi estuarine sediments from the mouth to the head region, with slight changes across seasons. The higher zinc concentration in the upper estuarine region during non-monsoonal months may be attributed to discharges from shipbuilding industries, agricultural, industrial and atmospheric emissions. Zinc accumulation in sediments can be influenced by factors such as sediment texture, organic matter content and anthropogenic activities.

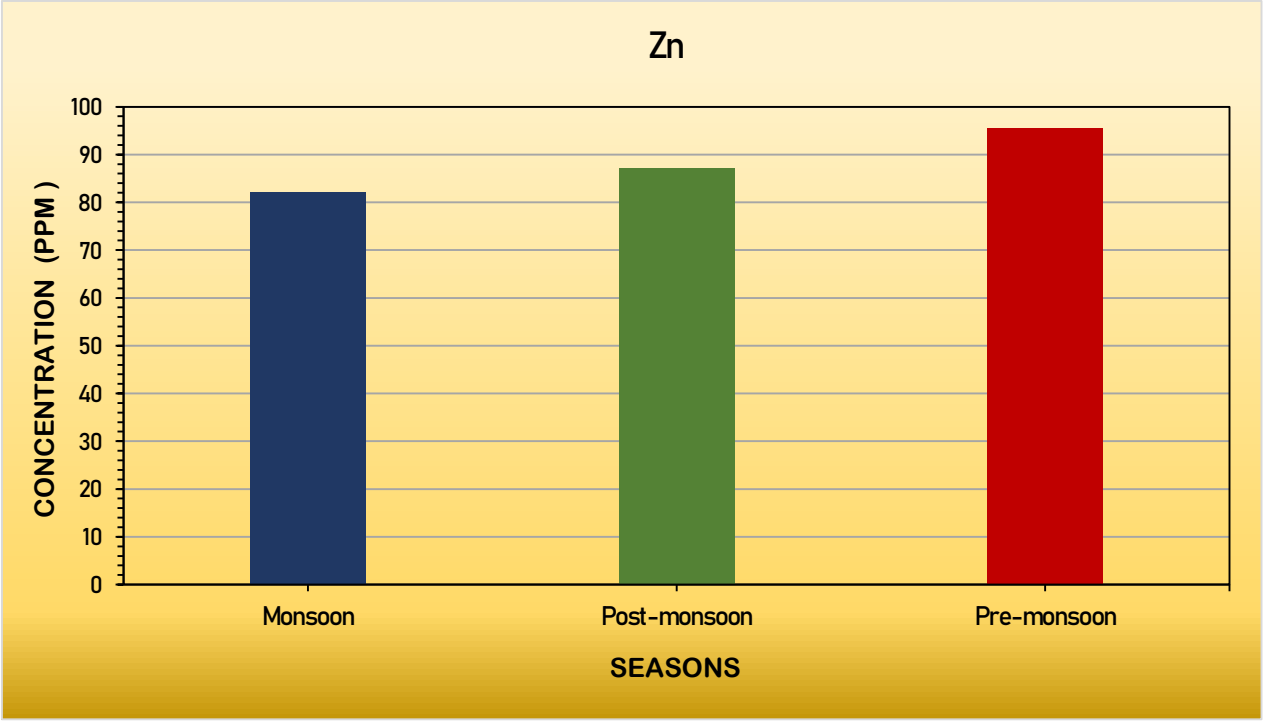

Fig. 8 – Depicts the seasonal variation of Zinc (Zn) in the coastal surface sediments of the Mandovi Estuary during the monsoon, post-monsoon and pre-monsoon seasons.

In coastal surface sediments collected from the Mandovi estuary, the concentration of zinc showed lower levels during the monsoon season. Subsequently, there was an increase in zinc concentration during the post-monsoon season, reaching its peak during the pre-monsoon season. The increased zinc concentration in the pre-monsoon season could be attributed to the release of metals from the overflow of sewage water rich in metals into the estuary **(Gaonkar and Matta, 2020)**. The seasonal variation of zinc **(Fig. 8)** in this study exhibited a contrasting trend from that reported by **Gaonkar et al., (2021)**.

4.1.4 Copper (Cu)

Copper is a reddish metal with a face-centered cubic crystalline structure. Copper reflects red and orange light while absorbing other frequencies in the visible spectrum. It is malleable, ductile, and an extremely good conductor of both heat and electricity. Copper can exist in oxidation states of +1 and +2, with +2 being the most common state. Both copper (I) oxide and copper (II) oxide are known. Among the numerous copper sulfides, the most important examples include Cu_2S and CuS. The cuprous halides with chlorine, bromine, and iodine are known, as are the cupric halides **(Holleman and Wilburg, 2001)**.

Copper is widely distributed in nature in a free state, in sulfides, arsenides, chlorides, and carbonates. Copper is used in making electrical wires, while its alloys, such as bronze and brass, find applications in various industries. Copper enters aquatic environments through the erosion of soil and mineral

deposits. Copper is easily bound to sediments and organic material and is only moderately soluble in water. Tubes made of copper and copper alloys are widely and increasingly used for domestic plumbing, heating systems, air conditioning, refrigerators, and in industries. Copper sulfate is used in fungicides, pesticides, nutritional supplements in animal feeds, and fertilizers. It also promotes growth and controls diseases in livestock and poultry **(WHO, 2004)**. Corrosion of copper by acids and bases will result in copper compounds finding their way to different environments and finally to food and drinking water **(Duruibe et al., 2007)**.

In the present study, the concentration of copper (Cu) in the coastal surface sediment of the Mandovi estuary ranges from 16.2125 to 38.6375 ppm **(Table 10)**, 19.7625 to 51.9125 ppm **(Table 11)** and 17.45 to 56.05 ppm **(Table 12)** during the monsoon, post-monsoon and pre-monsoon seasons, respectively. Furthermore, the present study discovered that the range and average copper concentrations in the Mandovi estuarine coastal surface sediments were relatively lower than those previously reported by **Gaonkar et al., (2021)**.

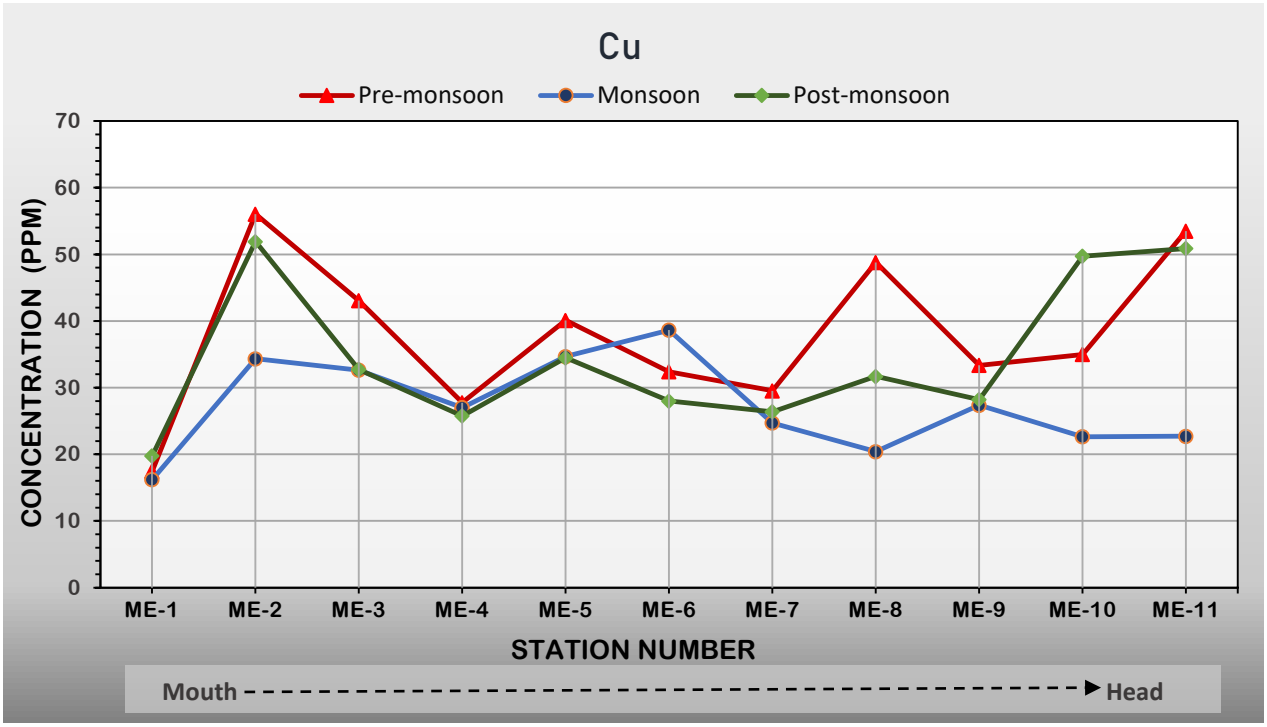

Fig. 9 – Shows the spatial variation of Copper (Cu) in the coastal surface sediments of the Mandovi Estuary during the pre-monsoon, monsoon and post-monsoon seasons.

During both the post-monsoon and pre-monsoon seasons, station 2 had the highest copper (Cu) concentration, while station 6 exhibited the highest copper (Cu) concentration during the monsoon season, as depicted in the graph **(Fig. 9)**. On the other hand, in all three seasons, station 1 showed the lowest copper concentration. Copper exhibited the highest concentration in the lower estuarine region during all three seasons of the study. The spatial distribution of Cu in the Mandovi estuary can be

attributed to the influence of sediment grain size and organic carbon (OC) on its dispersion. Interestingly, copper exhibited higher concentrations at station 8 during the pre-monsoon season. Copper showed a significantly higher concentration in the upstream region, which might be due to the various activities in the harbor, such as loading and unloading of cargo, boat cleaning and maintenance, and antifouling paint applications, which are known to increase the Cu load in an aquatic environment **(WHO, 1998; Silambarasan et al., 2012)**. Furthermore, copper has the ability to form organic complexes, precipitate as an insoluble form, and subsequently get deposited in estuarine sediments **(Silambarasan et al., 2012)**.

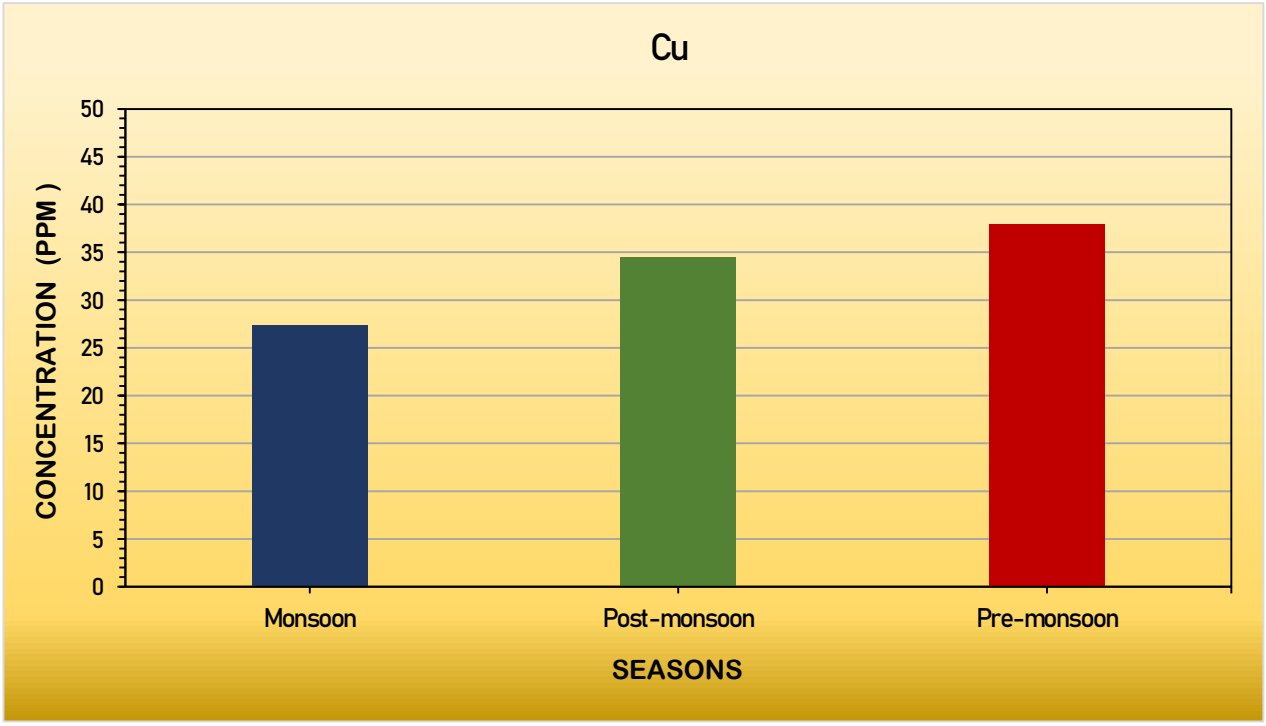

Fig. 10 – Depicts the seasonal variation of Copper (Cu) in the coastal surface sediments of the Mandovi Estuary during the monsoon, post-monsoon and pre-monsoon seasons.

Seasonal variation of Cu in the surface sediments of the Mandovi estuary **(Fig. 10)**: the highest average copper concentrations were found during the pre-monsoon season. This increase in copper levels may be attributed to the high saline conditions, potentially leading to the precipitation of dissolved Cu **(Ananthan et al., 2005, 2006)**. However, the average concentration of copper in the Mandovi estuary was significantly lower during the monsoon season compared to the postmonsoon season. Overall, the high concentration of copper (Cu) during the non-monsoonal months can be attributed to factors such as its high organic matter content and its extensive use in antifouling paints **(Ananthan et al., 2005, 2006)**.

4.1.5 Cobalt (Co)

Cobalt, though widely distributed, makes up only 0.001% of the Earth's crust. Cobalt can be found in trace amounts in soils, plants, animals, ferromanganese crusts deep in the oceans, the sun and stellar atmospheres, natural waters mixed with other elements such as cobaltite, skutterudite, smaltite, heterogenite and erythrite, as well as native nickel-iron on land and in meteorites.

Pure cobalt does not exist on Earth, although cobalt-bearing minerals are found globally. Cobalt ore is not often mined for its cobalt content. Rather, it is often recovered as a byproduct of the mining of iron, nickel, copper, silver, manganese, zinc, and arsenic, all of which contain trace amounts of cobalt. Concentrating and extracting cobalt from these ores requires complex processing. Dissolved cobalt has a scavenged profile; its concentration is high near the surface due to significant atmospheric input, and it drops with depth as dissolved cobalt is sorbed onto sinking particles and removed to ocean sediments (scavenging).

In the current study, the concentration of cobalt in the coastal surface sediment of the Mandovi estuary varied from 15.8875 to 30.3875 ppm **(Table 10)**, from 13.475 to 35.625 ppm **(Table 11)** and from 12 to 32.3625 ppm **(Table 12)**, during monsoon, post-monsoon and pre-monsoon seasons, respectively.

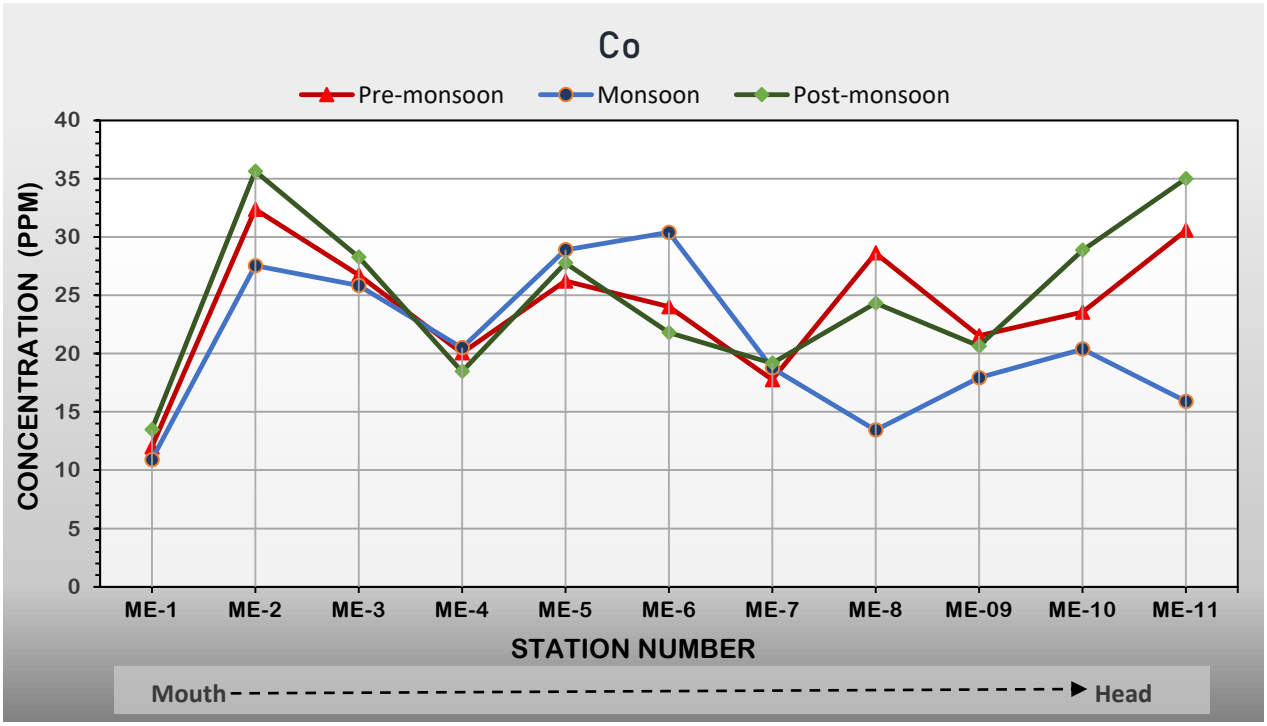

Fig. 11 – Shows the spatial variation of cobalt (Co) in the coastal surface sediments of the Mandovi Estuary during the pre-monsoon, monsoon and post-monsoon seasons.

Based on the spatial variation of cobalt (Co) **(Fig. 11)**, station 2 shows a high cobalt concentration during the pre-monsoon and post-monsoon seasons, while station 6 exhibits the highest value in the monsoon

season. In contrast, station 1 had the lowest values in the pre-monsoon and post-monsoon seasons, whereas station 11 showed the lowest values during the monsoon season. The cobalt distribution in the coastal surface sediment of the Mandovi estuary shows an uneven pattern from the mouth (downstream) to the head region (upstream). In non-monsoonal months, a relatively higher cobalt concentration was detected, possibly due to increased biological productivity in the estuary. Overall, the cobalt distribution from the mouth to the head region showed a consistent pattern across all seasons. The movement of sediment, river discharge and deposition patterns along the estuary directly influence cobalt distribution, leading to the irregular trend observed. Moreover, industrial activities and human influences along the estuary have a significant impact on how cobalt is distributed in the sediment. As a result, these factors can cause cobalt to accumulate in specific estuarine areas, leading to the irregular distribution trend observed.

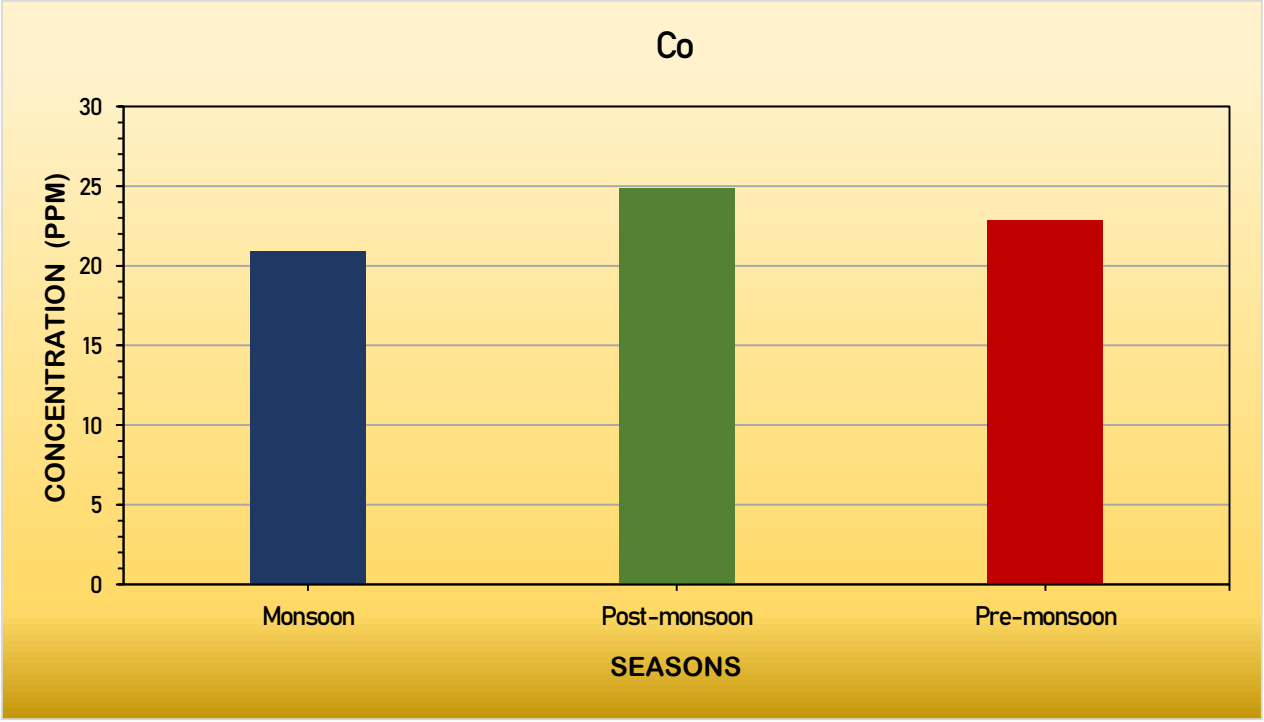

Fig. 12 – Depicts the seasonal variation of cobalt (Co) in the coastal surface sediments of the Mandovi Estuary during the monsoon, post-monsoon and pre-monsoon seasons.

The cobalt concentration in coastal surface sediments collected from the Mandovi estuary is highest during the post-monsoon season, followed by the pre-monsoon season and finally the monsoon season **(Fig. 12)**. Furthermore, during the post-monsoon season, increased biological activity in the estuary can elevate cobalt levels in the water through uptake by organisms such as phytoplankton. In the pre-monsoon season, a rise in biological productivity within the estuary might have resulted in an increase in cobalt levels. The elevated cobalt levels during the monsoon season may be due to the influx of increased particulate matter and suspended sediment load from the river **(Senthilnathan and Balasubramanian, 1999)**.

4.2 PROCESSED DATA FOR THE ZUARI ESTUARY

Table 13 – Data on the variation of trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Zuari estuary, Goa, during the monsoon season.

STATION NUMBER	Mn (%)	Fe (%)	Zn (ppm)	Cu (ppm)	Co (ppm)
ZE- 1	0.3792	9.2742	195.075	104.05	41.9
ZE- 2	0.4196	9.0964	225.9875	106.8	40.925
ZE- 3	0.3158	9.0208	134.3875	62.025	29.725
ZE- 4	0.4211	7.9899	97.1625	44.3875	26.65
ZE- 5	0.4397	4.2426	72.15	29.2875	18.4875
ZE- 6	0.1798	4.3788	80.15	24.275	15.2
ZE- 7	0.1721	7.3370	89.1625	55.8875	26.4125
ZE- 8	0.1502	5.8492	69.875	28.7875	15.9375
ZE- 9	0.1938	4.5312	63.2	23.7375	13.5125
ZE- 10	0.0926	4.1245	79.725	21.95	10.6
ZE- 11	0.0434	4.3320	59.8875	24.8125	10.3
AVERAGE CONCENTRATION	0.2552 %	6.3797 %	106.0693 ppm	47.8182 ppm	22.6955 ppm
MINIMUM CONCENTRATION	0.0434 %	4.1245 %	59.8875 ppm	21.95 ppm	10.3 ppm
MAXIMUM CONCENTRATION	0.4397 %	9.2742 %	225.9875 ppm	106.8 ppm	41.9 ppm
STANDARD DEVIATION	0.1435 %	2.1861 %	55.9164 ppm	31.5559 ppm	11.3306 ppm

***ZE-** Zuari Estuary

Table 14 – Data on the variation of trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Zuari estuary, Goa, during the post-monsoon season.

STATION NUMBER	Mn (%)	Fe (%)	Zn (ppm)	Cu (ppm)	Co (ppm)
ZE- 1	0.3256	7.9758	156.25	91.6	35.95
ZE- 2	0.4019	9.0715	176.575	91.875	39
ZE- 3	0.2478	6.5902	104.6375	48.3875	24.4125
ZE- 4	0.3482	8.6218	157.05	94.45	32.85
ZE- 5	0.3473	3.5828	75.3125	20.3375	15.9
ZE- 6	0.2062	6.1310	86	32.15	18.3
ZE- 7	0.2582	4.2569	73.0875	21.2375	13.9625
ZE- 8	0.1489	5.3764	99.2125	25.9625	14.575
ZE- 9	0.1622	6.4891	97.65	33.4625	20.425
ZE- 10	0.1511	5.0590	76.25	24.1375	13.1
ZE- 11	0.1495	4.6540	84.5625	22.375	11.2625
AVERAGE CONCENTRATION	0.2497 %	6.1644 %	107.8716 ppm	45.9977 ppm	21.7943 ppm
MINIMUM CONCENTRATION	0.1495 %	3.5828 %	73.0875 ppm	20.3375 ppm	11.2625 ppm
MAXIMUM CONCENTRATION	0.4019 %	9.0715 %	176.575 ppm	94.45 ppm	39 ppm
STANDARD DEVIATION	0.0938 %	1.8024 %	37.3640 ppm	30.9764 ppm	9.8706 ppm

***ZE-** Zuari Estuary

Table 15 – Data on the variation of trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Zuari estuary, Goa, during the pre-monsoon season.

STATION NUMBER	Mn (%)	Fe (%)	Zn (ppm)	Cu (ppm)	Co (ppm)
ZE- 1	0.3827	8.4991	162.9625	91.625	37.2625
ZE- 2	0.3621	8.1096	153.7	83.975	35.9625
ZE- 3	0.2547	7.2450	78.1375	38.25	23.2875
ZE- 4	0.4415	7.1262	187.5125	139.6875	29.1
ZE- 5	0.2343	3.0999	72.15	26.125	14.8375
ZE- 6	0.2192	4.7464	86.3375	30.5625	17.95
ZE- 7	0.2604	3.6361	76.8625	23.725	13.8875
ZE- 8	0.1177	5.0404	82.55	30.6	15.9625
ZE- 9	0.1324	5.0562	87.725	32.5125	19.225
ZE- 10	0.1756	5.5105	83.45	29.825	18.7875
ZE- 11	0.2351	10.0846	78.875	37.625	25.2
AVERAGE CONCENTRATION	0.2558 %	6.1958 %	104.5693 ppm	51.3193 ppm	22.8602 ppm
MINIMUM CONCENTRATION	0.1177 %	3.0999 %	72.15 ppm	23.725 ppm	13.8875 ppm
MAXIMUM CONCENTRATION	0.4415 %	10.0846 %	187.5125 ppm	139.6875 ppm	37.2625 ppm
STANDARD DEVIATION	0.1020 %	2.1771 %	41.7465 ppm	37.3233 ppm	8.1857 ppm

***ZE-** Zuari Estuary

4.2.1 Manganese (Mn)

Manganese is a pinkish-gray, chemically active element. It's a hard brittle metal. Manganese can be found in a variety of salts and mineral complexes found in rocks, soil, and bodies of water. Manganese is most commonly found as a dioxide, carbonate, or silicate. Its oxidation states range from -3 to +7. The most important oxidation states for aquatic systems are manganous (Mn^{2+}) and mangatic (Mn^{4+}). Manganese accounts for around 0.1% of the earth's crust, making it the 12th most abundant element, and the most important manganese ore is pyrusite **(Dill, 2010)**. Other manganese ores are typically found in trace concentrations in iron ores. Manganese exists in two forms: organic and inorganic.

Inorganic manganese is typically found in water and soil, while organic manganese is found in living organisms as a necessary trace element for biological functions. Manganese plays a crucial role in various biochemical processes, such as photosynthesis, respiration, and nitrogen metabolism. Additionally, manganese is essential for the production of enzymes that are involved in antioxidant defense and bone formation. Overall, manganese is a vital element for both environmental and biological systems. It is also used in the production of steel and other alloys due to its ability to increase strength and toughness.

In the industrial sector, manganese is widely utilized in the manufacturing of batteries, ceramics, and fertilizers. Its properties make it a valuable component in the production of glass, paints, and even medications. Furthermore, manganese is crucial in the removal of harmful pollutants from the environment, making it an important player in the field of environmental remediation. Its versatility and importance in various industries highlight the significance of manganese in both human activities and natural ecosystems.

In the present study, the concentration of manganese (Mn) in the coastal surface sediment of the Zuari estuary ranges from 0.0434 % to 0.4397 % **(Table 13)**, from 0.1495 % to 0.4019 % **(Table 14)** and from 0.1177 % to 0.4415 % **(Table 15)** during the monsoon, post-monsoon and pre-monsoon seasons, respectively. Furthermore, the present study discovered that the range and average manganese concentrations in the Zuari estuarine coastal surface sediments were higher than those previously reported by **Gaonkar and Matta, (2020)**.

During both the monsoon and pre-monsoon seasons, stations 5 and 4 had the highest manganese concentrations, whereas stations 11 and 8 had the lowest levels, respectively, as depicted in the plotted graph **(Fig. 13)**. Conversely, station 2 showed the highest manganese concentration during the post-monsoon season, whereas stations 8 and 11 had the lowest levels. The higher manganese levels in the upper estuary are probably caused by activities like ore processing plants and accidental spillage of ferro-

manganese ore at loading points in this area. During monsoon rains, the estuaries receive significant amounts of sediment load, and the substantial influx of ore notably elevated the manganese levels observed in the upper estuary during this period. Conversely, in the lower estuarine region, the higher manganese concentration may result from the precipitation of manganese due to the elevated salinity level. The behavior of manganese within the estuarine region differs from that of other metals. At lower salinity (10 ppt), Mn is present in the solution phase **(Kerdijk and Salomons, 1981)**, and at higher salinity (18 ppt), Mn flocculates and finally precipitates **(Balachandran et al., 2005)**. This behavior of manganese is prominently observed in the Zuari estuary, where higher salinity is consistently maintained from the estuary's mouth to the slightly upstream end of the Cumbharjua canal.

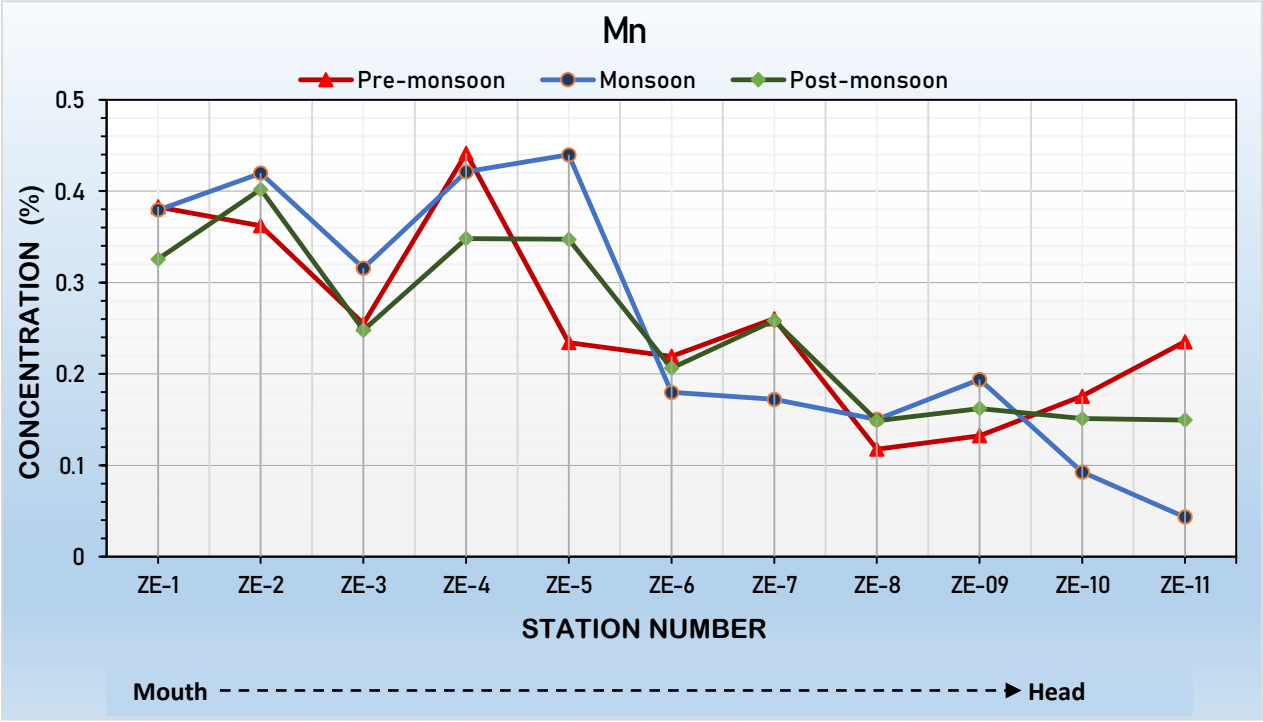

Fig. 13 – Shows the spatial variation of manganese (Mn) in the coastal surface sediments of the Zuari Estuary during the pre-monsoon, monsoon and post-monsoon seasons.

The seasonal variation of manganese concentration **(Fig. 14)** in coastal surface sediments from the Zuari estuary exhibited stable concentrations throughout the pre-monsoon, monsoon and post-monsoon seasons, with a slightly decreased amount noted in the post-monsoon season. The increased Mn levels during the monsoon season could be a result of heavy freshwater run-off due to rainfall, carrying mining waste into the estuarine region. The higher Mn levels in the post-monsoon season could be attributed to the influx of saline water and organic matter, influencing the deposition of Mn in the estuary **(Dessai and Nayak, 2009)**. Overall, the stable manganese levels in the sediments of the Zuari estuary may suggest a balanced ecosystem, maintained by diverse biogeochemical processes that control metal distribution.

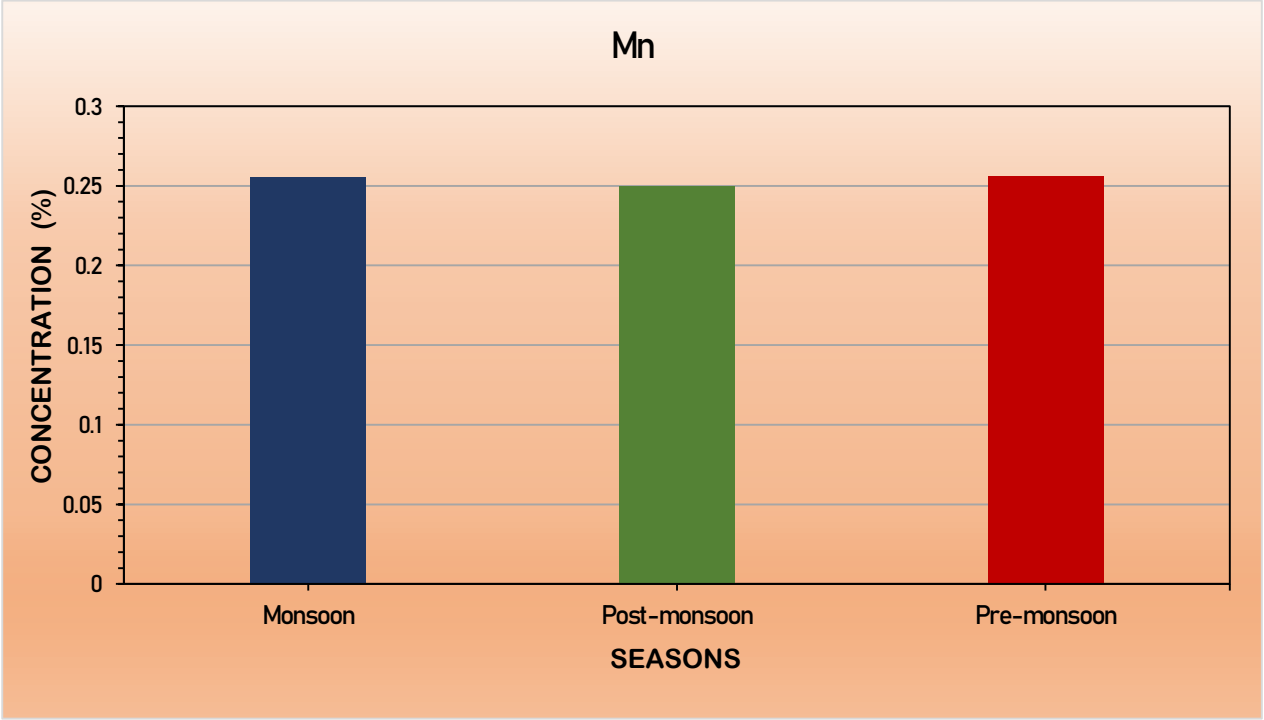

Fig. 14 – Depicts the seasonal variation of Manganese (Mn) in the coastal surface sediments of the Zuari Estuary during the monsoon, post-monsoon and pre-monsoon seasons.

4.2.2 Iron (Fe)

Iron (Fe) is the fourth most abundant element in the Earth's crust and may be present in natural waters in varying quantities depending upon the geology of the area and other chemical components of the water **(USEPA, 1986)**. The most common oxidation states of iron in water are the ferrous (Fe^{2+}) and the ferric (Fe^{3+}) states, although other forms may be present in organic and inorganic wastewater streams. In surface waters, iron is generally present in the ferric state; in reducing waters, the ferrous form can persist. In presence of oxygen , iron is often found as colloidal suspensions of ferric hydroxide, which may remain suspended in water or settled and harden **(CCREM, 1987)**.

Iron is an abundant earth metal that participates in biogeochemical reactions in marine sediments. Microorganisms use iron for a variety of activities, including cell development, energy conservation, and metabolic activity. Iron is a necessary trace element for both plants and animals, and most species require it for growth and development. Therefore, iron deficiency could cause adverse biological effects. **(Diaz, 2021)**.

In the present study, the concentration of Iron (Fe) in the coastal surface sediment of the Zuari estuary ranges from 4.1245 % to 9.2742 % **(Table 13)**, 3.5828 % to 9.0715 % **(Table 14)** and 3.0999 % to 10.0846 % **(Table 15)** during the monsoon, post-monsoon and pre-monsoon seasons, respectively.

Similarly, like manganese, the iron concentrations in the coastal surface sediments of the Zuari estuary were found to be higher in this study as compared to the findings of **Gaonkar and Matta, (2020)**.

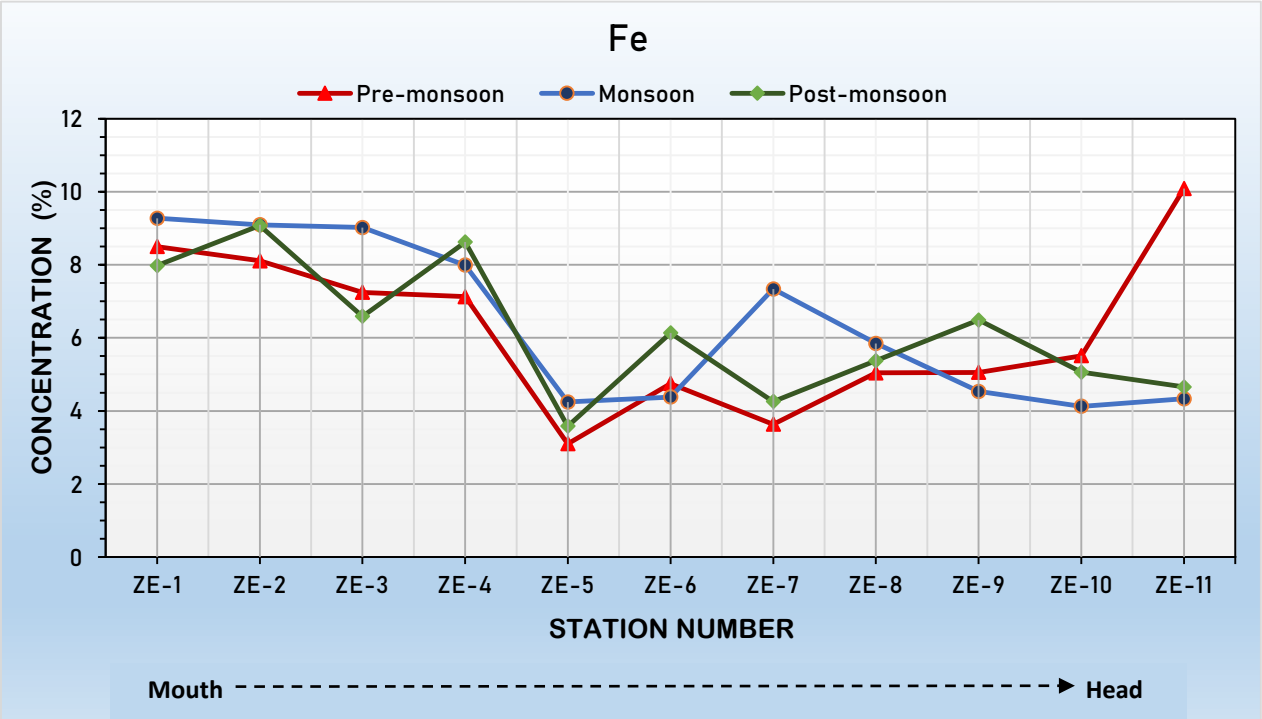

Fig. 15 – Shows the spatial variation of Iron (Fe) in the coastal surface sediments of the Zuari Estuary during the pre-monsoon, monsoon and post-monsoon seasons.

During the post-monsoon and pre-monsoon seasons, stations 2 and 11 had the highest iron (Fe) concentrations, while station 5 had the lowest Fe concentrations in both seasons; this is depicted by the plotted graph **(Fig. 15)**. During the monsoon season, station 1 exhibited the highest iron (Fe) concentration, while station 10 had the lowest levels. In the lower estuarine region, a higher concentration of iron was found, which could be due to the factors such as sediment grain size and organic carbon (OC) content **(Gopal et al., 2017)**. Additionally, sediment resuspension at higher salinities might have influenced the higher levels of iron at stations in this region. In general, dissolved iron flocculates at lower salinities, and this flocculation decreases with an increase in salinity, and finally it is precipitated **(Sholkovitz, 1987; Joseph and Chacko, 2006)**. Slightly higher iron values in the upper estuarine region could be due to past mining activities, particularly open-cast iron mining in the northern area, which had previously added extra iron to the estuarine system. Overall, materials from an iron ore processing plant and ore spills at the loading points could be responsible for the higher concentration of iron (Fe) reported at some stations. Currently, iron ore mining is not active in Goa. However, the metal released and absorbed by the sediments of the Zuari estuary in the past remains unsequestered **(Huang et al., 2012)**, and therefore, it can be mobilized.

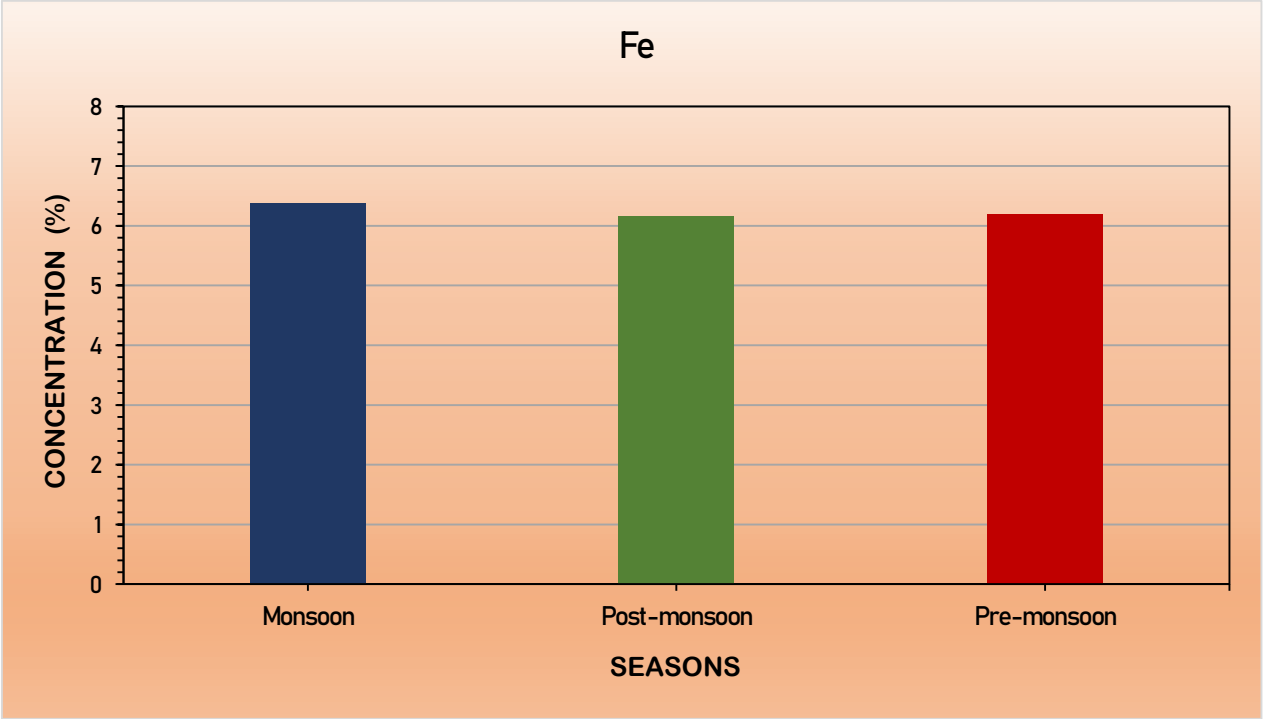

Fig. 16 – Depicts the seasonal variation of Iron (Fe) in the coastal surface sediments of the Zuari Estuary during the monsoon, post-monsoon and pre-monsoon seasons.

The seasonal variation of Fe **(Fig. 16)** in the coastal surface sediments collected from the Zuari estuary showed similar concentrations during the monsoon, post-monsoon, and pre-monsoon seasons, with a slightly higher value during the monsoon season. A higher concentration of iron (Fe) during monsoon season may be due to higher inputs from land run-off and the influx of metal-rich fresh water **(Singh et al., 2009)**. The increased particulate matter along with the suspended sediment load brought in by the river would also be a possible reason for the slightly higher values of iron during the monsoon season **(Senthilnathan and Balasubramanian, 1994)**. Higher Fe concentrations during the post-monsoon season can be attributed to metals being mobilized as a result of excessive inundation of the estuary with metal rich waste water **(Gaonkar and Matta, 2020)**. In contrast, the high concentration of Fe during the pre-monsoon season can be linked to the adsorption onto sediments due to the low water volume, which is associated with a high rate of evaporation, the presence of high organic carbon content, and the fine-grained nature of the sediments **(Obasohan, 2008)**.

4.2.3 Zinc (Zn)

Zinc occurs naturally in air, water, and soil, but human activities are increasing zinc concentrations unnaturally by adding zinc to the environment. Industrial activities such as mining, coal, waste combustion, and steel processing are the primary sources of zinc addition. Zinc is one of the most easily transported metals in natural waterways, moving in dissolved and combined forms with suspended

particles **(Mance and Yates, 1984)**. Zinc (Zn) is mainly found in its dissolved form in river water. A higher percentage of the zinc is absorbed by suspended particles in estuaries where suspended particle concentrations are higher. By means of microbial breakdown of organic matter and displacement by calcium and magnesium, zinc can be liberated from particles in low-salinity estuarine environments. When turbidity is at its highest, flocculated particles and zinc from suspended sediment will be deposited where they might concentrate, especially in anaerobic sediments. Numerous zinc ions exist in seawater in dissolved form as both inorganic and organic compounds.

Zinc is vital for living organisms as it plays a crucial role in various physiological processes like controlling ligand exchange and contributing to nucleic acid metabolism and gene expression. Lack of this element can result in inhibited growth, delayed maturation, weakened immunity, and neurosensory disorders. Conversely, an excessive intake of this element can lead to anemia.

In the present study, the concentration of zinc (Zn) in the coastal surface sediment of the Zuari estuary ranges from 59.8875 to 225.9875 ppm **(Table 13)**, 73.0875 to 176.575 ppm **(Table 14)** and 72.15 to 187.5125 ppm **(Table 15)** during the monsoon, post-monsoon and pre-monsoon seasons, respectively. Similarly, like manganese and iron, the zinc concentrations in the coastal surface sediments of the Zuari estuary were found to be slightly higher in this study as compared to the findings of **Gaonkar and Matta, (2020)**.

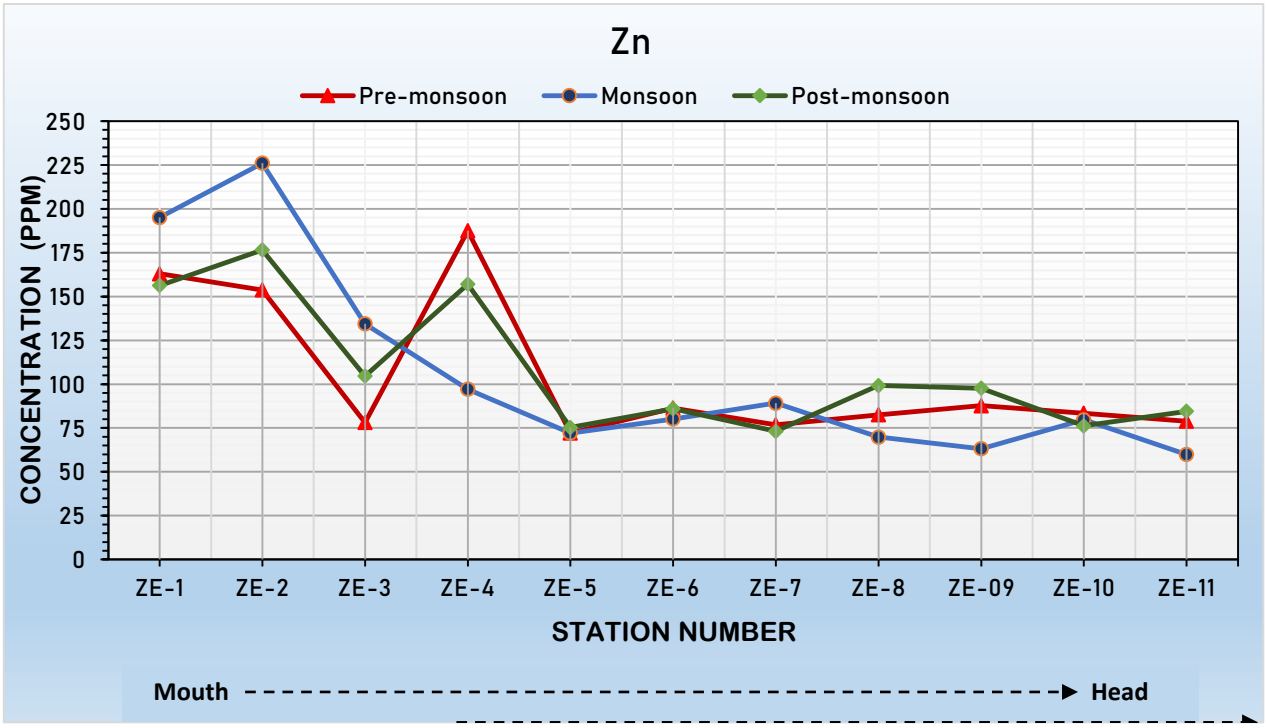

Fig. 17 – Shows the spatial variation of Zinc (Zn) in the coastal surface sediments of the Zuari Estuary during the pre-monsoon, monsoon and post-monsoon seasons.

During the monsoon and post-monsoon seasons, stations 2 had the highest zinc (Zn) concentrations, and stations 7 and 11 had the lowest zinc concentrations, respectively. Which is shown in the graph **(Fig. 17)**. During the pre-monsoon season, station 4 exhibited the highest zinc concentration, while station 5 had the lowest levels. Notably, Zn recorded higher values in the lower estuarine region as compared to the middle and upper estuarine regions. Overall, the zinc concentration in the collected surface sediments remained relatively stable from station 5 to station 11. **Gaonkar and Matta, (2020)** reported a similar spatial variation of zinc in the surface sediments of the Zuari estuary, attributing it to discharge from shipbuilding industries, atmospheric emissions, and other industrial activities. Zinc can enter the aquatic environment from a number of sources, including industrial discharges, sewage effluent, municipal routes, automobiles, agricultural use of pesticides and fungicides containing $ZnSO_4$, and run-off along with organic wastes **(Boxall et al., 2000; Silambarasan et al., 2012)**.

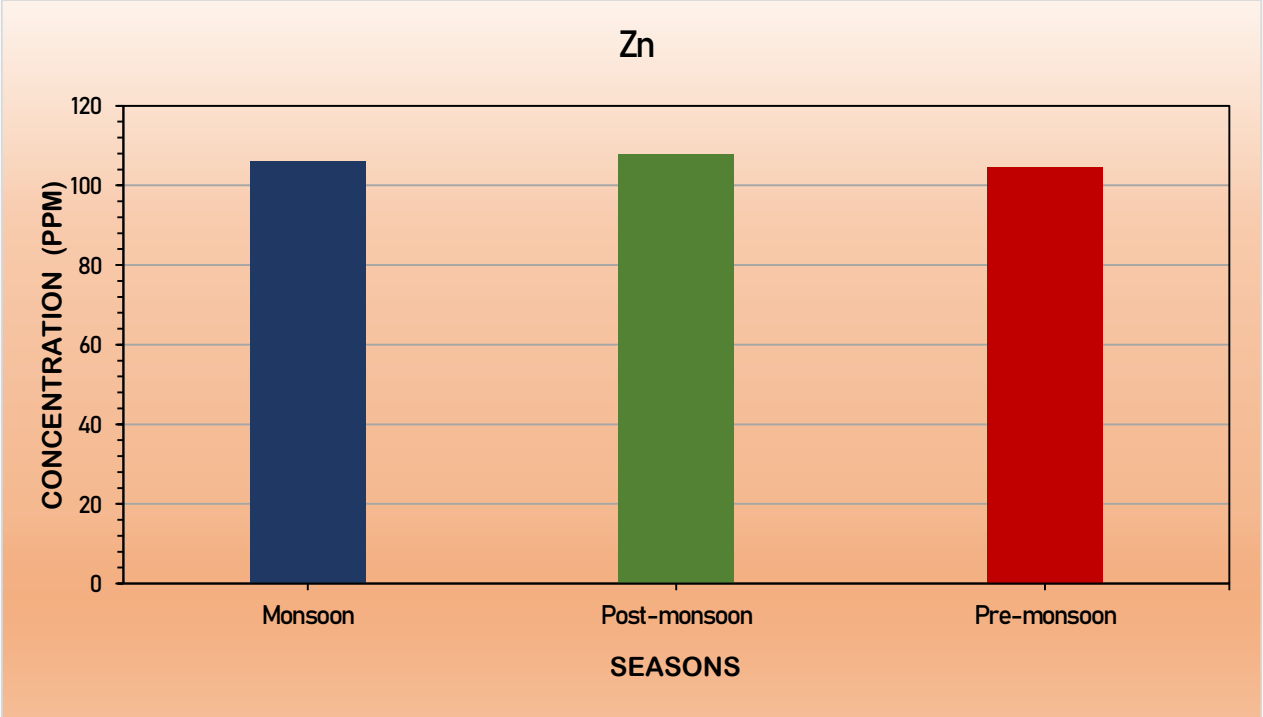

Fig. 18 – Depicts the seasonal variation of Zinc (Zn) in the coastal surface sediments of the Zuari Estuary during the monsoon, post-monsoon and pre-monsoon seasons.

The seasonal variation of Zn **(Fig. 18)** in coastal surface sediments collected from the Zuari estuary indicated lower concentrations during the pre-monsoon season; however, the concentration of zinc increased again during the post-monsoon season. A slightly higher Zn concentration during the monsoon season than the pre-monsoon season could be attributed to heavy freshwater runoff, which resulted in a high load of suspended or finer sediments and organic matter, facilitating the binding of Zn in sediments in addition to anthropogenic input **(Gaonkar et al., 2021)**.

4.2.4 Copper (Cu)

Copper is an abundant trace element found naturally in the Earth's crust and surface waters. Copper is a reddish metal with a distinct crystal structure. Copper naturally exists as a pure metal with great thermal and electrical conductivity. Copper commonly has an oxidation state of +2, but it can also exist in the +1 state. The main ores are oxides, sulfides, and halides. Copper plays a vital role in carbohydrate metabolism and the normal function of over 30 enzymes in various organisms, even at low concentrations (5–20 ppm). Copper is also required for the production of hemocyanin and hemoglobin, pigments that transport oxygen in the blood of vertebrates and crustaceans. Copper concentrations greater than 20 ppm can be harmful. Copper readily binds to sediments and organic materials, exhibiting moderate solubility in water **(Wekesa, 2015)**.

Copper is necessary for the well-being of plants and animals but not for microbes, leading to the low biodegradability of copper compounds. Copper is commonly present in aquatic systems due to a combination of natural occurrences and human activities. Copper occurs naturally in aquatic systems through geological deposits, volcanic processes, weathering and the erosion of rocks and soil. Mining, agriculture, metal and electrical manufacturing, pesticide application and various other human activities serve as anthropogenic sources of copper. Antifouling paints are used to coat ship hulls, buoys, and undersea surfaces, and as a contaminant from decking, pilings are a major source of copper in the marine environment. Some maritime buildings made of chromated copper arsenate (CCA)-treated timbers can also be a anthropogenic source of copper **(EPA, 2007)**.

In the present study, the concentration of copper (Cu) in the coastal surface sediment of the Zuari estuary ranges from 21.95 to 106.8 ppm **(Table 13)**, 20.3375 to 94.45 ppm **(Table 14)** and 23.725 to 139.6875 ppm **(Table 15)** during the monsoon, post-monsoon and pre-monsoon seasons, respectively. Similarly, like Zinc, the copper concentrations in the coastal surface sediments of the Zuari estuary were found to be slightly higher in this study as compared to the findings of **Gaonkar and Matta, (2020)**.

During the post-monsoon and pre-monsoon seasons, stations 4 had the highest copper (Cu) concentrations, and stations 5 and 7 had the lowest copper concentrations, respectively. Which is shown in the graph **(Fig. 19)**. During the monsoon season, station 2 exhibited the highest copper (Cu) concentration, while station 10 had the lowest levels. Copper showed an increasing trend from upstream to downstream, like in Fe, Mn, and Zn. Relatively higher values in the lower estuarine region can be attributed to the nature of the texture and organic matter content of the sediments. Moreover, Cu has the ability to form organic complexes, accelerate out as an insoluble form, and consequently get deposited in estuarine sediments **(Silambarasan et al., 2012)**. Simillary to spatial variation of zinc in the surface sediments of Zuari estuary copper concentration in the collected surface sediments remained relatively

stable from station 5 to station 11. **Gaonkar and Matta, (2020)** reported a similar spatial variation of zinc in the surface sediments of the Zuari estuary.

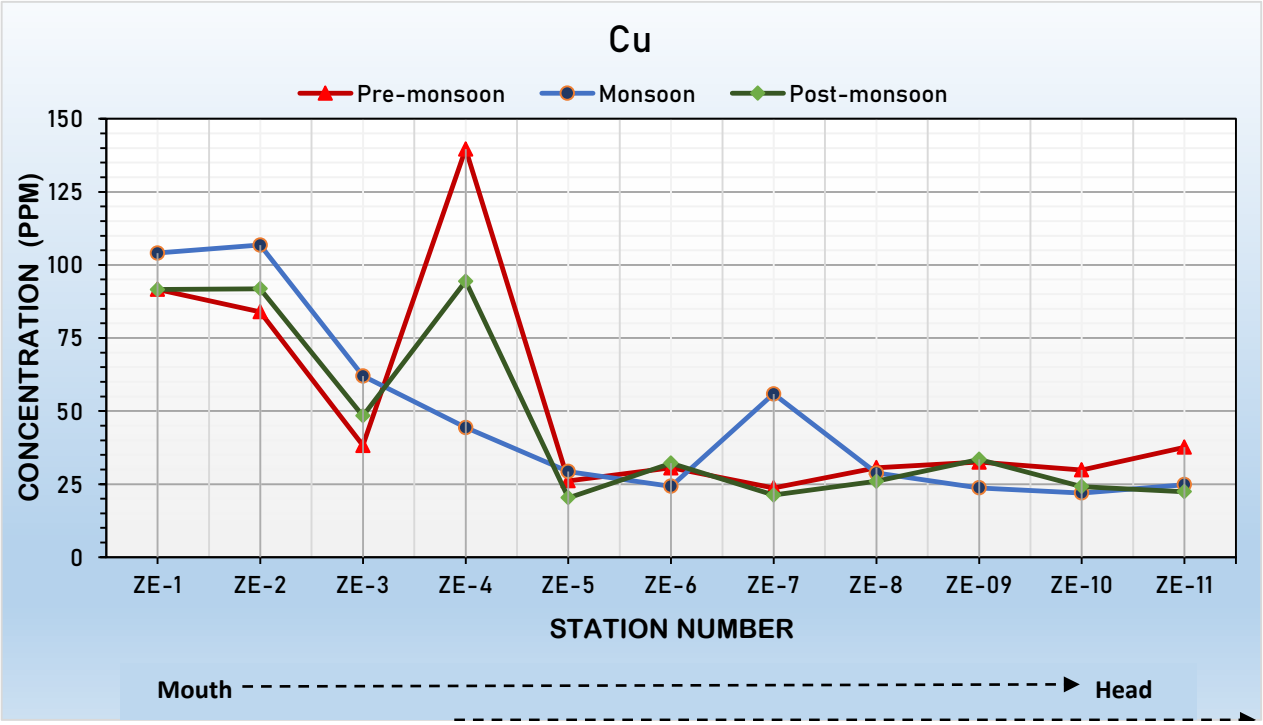

Fig. 19 – Shows the spatial variation of Copper (Cu) in the coastal surface sediments of the Zuari Estuary during the pre-monsoon, monsoon and post-monsoon seasons.

Interestingly, the spatial variation of Cu registered the highest concentrations at station 4 in the pre-monsoon season. Various activities in the harbor such as loading and unloading of cargo, cleaning of boats and maintenance, antifouling paint applications, etc., which are known to increase the Cu load in an aquatic environment since Cu-based biocides long-used on recreational boats have become the primary antifouling coating option for recreational boats **(WHO, 1998; Silambarasan et al., 2012)**.

Seasonal variation of Cu in the surface sediments of the Zuari estuary **(Fig. 20)**; higher copper concentrations were found during the pre-monsoon season. This increase in copper levels may be attributed to the high saline conditions, potentially leading to the precipitation of dissolved Cu **(Ananthan et al., 2005, 2006)**. During the post-monsoon season, the concentration of Cu was lower compared to the monsoon season. The higher copper concentrations observed during the monsoon season may be due to the influx of land-based materials such as runoff from agricultural areas, shipbuilding harbors and industrial discharges.

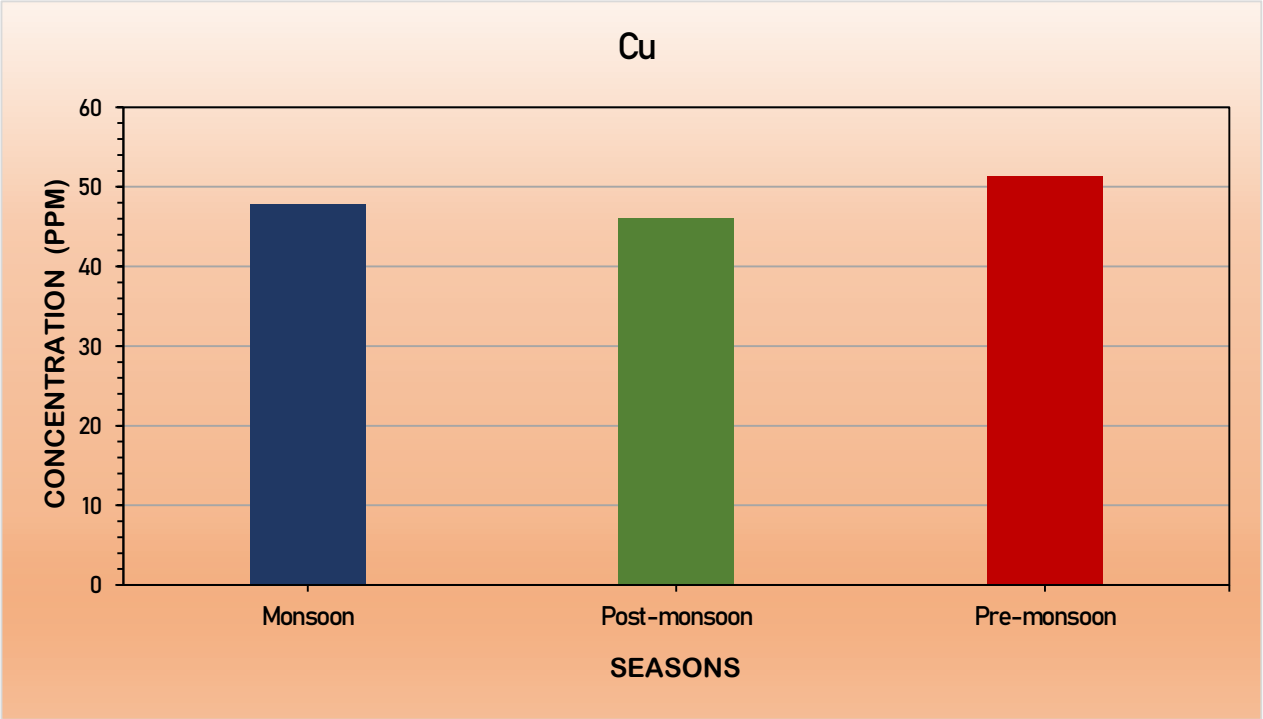

Fig. 20 – Depicts the seasonal variation of copper (Cu) in the coastal surface sediments of the Zuari Estuary during the monsoon, post-monsoon and pre-monsoon seasons.

4.2.5 Cobalt (Co)

Cobalt though widely dispersed, makes up only 0.001 % of the earths crust. The majority of cobalt in the earth's crust is found in minerals such as cobaltite, smaltite, and skutterudite. In addition to natural processes, human activities such as mining and industrial processes have also contributed to the distribution of cobalt in the environment. Overall, the cycling of cobalt between the atmosphere, surface water, and ocean sediments plays a crucial role in regulating its availability and abundance in different parts of the Earth.

Understanding the sources and sinks of cobalt in the environment is essential for assessing its potential impact on ecosystems and human health. In recent years, there has been growing concern over the environmental and health risks associated with cobalt exposure, particularly in regions where mining and industrial activities are prevalent.

One important aspect of cobalt's environmental impact is its ability to bioaccumulate in organisms, leading to potential toxicity in higher trophic levels of the food chain. Additionally, cobalt can leach into water sources and soil, posing a risk to both aquatic and terrestrial ecosystems. Studies have shown that exposure to high levels of cobalt can have detrimental effects on the health of organisms, including developmental abnormalities, reproductive issues, and neurological disorders.

In the present study, the concentration of cobalt (Co) in the coastal surface sediment of the Zuari estuary varies from 10.3 ppm to 41.9 ppm **(Table 13)**, 11.2625 ppm to 39 ppm **(Table 14)** and 13.8875 ppm to 37.2625 ppm **(Table 15)**, during the monsoon, post-monsoon and pre-monsoon season, respectively.

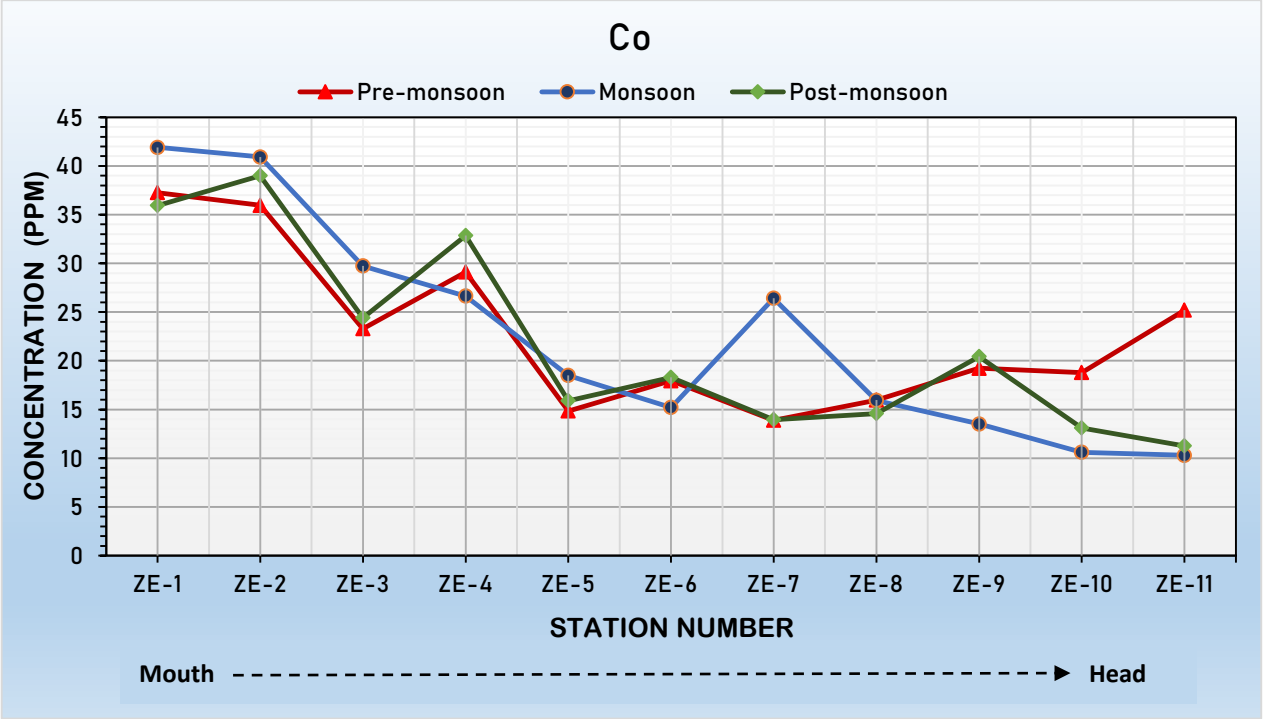

Fig. 21 – Shows the spatial variation of cobalt (Co) in the coastal surface sediments of the Zuari Estuary during the pre-monsoon, monsoon and post-monsoon seasons.

In the plotted graph **(Fig. 21)**, cobalt concentration peaked at station 1 in the monsoon season, while the highest concentrations of cobalt were observed at stations 1 and 2 in the pre-monsoon and post-monsoon seasons, respectively. The way cobalt is spread in the coastal sediment of the Zuari estuary shows an uneven pattern from the estuary's entrance to its upper reaches (from downstream to upstream). Factors such as sediment movement, river discharge, and deposition patterns along the estuary directly influence the distribution of cobalt, leading to the observed irregular trend. Moreover, industrial operations and human influences along the estuary can also greatly affect the spatial distribution of cobalt in the sediment. These factors can contribute to the accumulation of cobalt in certain areas of the estuary, leading to the observed irregular trend in its distribution.

Seasonal variation of cobalt **(Fig. 22)** in coastal surface sediments collected from the Zuari estuary revealed similar concentrations of cobalt during the pre-monsoon, monsoon, and post-monsoon seasons, with the post-monsoon season showing a slightly lower concentration. The results suggest that cobalt levels in sediments remain mostly constant throughout the year, with slight variations during different seasons. This is probably because cobalt is consistently supplied from sources like weathering of rock and anthropogenic activities. The stability of cobalt levels in sediments indicates a balance between input

and removal of cobalt within the estuary. Moreover, in the post-monsoon season, the higher biological activity in the estuary can raise the cobalt concentration in the water due to uptake by organisms like phytoplankton. The higher cobalt values during the monsoon season could be attributed to the increased particulate matter and suspended sediment load brought in by the river **(Senthilnathan and Balasubramanian, 1999)**.

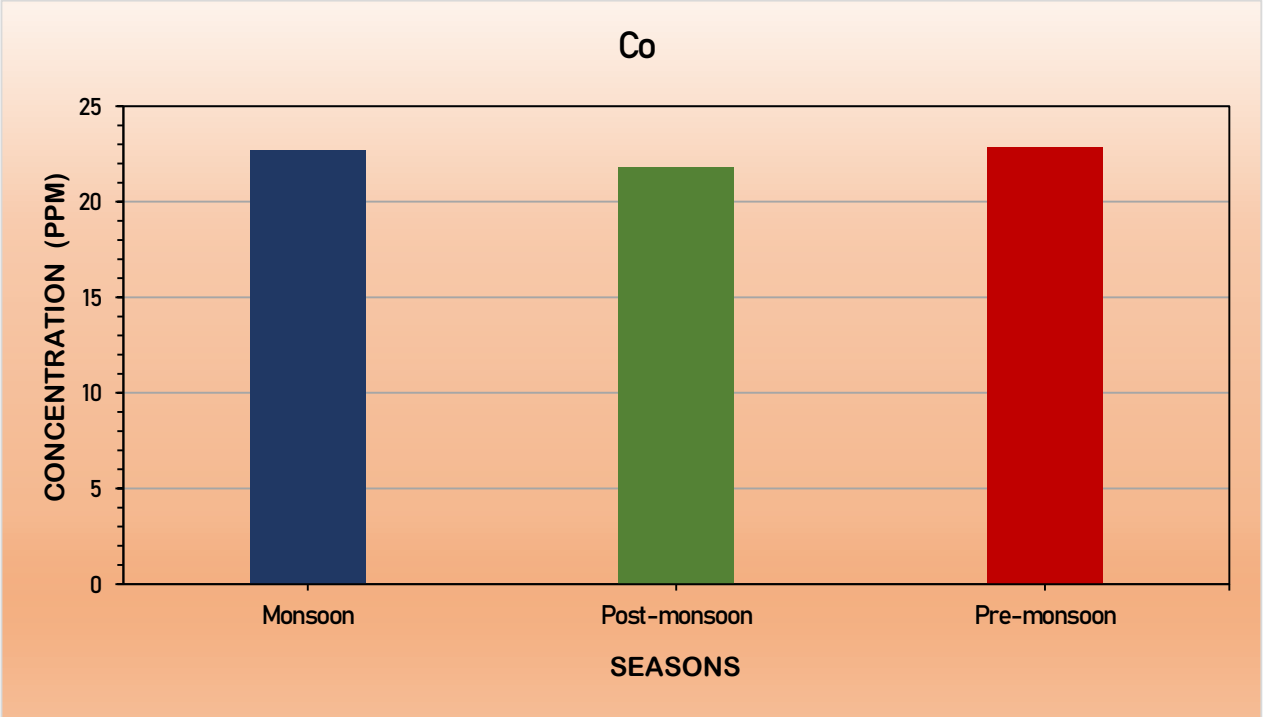

Fig. 22 – Depicts the seasonal variation of cobalt (Co) in the coastal surface sediments of the Zuari Estuary during the monsoon, post-monsoon and pre-monsoon seasons.

4.3 POLLUTION INDICES DATA FOR THE MANDOVI ESTUARINE SEDIMENT

- **Geo-accumulation index (Igeo) -**

Table 16 – Geo-accumulation index (Igeo) data on the variation of trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Mandovi estuary, Goa, during the monsoon season.

STATION NUMBER	Mn (ASV=850 ppm)	Fe (ASV=47200 ppm)	Zn (ASV=95 ppm)	Cu (ASV=45 ppm)	Co (ASV=19 ppm)
ME- 1	1.2887	-0.6247	-1.1514	-2.0578	-1.3866
ME- 2	2.8640	1.1132	-0.4392	-0.9751	-0.0496
ME- 3	1.8671	0.4906	-0.6228	-1.0484	-0.1422
ME- 4	1.9423	0.5512	-0.7265	-1.3219	-0.4762
ME- 5	2.2315	1.2957	-0.5266	-0.9615	0.0195
ME- 6	1.6518	1.6893	-0.5157	-0.8049	0.0925
ME- 7	1.8190	0.5558	-0.7741	-1.4496	-0.6031
ME- 8	1.2458	0.3189	-1.1613	-1.7254	-1.0847
ME- 9	1.1731	0.6232	-1.0933	-1.3020	-0.6690
ME- 10	1.9671	0.7849	-0.8083	-1.5754	-0.4833
ME- 11	0.5897	0.2949	-1.2238	-1.5722	-0.8431
AVERAGE CONCENTRATION	1.6946	0.6448	-0.8221	-1.3449	-0.5114

***ME** - Mandovi Estuary ***ASV –** Average Shale Value

Table 17 – Geo-accumulation index (Igeo) data on the variation of trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Mandovi estuary, Goa, during the post-monsoon season.

STATION NUMBER	Mn (ASV=850 ppm)	Fe (ASV=47200 ppm)	Zn (ASV=95 ppm)	Cu (ASV=45 ppm)	Co (ASV= 19 ppm)
ME- 1	2.4301	0.1419	-1.1608	-1.7721	-1.0807
ME- 2	2.5662	1.3270	-0.4318	-0.3788	0.3219
ME- 3	2.6796	0.7749	-0.8234	-1.0439	-0.0114
ME- 4	1.9334	0.2988	-0.9804	-1.3903	-0.6264
ME- 5	2.4530	1.1251	-0.7057	-0.9688	-0.0378
ME- 6	1.8381	0.5563	-0.9400	-1.2695	-0.3866
ME- 7	2.0046	0.6780	-1.0615	-1.3557	-0.5717
ME- 8	2.0025	0.9324	-0.8438	-1.0910	-0.2285
ME- 9	1.2476	0.9846	-0.0241	-1.2586	-0.4657
ME- 10	2.2692	1.7691	-0.5486	-0.4406	0.0182
ME- 11	3.2470	1.8954	-0.6787	-0.4079	0.2964
AVERAGE CONCENTRATION	2.2428	0.9530	-0.7453	-1.0343	-0.2520

***ME -** Mandovi Estuary ***ASV –** Average Shale Value

Table 18 – Geo-accumulation index (Igeo) data on the variation of trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Mandovi estuary, Goa, during the pre-monsoon season.

STATION NUMBER	Mn (ASV=850 ppm)	Fe (ASV=47200 ppm)	Zn (ASV=95 ppm)	Cu (ASV= 45 ppm)	Co (ASV=19 ppm)
ME- 1	1.3083	-0.6480	-1.0471	-1.9517	-1.2479
ME- 2	2.8820	1.5709	-0.3345	-0.2682	0.1834
ME- 3	2.4684	0.9508	-0.3906	-0.6489	-0.0921
ME- 4	2.0616	0.3528	-0.7323	-1.2818	-0.5074
ME- 5	2.2458	1.2610	-0.4662	-0.7513	-0.1207
ME- 6	1.9334	0.9962	-0.5196	-1.0594	-0.2464
ME- 7	1.2642	0.3771	-0.8492	-1.1923	-0.6821
ME- 8	2.0818	1.3334	-0.4075	-0.4684	0.0057
ME- 9	1.5878	1.0093	-0.7739	-1.0172	-0.4050
ME- 10	1.8262	1.3210	-0.7260	-0.9486	-0.2752
ME- 11	3.1710	1.2538	-0.3090	-0.3353	0.1008
AVERAGE CONCENTRATION	2.0755	0.8889	-0.5960	-0.9021	-0.2988

***ME -** Mandovi Estuary ***ASV –** Average Shale Value

- **Contamination factor (CF) -**

Table 19 – Contamination factor (CF) data for the trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Mandovi estuary, Goa, during the monsoon season.

STATION NUMBER	Mn (ASV=850 ppm)	Fe (ASV=47200 ppm)	Zn (ASV=95 ppm)	Cu (ASV=45 ppm)	Co (ASV=19 ppm)
ME- 1	3.6647	0.9728	0.6753	0.3603	0.5737
ME- 2	10.9206	3.2448	1.1063	0.7631	1.4493
ME- 3	5.4721	2.1076	0.9741	0.7253	1.3592
ME- 4	5.7647	2.1979	0.9066	0.6	1.0783
ME- 5	7.0441	3.6823	1.0413	0.7703	1.5204
ME- 6	4.7132	4.8375	1.0492	0.8586	1.5993
ME- 7	5.2926	2.2049	0.8771	0.5492	0.9875
ME- 8	3.5574	1.8710	0.6707	0.4536	0.7072
ME- 9	3.3824	2.3104	0.7030	0.6083	0.9434
ME- 10	5.8647	2.5844	0.8566	0.5033	1.0730
ME- 11	2.2574	1.8402	0.6422	0.5044	0.8362
AVERAGE CONCENTRATION	5.2667	2.5322	0.8638	0.6088	1.1025

***ME -** Mandovi Estuary ***ASV –** Average Shale Value

Table 20 – Contamination factor (CF) data for the trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Mandovi estuary, Goa, during the post-monsoon season.

STATION NUMBER	Mn (ASV=850 ppm)	Fe (ASV=47200 ppm)	Zn (ASV=95 ppm)	Cu (ASV=45 ppm)	Co (ASV=19 ppm)
ME- 1	8.0838	1.6551	0.6709	0.4392	0.7092
ME- 2	8.8838	3.7632	1.1120	1.1536	1.875
ME- 3	9.6103	2.5667	0.8476	0.7275	1.4882
ME- 4	5.7294	1.8452	0.7603	0.5722	0.9717
ME- 5	8.2132	3.2718	0.9197	0.7664	1.4612
ME- 6	5.3632	2.2058	0.7818	0.6222	1.1474
ME- 7	6.0191	2.3999	0.7187	0.5861	1.0092
ME- 8	6.0103	2.8628	0.8358	0.7042	1.2803
ME- 9	3.5618	2.9681	1.4751	0.6269	1.0862
ME- 10	7.2309	5.1128	1.0255	1.1053	1.5191
ME- 11	14.2412	5.5802	0.9371	1.1306	1.8421
AVERAGE CONCENTRATION	7.5406	3.11200.	0.9168	0.7667	1.3081

***ME -** Mandovi Estuary ***ASV –** Average Shale Value

Table 21 – Contamination factor (CF) data for the trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Mandovi estuary, Goa, during the pre-monsoon season.

STATION NUMBER	Mn (ASV=850 ppm)	Fe (ASV=47200 ppm)	Zn (ASV=95 ppm)	Cu (ASV=45 ppm)	Co (ASV=19 ppm)
ME- 1	3.7147	0.9573	0.7259	0.3878	0.6316
ME- 2	11.0574	4.4563	1.1896	1.2456	1.7033
ME- 3	8.3015	2.8994	1.1442	0.9567	1.4072
ME- 4	6.2618	1.9156	0.9029	0.6169	1.0553
ME- 5	7.1147	3.5950	1.0858	0.8911	1.3796
ME- 6	5.7294	2.9920	1.0463	0.7197	1.2645
ME- 7	3.6029	1.9482	0.8326	0.6564	0.9349
ME- 8	6.35	3.7801	1.1309	1.0842	1.5059
ME- 9	4.5088	3.0195	0.8772	0.7411	1.1329
ME- 10	5.3191	3.7475	0.9068	0.7772	1.2395
ME- 11	13.5103	3.5769	1.2108	1.1889	1.6086
AVERAGE CONCENTRATION	6.8610	2.9898	1.0048	0.8423	1.2603

***ME -** Mandovi Estuary ***ASV –** Average Shale Value

- **Pollution load index (PLI) -**

Table 22 – Pollution load index (PLI) data for the trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Mandovi estuary, Goa.

STATION NUMBER	MONSOON	POST-MONSOON	PRE-MONSOON
ME- 1	0.8697	1.2283	0.9124
ME- 2	2.1252	2.4047	2.6238
ME- 3	1.6176	1.8662	2.0598
ME- 4	1.4935	1.3491	1.4779
ME- 5	1.9954	1.9428	2.0261
ME- 6	2.0105	1.4586	1.7481
ME- 7	1.4089	1.4376	1.2910
ME- 8	1.0745	1.6694	2.1346
ME- 9	1.2582	1.6040	1.5857
ME- 10	1.4763	2.2949	1.7708
ME- 11	1.0239	2.7423	2.5690

***ME** - Mandovi Estuary

- **Contamination degree (Cd) -**

Table 23 – Contamination degree (Cd) data for the trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Mandovi estuary, Goa.

STATION NUMBER	MONSOON	POST-MONSOON	PRE-MONSOON
ME- 1	6.2468	11.5582	6.4173
ME- 2	17.4841	16.7876	19.6522
ME- 3	10.6383	15.2403	14.709
ME- 4	10.5475	9.8788	10.7525
ME- 5	14.0584	14.6323	14.0662
ME- 6	13.0578	10.1204	11.7519
ME- 7	9.9113	10.733	7.975
ME- 8	7.2599	11.6934	13.8511
ME- 9	7.9475	9.7181	10.2795
ME- 10	10.882	15.9936	11.9901
ME- 11	6.0804	23.7312	21.0955

***ME** - Mandovi Estuary

- **Modified degree of contamination (mCd) -**

Table 24 – Modified degree of contamination (mCd) data for the trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Mandovi estuary, Goa.

STATION NUMBER	MONSOON	POST-MONSOON	PRE-MONSOON
ME- 1	1.2494	2.3116	1.2835
ME- 2	3.4968	3.3575	3.9304
ME- 3	2.1277	3.0481	2.9418
ME- 4	2.1095	1.9758	2.1505
ME- 5	2.8117	2.9265	2.8132
ME- 6	2.6116	2.0241	2.3504
ME- 7	1.9823	2.1466	1.595
ME- 8	1.4520	2.3387	2.7702
ME- 9	1.5895	1.9436	2.0559
ME- 10	2.1764	3.1987	2.3980
ME- 11	1.2161	4.7462	4.2191

***ME** - Mandovi Estuary

- **Potential contamination index (Cp) -**

Table 25 – Potential contamination index (Cp) data for the trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Mandovi estuary, Goa.

TRACE ELEMENTS	MONSOON	POST-MONSOON	PRE-MONSOON
Mn	10.9206	14.2412	13.5103
Fe	4.8375	5.5802	4.4563
Zn	1.1063	1.4751	1.2108
Cu	0.8586	1.1536	1.2456
Co	1.5993	1.875	1.7033

- **Potential ecological risk index -**

Table 26 – Evaluation on potential risk of trace metals pollution in coastal surface sediments of the Mandovi estuary during monsoon season.

STATION NUMBER	Ecological risk for single metal E_r^i				RISK INDEX
	Mn	Zn	Cu	Co	
ME- 1	3.6647	0.6753	1.8015	2.8685	9.01
ME- 2	10.9206	1.1063	3.8155	7.2465	23.0889
ME- 3	5.4721	0.9741	3.6265	6.796	16.8687
ME- 4	5.7647	0.9066	3	5.3915	15.0628
ME- 5	7.0441	1.0413	3.8515	7.602	19.5389
ME- 6	4.7132	1.0492	4.293	7.9965	18.0519
ME- 7	5.2926	0.8771	2.746	4.9375	13.8532
ME- 8	3.5574	0.6707	2.268	3.536	10.0321
ME- 9	3.3824	0.7030	3.0415	4.717	11.8439
ME- 10	5.8647	0.8566	2.5165	5.365	14.6028
ME- 11	2.2574	0.6422	2.522	4.181	9.6026
MEAN	5.2667	0.8638	3.0438	5.5125	

***ME** - Mandovi Estuary

Table 27 – Evaluation on potential risk of trace metals pollution in coastal surface sediments of the Mandovi estuary during post-monsoon season.

STATION NUMBER	Ecological risk for single metal E_r^i				RISK INDEX
	Mn	Zn	Cu	Co	
ME- 1	8.0838	0.6709	2.196	3.546	14.4967
ME- 2	8.8838	1.1120	5.768	9.375	25.1388
ME- 3	9.6103	0.8476	3.6375	7.441	21.5364
ME- 4	5.7294	0.7603	2.861	4.8585	14.2092
ME- 5	8.2132	0.9197	3.832	7.306	20.2709
ME- 6	5.3632	0.7818	3.111	5.737	14.993
ME- 7	6.0191	0.7187	2.9305	5.046	14.7143
ME- 8	6.0103	0.8358	3.521	6.4015	16.7686
ME- 9	3.5618	1.4751	3.1345	5.431	13.6024
ME- 10	7.2309	1.0255	5.5265	7.5955	21.3784
ME- 11	14.2412	0.9371	5.653	9.2105	30.0418
MEAN	7.5406	0.9168	3.8337	6.5407	

***ME -** Mandovi Estuary

Table 28 – Evaluation on potential risk of trace metals pollution in coastal surface sediments of the Mandovi estuary during pre-monsoon season.

STATION NUMBER	Ecological risk for single metal E_r^i				RISK INDEX
	Mn	Zn	Cu	Co	
ME- 1	3.7147	0.7259	1.939	3.158	9.5376
ME- 2	11.0574	1.1896	6.228	8.5165	26.9915
ME- 3	8.3015	1.1442	4.7835	7.036	21.2652
ME- 4	6.2618	0.9029	3.0845	5.2765	15.5257
ME- 5	7.1147	1.0858	4.4555	6.898	19.554
ME- 6	5.7294	1.0463	3.5985	6.3225	16.6967
ME- 7	3.6029	0.8326	3.282	4.6745	12.392
ME- 8	6.35	1.1309	5.421	7.5295	20.4314
ME- 9	4.5088	0.8772	3.7055	5.6645	14.756
ME- 10	5.3191	0.9068	3.886	6.1975	16.3094
ME- 11	13.5103	1.2108	5.9445	8.043	28.7086
MEAN	6.8610	1.0048	4.2116	6.3015	

***ME -** Mandovi Estuary

4.3.1 Geo-accumulation index (Igeo)

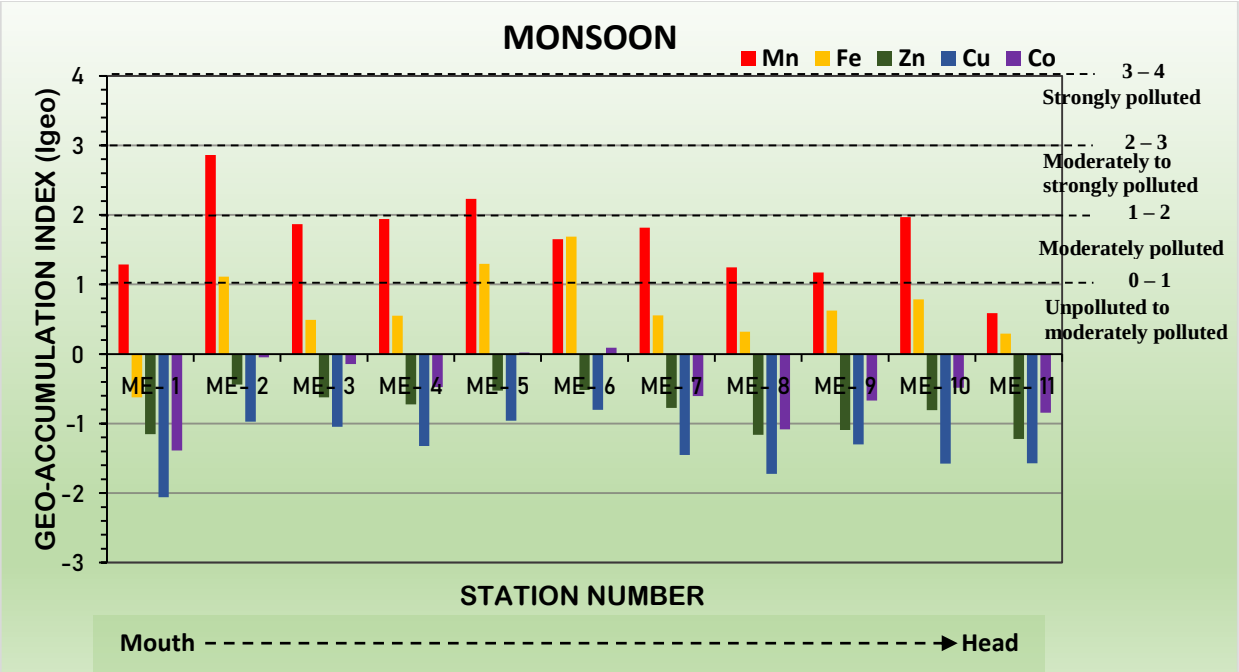

Fig. 23 - Plots showing Igeo values for each metal in the coastal surface sediments of the Mandovi estuary during monsoon season.

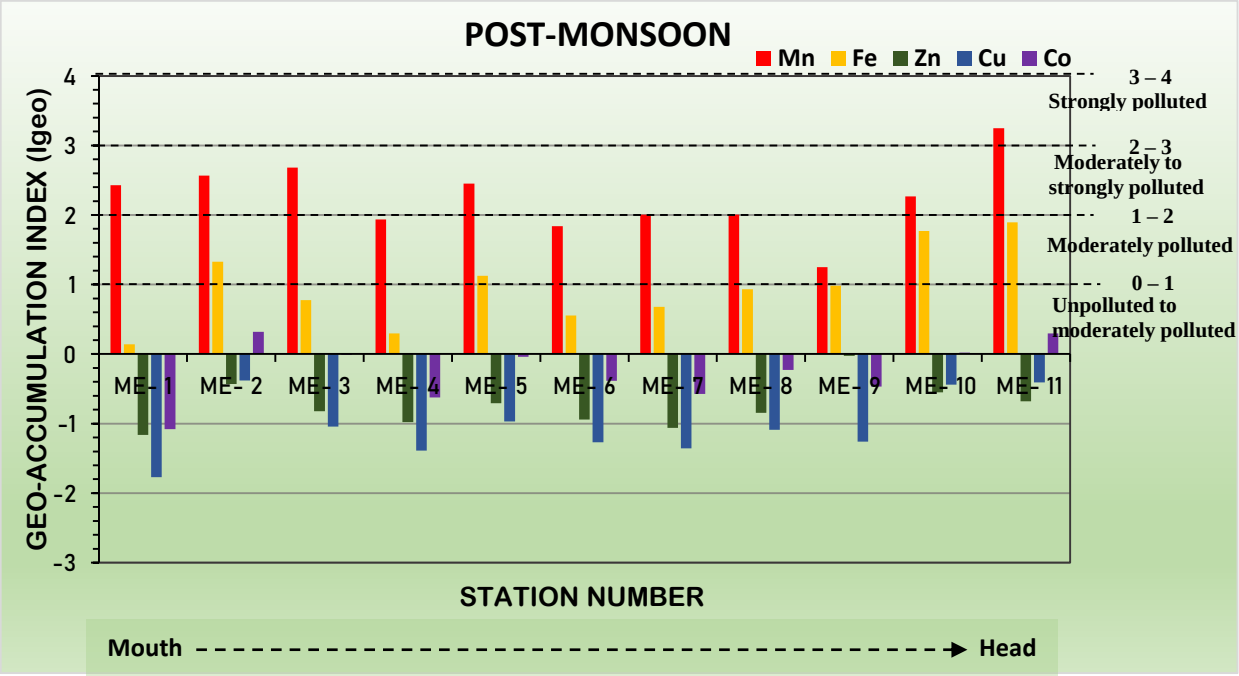

Fig. 24 - Plots showing Igeo values for each metal in the coastal surface sediments of the of the Mandovi estuary during post-monsoon season.

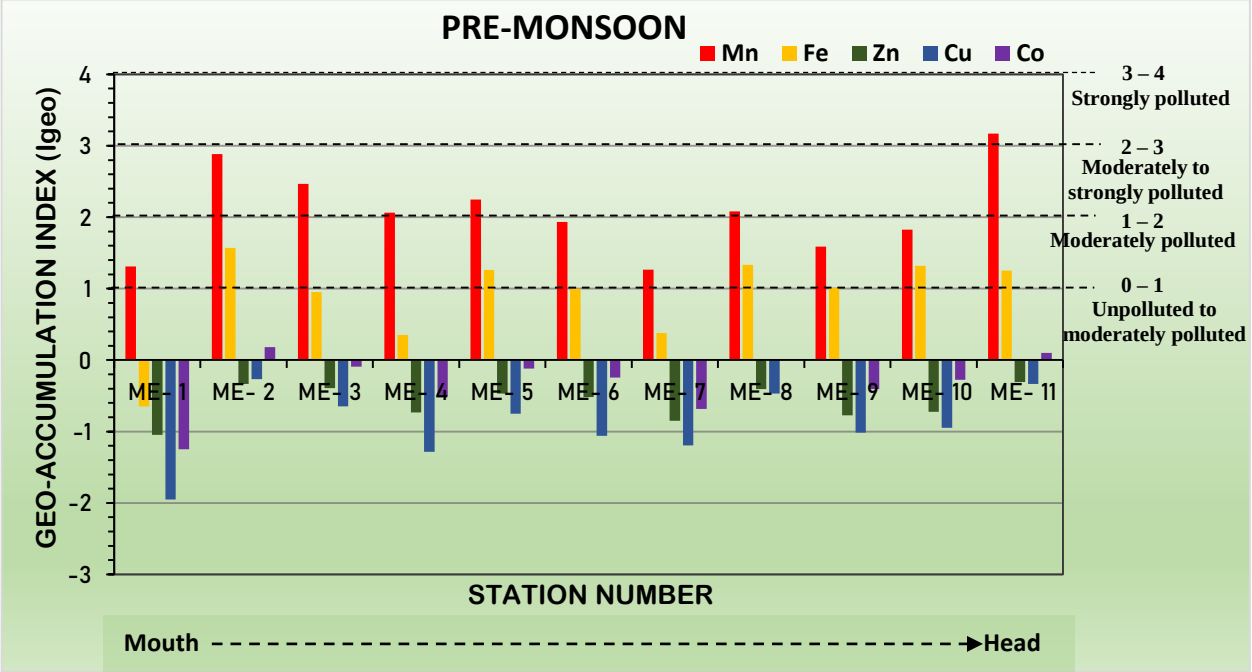

Fig. 25 - Plots showing Igeo values for each metal in the coastal surface sediments of the Mandovi estuary during pre-monsoon season.

The average Igeo values in the Mandovi estuarine surface sediments for Mn in the monsoon, post-monsoon, and pre-monsoon seasons were 1.6946, 2.2428 and 2.0755 **(Table 16, 17** and **18)**, respectively. The corresponding values for Fe were 0.6448, 0.9530 and 0.8889 **(Table 16, 17** and **18)**. The levels of pollution in the estuarine sediments of the Mandovi estuary for Mn ranged from moderately to strongly polluted across all three seasons **(Figs. 23, 24** and **25)**. However, during the monsoon season, station 11 sediments were free of manganese pollution but later increased to strongly polluted levels during the post-monsoon season. In contrast, Fe showed pollution levels ranging from unpolluted to moderate across all three seasons. Apart from Mn and Fe, the sediments remained free from pollution by zinc (Zn), copper (Cu) and cobalt (Co) throughout all three seasons.

The higher Igeo values of Mn and Fe can be attributed to anthropogenic inputs such as industrial discharge, sewage waste, antifouling coatings from fishing boats, boat exhaust and barges used to transport Fe-Mn ore. The elevated levels of manganese in station 11 sediments during the post-monsoon season indicate a significant contamination source in that specific area. The presence of Fe at levels ranging from unpolluted to moderate levels implies a more regulated input compared to the input of manganese. In summary, the sediments in the study area exhibit different pollution levels based on the season and specific region.

4.3.2 Contamination factor (CF)

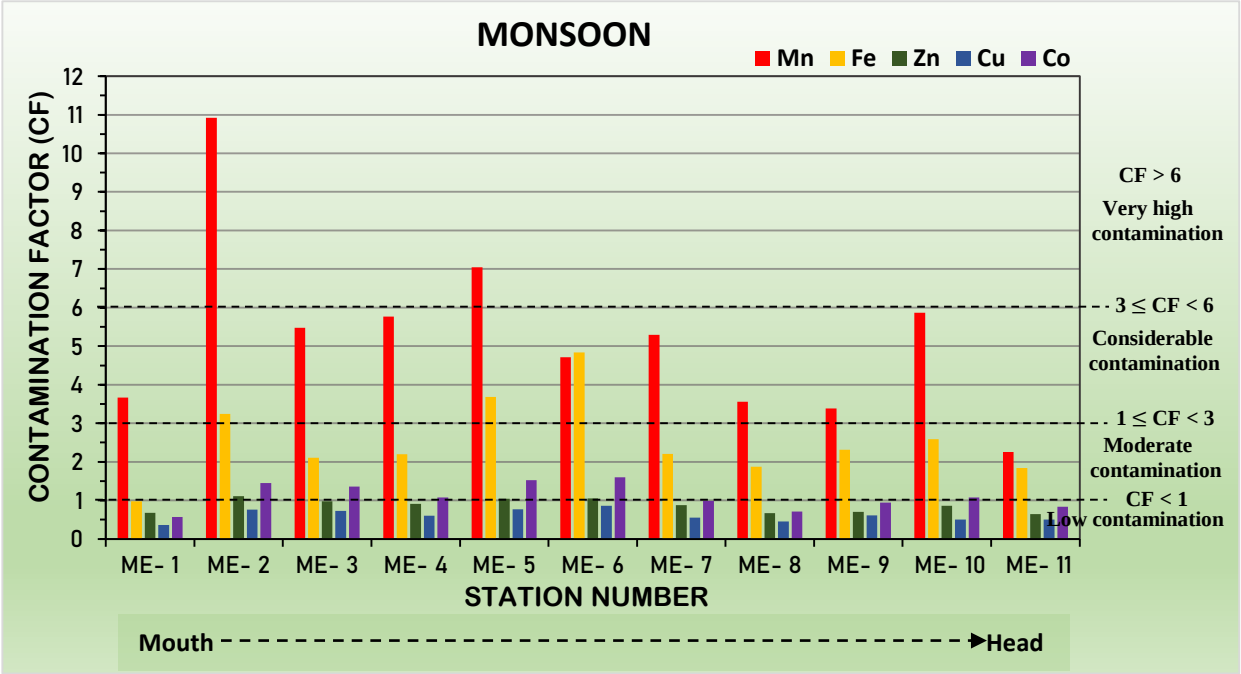

Fig. 26 - Plots showing Contamination factor (CF) values for each metal in the coastal surface sediments of the Mandovi estuary during monsoon season.

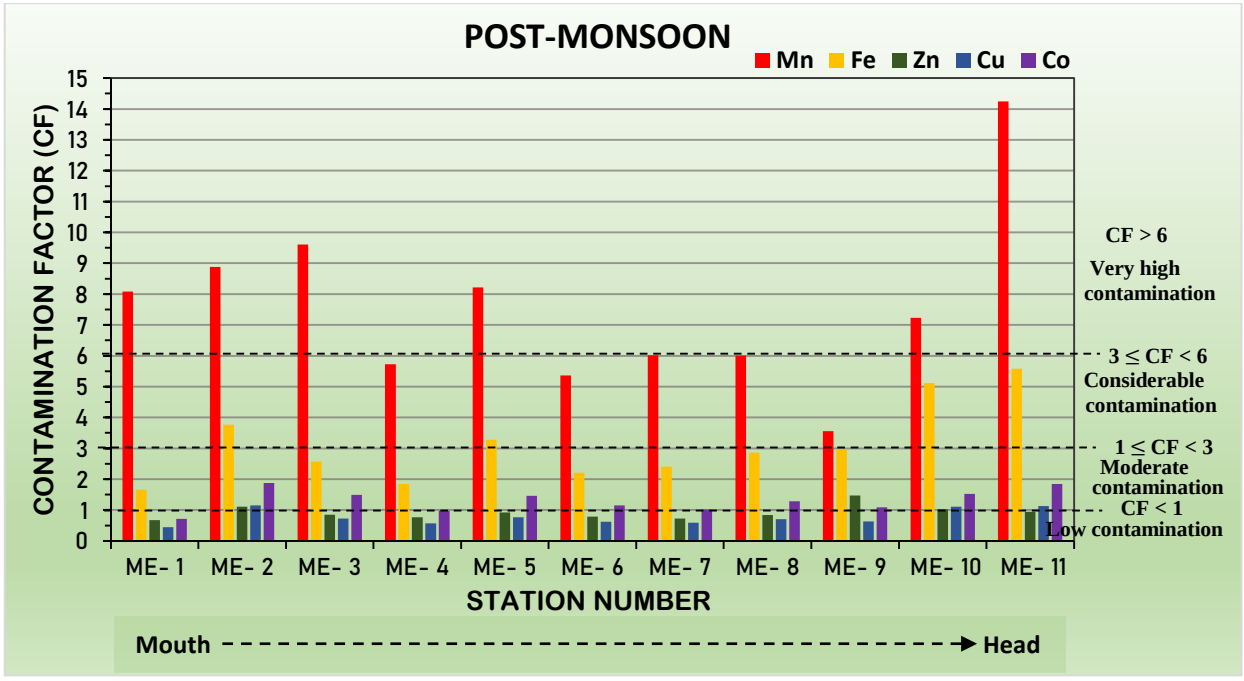

Fig. 27 - Plots showing Contamination factor (CF) values for each metal in the coastal surface sediments of the Mandovi estuary during post-monsoon season.

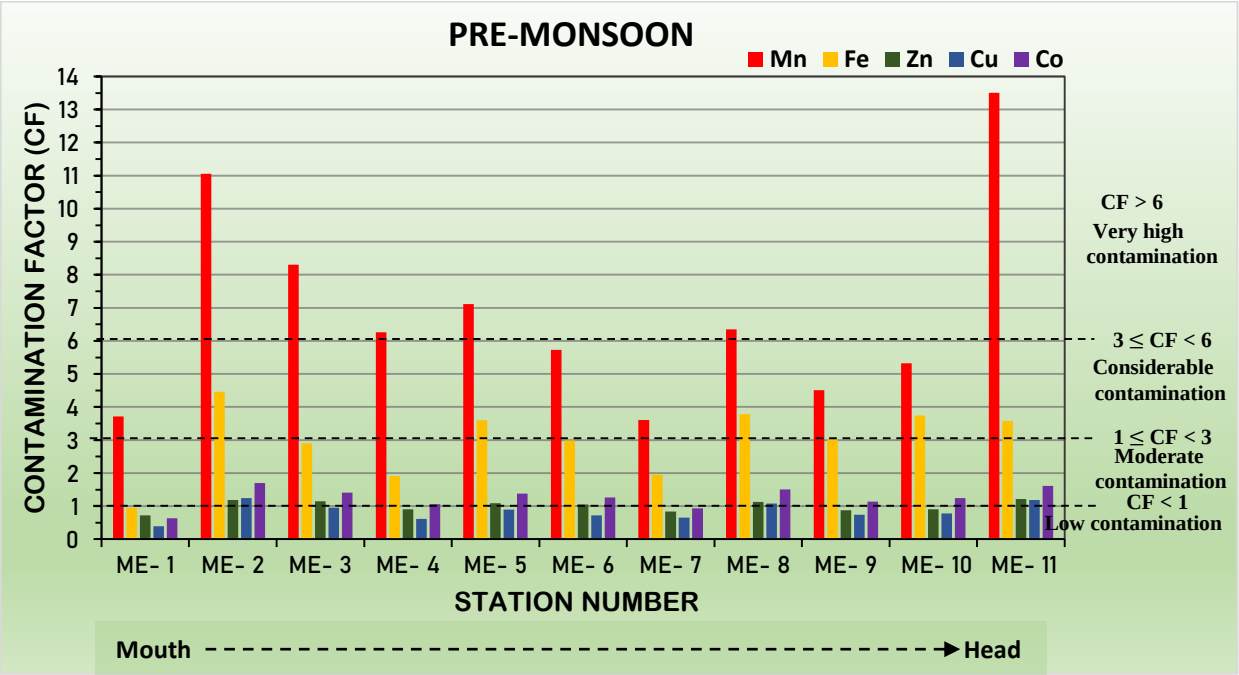

Fig. 28 - Plots showing Contamination factor (CF) values for each metal in the coastal surface sediments of the Mandovi estuary during pre-monsoon season.

Contamination factor values for the monsoon, post-monsoon and pre-monsoon seasons are displayed in **Tables 19, 20** and **21**, respectively. The variation of contamination factor values for each metal during the monsoon, post-monsoon and pre-monsoon seasons is depicted in **Figs. 26, 27** and **28**, respectively. In the Mandovi estuary, Mn showed a considerable to very high contamination level across all seasons and stations except at station 11. At station 11, the sediment sample exhibited a moderate contamination level during the monsoon season. However, in the post-monsoon and pre-monsoon seasons, the sediment sample showed very high contamination levels. Conversely, Fe displayed a moderate to considerable contamination level across all seasons and stations, with the exception of station 1. At station 1, Fe exhibited a low contamination level during both the monsoon and pre-monsoon seasons. Apart from Mn and Fe, the sediments remained uncontaminated by zinc (Zn), copper (Cu) and cobalt (Co) throughout all three seasons and across all stations. Nevertheless, cobalt displayed moderate contamination levels at specific stations throughout the different seasons.

The elevated contamination factors of Mn and Fe can be attributed to the ore input from intensive mining activities previously conducted in Goa. Additionally, industrial waste discharge, ongoing developmental activities along riverbanks, and sewage discharge could contribute to the increased levels of Mn and Fe in the sediments. The moderate contamination of cobalt at certain stations suggests localized sources of pollution in those areas.

4.3.2 Pollution load index (PLI)

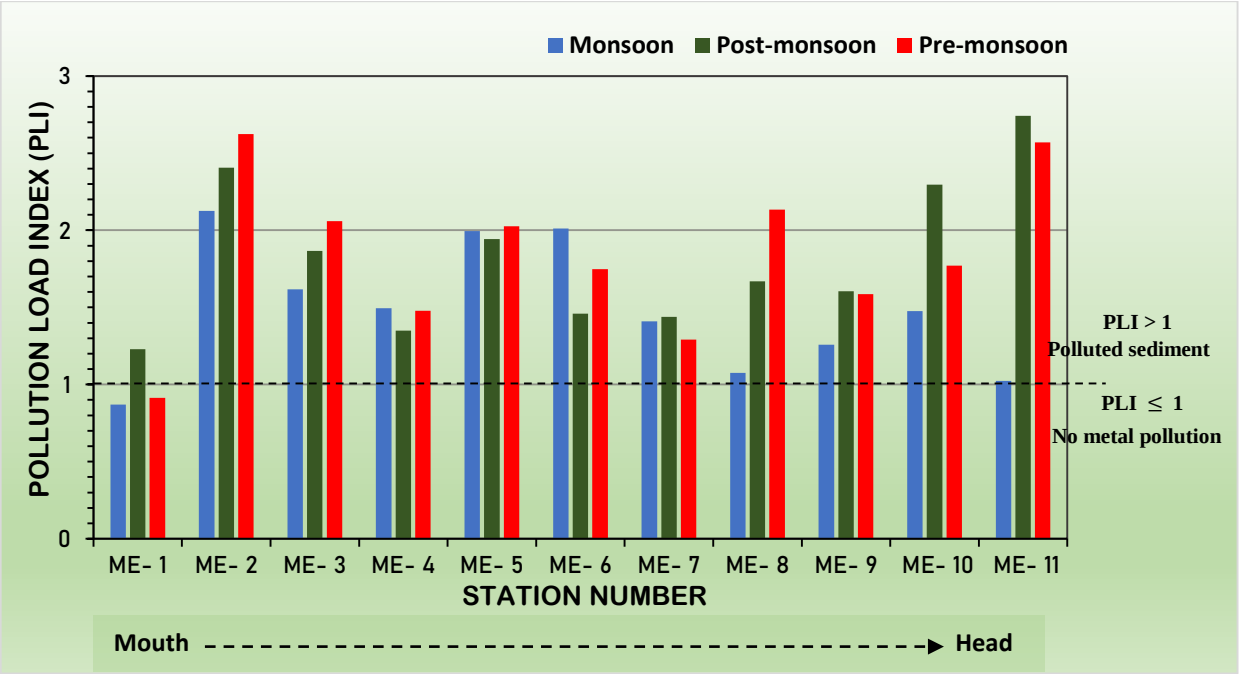

Fig. 29 - Plots showing Pollution load index (PLI) values for each season in the coastal surface sediments of the Mandovi estuary.

Pollution load index values are presented in **Table 22** and **Fig. 29** represents the variation of PLI values for each season in the Mandovi estuarine sediments. Notably, PLI values across all stations and seasons were greater than 1. Except at station 1, where PLI values were less than 1 during monsoon and pre-monsoon seasons. The sampling stations with values greater than 1 suggest that the sediments are polluted with metals. This could be due to various anthropogenic activities such as industrial discharge, agricultural runoff, urban waste disposal, developmental activities, etc.

4.3.4 Contamination degree (Cd)

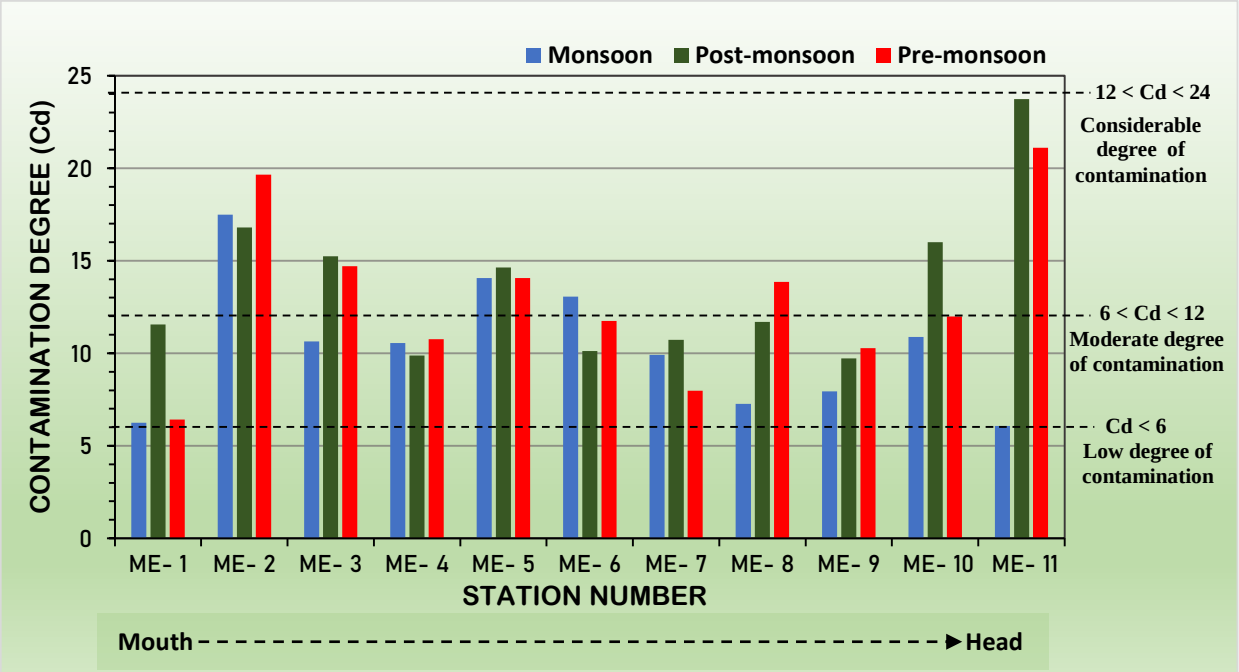

Fig. 30 - Plots showing Contamination degree (Cd) values for each season in the coastal surface sediments of the Mandovi estuary.

The results of the contamination degree (Cd) are presented in **Table 23** and **Fig. 30** represents the variation in contamination degree values for each season. The analysis revealed that the Mandovi estuary sediments were moderately to considerably contaminated. Stations 2 and 5 showed a considerable degree of contamination across all seasons; stations 3 and 11 showed a considerable degree of contamination during the post-monsoon and pre-monsoon seasons, whereas stations 6, 8 and 10 showed a considerable degree of contamination during the monsoon, pre-monsoon and post-monsoon seasons, respectively. In conclusion, the Madovi estuary sediments are significantly affected by contamination, with specific stations consistently displaying elevated contamination levels year-round.

4.3.5 Modified degree of contamination (mCd)

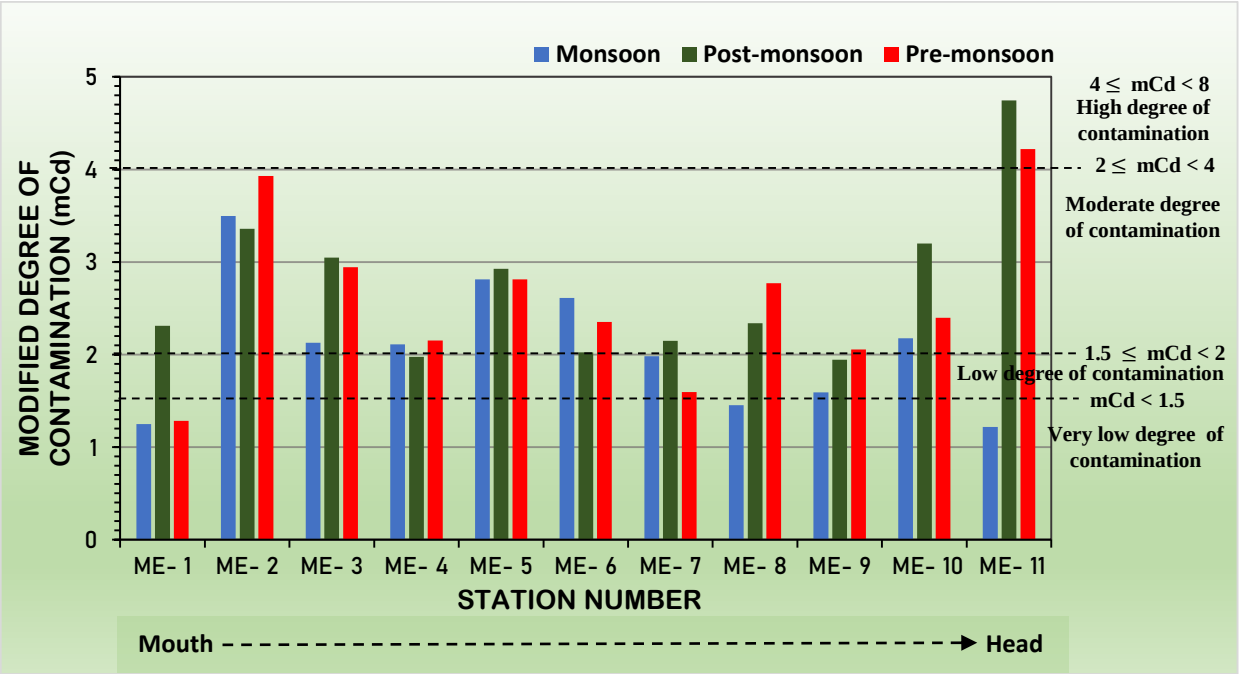

Fig. 31 - Plots showing Modified degree of contamination (mCd) values for each season in the coastal surface sediments of the Mandovi estuary.

Contamination levels were determined using a formula developed by **Abrahim and Parker, (2008)**, modified from **Hakanson, (1980)**. The mCd ranged from 1.2161 to 3.4968 during the monsoon season, 1.9436 to 4.7462 in the post-monsoon season, and 1.2835 to 4.2191 in the pre-monsoon season **(Table 24)**.

Fig. 31 shows how the level of contamination changes across seasons and locations in the Mandovi estuary. Overall, contamination levels in the study area indicate a low to moderate degree, except for stations 1 with very low contamination during the monsoon and pre-monsoon seasons and stations 8 and 11 with very low contamination during the monsoon season. However, station 11 exhibited a high degree of contamination during the post-monsoon and pre-monsoon seasons. In summary, the mCd values show that contamination levels vary across different seasons in the study area. This variability in contamination levels could be attributed to factors like human activities, industrial discharges, agricultural runoff and developmental activities.

4.3.6 Potential contamination index (Cp)

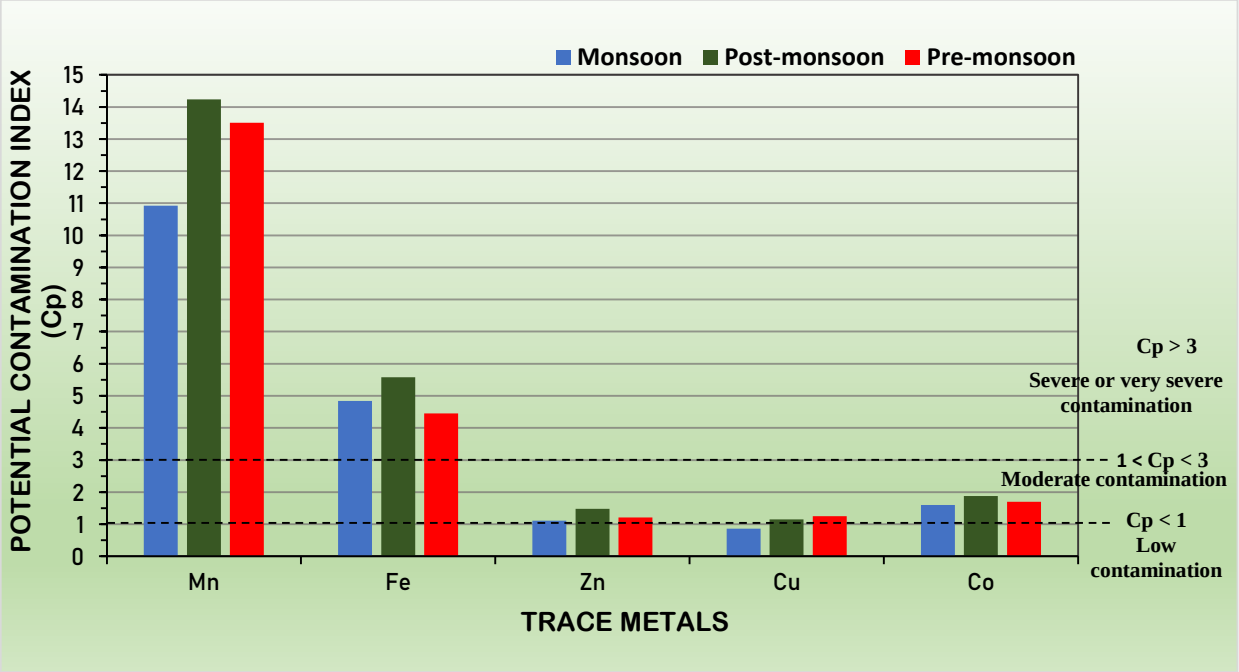

Fig. 32 - Plots showing Potential contamination index (Cp) values for each season in the coastal surface sediments of the Mandovi estuary.

The potential contamination index (Cp) was measured for Mn, Fe, Zn, Cu and Co for monsoon, post-monsoon and pre-monsoon seasons in the Mandovi estuarine sediments and the results are reported in **Table 25**. The variations of the Cp values are depicted in **Fig. 32**. Mn and Fe exhibited severe or very severe contamination in all three seasons, whereas Zn, Cu and Co displayed a moderate level of contamination. In contrast, Cu exhibited a low degree of contamination during the monsoon season. The order of element contamination was as follows: Mn > Fe > Co > Zn > Cu in the monsoon and post-monsoon seasons, and Mn > Fe > Co > Cu > Zn in the pre-monsoon season. In all three seasons, Mn exhibited a very severe contamination level in the Mandovi estuarine sediments. The significant levels of Mn and Fe contamination in the Mandovi estuarine sediments are concerning, particularly given their very severe contamination levels throughout all three seasons, suggesting a consistent source of Mn and Fe in the estuarine sediments.

4.3.7 Potential ecological risk index

Tables 26, 27 and **28** provide the values of the potential ecological risk factor (E_r^i) and the ecological risk index (RI) for the monsoon, post-monsoon and pre-monsoon seasons, respectively. The average values of Mn, Zn, Cu and Co were consistently below 40 during all three seasons, indicating a low ecological risk in the Mandovi estuary. Across all three seasons, the sequence of potential ecological risk coefficients decreases as follows: Mn > Co > Cu > Zn. The risk index varied from 9.01 to 23.0889 in the monsoon season, 13.6024 to 30.0418 in the post-monsoon season and 9.5376 to 28.7086 in the pre-monsoon season, indicating a low risk level at all sampling stations with RI values below 95.

Based on the data, it is clear that there is no significant environmental risk present in the Mandovi estuary. Nevertheless, the environmental risk assessment indicated a relatively lower risk during the monsoon season compared to other seasons.

4.4 POLLUTION INDICES DATA FOR THE ZUARI ESTUARINE SEDIMENT

- **Geo-accumulation index (Igeo) -**

Table 29 – Geo-accumulation index (Igeo) data on the variation of trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Zuari estuary, Goa, during the monsoon season.

STATION NUMBER	Mn (ASV=850 ppm)	Fe (ASV=47200 ppm)	Zn (ASV=95 ppm)	Cu (ASV=45 ppm)	Co (ASV= 19 ppm)
ZE- 1	1.5726	0.3895	0.4531	0.6243	0.5560
ZE- 2	1.7186	0.3615	0.6653	0.6620	0.5220
ZE- 3	1.3086	0.3495	-0.0846	-0.1220	0.0607
ZE- 4	1.7235	0.1744	-0.5525	-0.6047	-0.0968
ZE- 5	1.7860	-0.7388	-0.9819	-1.2046	-0.6244
ZE- 6	0.4960	-0.6932	-0.8302	-1.4754	-0.9069
ZE- 7	0.4324	0.0514	-0.6764	-0.2724	-0.1097
ZE- 8	0.2363	-0.2755	-1.0281	-1.2294	-0.8385
ZE- 9	0.6042	-0.6438	-1.1730	-1.5077	-0.8775
ZE- 10	-0.4620	-0.7795	-0.8379	-1.6207	-1.4269
ZE- 11	-1.5535	-0.7087	-1.2506	-1.4438	-1.4683
AVERAGE CONCENTRATION	0.7148	-0.2285	-0.5724	-0.7449	-0.4737

***ZE -** Zuari Estuary ***ASV –** Average Shale Value

Table 30 – Geo-accumulation index (Igeo) data on the variation of trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Zuari estuary, Goa, during the post-monsoon season.

STATION NUMBER	Mn (ASV=850 ppm)	Fe (ASV=47200 ppm)	Zn (ASV=95 ppm)	Cu (ASV=45 ppm)	Co (ASV= 19 ppm)
ZE- 1	1.3527	0.1719	0.1329	0.4405	0.3350
ZE- 2	1.6562	0.3576	0.3093	0.4448	0.4525
ZE- 3	0.9584	-0.1034	-0.4456	-0.4802	-0.2233
ZE- 4	1.4496	0.2842	0.1403	0.4847	0.2049
ZE- 5	1.4457	-0.9827	-0.9200	-1.7307	-0.8419
ZE- 6	0.6935	-0.2076	-0.7286	-1.0701	-0.6391
ZE- 7	1.0179	-0.7340	-0.9633	-1.6683	-1.0294
ZE- 8	0.2236	-0.3971	-0.5224	-1.3785	-0.9675
ZE- 9	0.3472	-0.1257	-0.5453	-1.0123	-0.4806
ZE- 10	0.2452	-0.4849	-0.9022	-1.4836	-1.1214
ZE- 11	0.2296	-0.6053	-0.7529	-1.5930	-1.3394
AVERAGE CONCENTRATION	0.8745	-0.257	-0.4725	-0.8224	-0.5136

***ZE -** Zuari Estuary ***ASV –** Average Shale Value

Table 31 – Geo-accumulation index (Igeo) data on the variation of trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Zuari estuary, Goa, during the pre-monsoon season.

STATION NUMBER	Mn (ASV=850 ppm)	Fe (ASV=47200 ppm)	Zn (ASV=95 ppm)	Cu (ASV=45 ppm)	Co (ASV= 19 ppm)
ZE- 1	1.5857	0.2636	0.1936	0.4408	0.3868
ZE- 2	1.5057	0.1959	0.1092	0.3151	0.3355
ZE- 3	0.9982	0.0332	-0.8669	-0.8194	-0.2914
ZE- 4	1.7919	0.0094	0.3960	1.0492	0.0301
ZE- 5	0.8779	-1.1915	-0.9819	-1.3695	-0.9417
ZE- 6	0.7817	-0.5769	-0.7229	-1.1431	-0.6670
ZE- 7	1.0301	-0.9614	-0.8906	-1.5085	-1.0372
ZE- 8	-0.1155	-0.4902	-0.7876	-1.1414	-0.8363
ZE- 9	0.0541	-0.4857	-0.6999	-1.0539	-0.5680
ZE- 10	0.4615	-0.3616	-0.7720	-1.1784	-0.6012
ZE- 11	0.8829	0.5103	-0.8533	-0.8432	-0.1775
AVERAGE CONCENTRATION	0.8958	-0.2777	-0.5342	-0.6593	-0.3971

***ZE -** Zuari Estuary ***ASV –** Average Shale Value

- **Contamination factor (CF) -**

Table 32 – Contamination factor (CF) data for the trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Zuari estuary, Goa, during the monsoon season.

STATION NUMBER	Mn (ASV=850 ppm)	Fe (ASV=47200 ppm)	Zn (ASV=95 ppm)	Cu (ASV=45 ppm)	Co (ASV=19 ppm)
ZE- 1	4.4618	1.9649	2.0534	2.3122	2.2053
ZE- 2	4.9368	1.9272	2.3788	2.3733	2.1540
ZE- 3	3.7154	1.9112	1.4146	1.3783	1.5645
ZE- 4	4.9537	1.6928	1.0228	0.9864	1.4026
ZE- 5	5.1728	0.8989	0.7595	0.6508	0.9730
ZE- 6	2.1154	0.9277	0.8437	0.5394	0.8
ZE- 7	2.0243	1.5544	0.9386	1.2419	1.3901
ZE- 8	1.7669	1.2392	0.7355	0.6397	0.8388
ZE- 9	2.2802	0.9600	0.6653	0.5275	0.7112
ZE- 10	1.0890	0.8738	0.8392	0.4878	0.5579
ZE- 11	0.5110	0.9178	0.6304	0.5514	0.5421
AVERAGE CONCENTRATION	3.0025	1.3516	1.1165	1.0626	1.1945

***ZE -** Zuari Estuary ***ASV –** Average Shale Value

Table 33 – Contamination factor (CF) data for the trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Zuari estuary, Goa, during the post-monsoon season.

STATION NUMBER	Mn (ASV= 850 ppm)	Fe (ASV=47200 ppm)	Zn (ASV=95 ppm)	Cu (ASV=45 ppm)	Co (ASV=19 ppm)
ZE- 1	3.8309	1.6898	1.6447	2.0356	1.8921
ZE- 2	4.7279	1.9219	1.8587	2.0417	2.0526
ZE- 3	2.9147	1.3962	1.1014	1.0753	1.2849
ZE- 4	4.0971	1.8266	1.6532	2.0989	1.7290
ZE- 5	4.0860	0.7591	0.7928	0.4519	0.8368
ZE- 6	2.4257	1.2989	0.9053	0.7144	0.9632
ZE- 7	3.0375	0.9019	0.7693	0.4719	0.7349
ZE- 8	1.7515	1.1391	1.0443	0.5769	0.7671
ZE- 9	1.9081	1.3748	1.0279	0.7436	1.075
ZE- 10	1.7779	1.0718	0.8026	0.5364	0.6895
ZE- 11	1.7588	0.9860	0.8901	0.4972	0.5928
AVERAGE CONCENTRATION	2.9378	1.3060	1.1355	1.0222	1.1471

***ZE -** Zuari Estuary ***ASV –** Average Shale Value

Table 34 – Contamination factor (CF) data for the trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Zuari estuary, Goa, during the pre-monsoon season.

STATION NUMBER	Mn (ASV=850 ppm)	Fe (ASV=47200 ppm)	Zn (ASV=95 ppm)	Cu (ASV=45 ppm)	Co (ASV=19 ppm)
ZE- 1	4.5022	1.8007	1.7154	2.0361	1.9612
ZE- 2	4.2596	1.7181	1.6179	1.8661	1.8928
ZE- 3	2.9963	1.5350	0.8225	0.85	1.2257
ZE- 4	5.1941	1.5098	1.9738	3.1042	1.5316
ZE- 5	2.7566	0.6568	0.7595	0.5806	0.7809
ZE- 6	2.5787	1.0056	0.9088	0.6792	0.9447
ZE- 7	3.0632	0.7704	0.8091	0.5272	0.7309
ZE- 8	1.3846	1.0679	0.8690	0.68	0.8401
ZE- 9	1.5574	1.0712	0.9234	0.7225	1.0118
ZE- 10	2.0654	1.1675	0.8784	0.6628	0.9888
ZE- 11	2.7662	2.1366	0.8303	0.8361	1.3263
AVERAGE CONCENTRATION	3.0113	1.3127	1.1007	1.1404	1.2032

***ZE -** Zuari Estuary ***ASV –** Average Shale Value

- **Pollution load index (PLI) -**

Table 35 – Pollution load index (PLI) data for the trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Zuari estuary, Goa.

STATION NUMBER	MONSOON	POST-MONSOON	PRE-MONSOON
ZE- 1	2.4692	2.1017	2.2331
ZE- 2	2.5862	2.3441	2.1100
ZE- 3	1.8498	1.4400	1.3156
ZE- 4	1.6401	2.1402	2.3625
ZE- 5	1.1746	0.9856	0.9098
ZE- 6	0.9350	1.1444	1.0862
ZE- 7	1.3851	0.9392	0.9405
ZE- 8	0.9712	0.9839	0.9400
ZE- 9	0.8861	1.1660	1.0240
ZE- 10	0.7369	0.8923	1.0678
ZE- 11	0.6156	0.8543	1.4033

***ZE -** Zuari Estuary

- **Contamination degree (Cd) -**

Table 36 – Contamination degree (Cd) data for the trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Zuari estuary, Goa.

STATION NUMBER	MONSOON	POST-MONSOON	PRE-MONSOON
ZE- 1	12.9976	11.0931	12.0156
ZE- 2	13.7701	12.6028	11.3545
ZE- 3	9.984	7.7725	7.4295
ZE- 4	10.0583	11.4048	13.3135
ZE- 5	8.455	6.9266	5.5344
ZE- 6	5.2262	6.3075	6.117
ZE- 7	7.1493	5.9155	5.9008
ZE- 8	5.2201	5.2789	4.8416
ZE- 9	5.1442	6.1294	5.2863
ZE- 10	3.8477	4.8782	5.7629
ZE- 11	3.1527	4.7249	7.8955

***ZE -** Zuari Estuary

- **Modified degree of contamination (mCd) -**

Table 37 – Modified degree of contamination(mCd) data for the trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Zuari estuary, Goa.

STATION NUMBER	MONSOON	POST-MONSOON	PRE-MONSOON
ZE- 1	2.5995	2.2186	2.4031
ZE- 2	2.7540	2.5206	2.2709
ZE- 3	1.9968	1.5545	1.4859
ZE- 4	2.0117	2.2810	2.6627
ZE- 5	1.691	1.3853	1.1069
ZE- 6	1.0452	1.2615	1.2234
ZE- 7	1.4299	1.1831	1.1802
ZE- 8	1.0440	1.0558	0.9683
ZE- 9	1.0288	1.2259	1.0573
ZE- 10	0.7695	0.9756	1.1526
ZE- 11	0.6305	0.9450	1.5791

***ZE -** Zuari Estuary

- **Potential contamination index (Cp) -**

Table 38 – Potential contamination index (Cp) data for the trace metals (Mn, Fe, Zn, Cu and Co) in coastal surface sediments of the Zuari estuary, Goa.

TRACE ELEMENTS	MONSOON	POST-MONSOON	PRE-MONSOON
Mn	5.1728	4.7279	5.1941
Fe	1.9649	1.9219	2.1366
Zn	2.3788	1.8587	1.9738
Cu	2.3733	2.0989	3.1042
Co	2.2053	2.0526	1.9612

- **Potential ecological risk index -**

Table 39 – Evaluation on potential risk of trace metals pollution in coastal surface sediments of the Zuari estuary during monsoon season.

STATION NUMBER	Ecological risk for single metal E_r^i				RISK INDEX
	Mn	Zn	Cu	Co	
ZE- 1	4.4618	2.0534	11.561	11.0265	29.1027
ZE- 2	4.9368	2.3788	11.8665	10.77	29.9521
ZE- 3	3.7154	1.4146	6.8915	7.8225	19.844
ZE- 4	4.9537	1.0228	4.932	7.013	17.9215
ZE- 5	5.1728	0.7595	3.254	4.865	14.0513
ZE- 6	2.1154	0.8437	2.697	4	9.6561
ZE- 7	2.0243	0.9386	6.2095	6.9505	16.1229
ZE- 8	1.7669	0.7355	3.1985	4.194	9.8949
ZE- 9	2.2802	0.6653	2.6375	3.556	9.139
ZE- 10	1.0890	0.8392	2.439	2.7895	7.1567
ZE- 11	0.5110	0.6304	2.757	2.7105	6.6089
MEAN	3.0025	1.1165	5.3130	5.9725	

***ZE -** Zuari Estuary

Table 40 – Evaluation on potential risk of trace metals pollution in coastal surface sediments of the Zuari estuary during post-monsoon season.

STATION NUMBER	Ecological risk for single metal E_r^i				RISK INDEX
	Mn	Zn	Cu	Co	
ZE- 1	3.8309	1.6447	10.178	9.4605	25.1141
ZE- 2	4.7279	1.8587	10.2085	10.263	27.0581
ZE- 3	2.9147	1.1014	5.3765	6.4245	15.8171
ZE- 4	4.0971	1.6532	10.4945	8.645	24.8898
ZE- 5	4.0860	0.7928	2.2595	4.184	11.3223
ZE- 6	2.4257	0.9053	3.572	4.816	11.719
ZE- 7	3.0375	0.7693	2.3595	3.6745	9.8408
ZE- 8	1.7515	1.0443	2.8845	3.8355	9.5158
ZE- 9	1.9081	1.0279	3.718	5.375	12.029
ZE- 10	1.7779	0.8026	2.682	3.4475	8.71
ZE- 11	1.7588	0.8901	2.486	2.964	8.0989
MEAN	2.9378	1.1355	5.1108	5.7354	

***ZE -** Zuari Estuary

Table 41 – Evaluation on potential risk of trace metals pollution in coastal surface sediments of the Zuari estuary during pre-monsoon season.

STATION NUMBER	Ecological risk for single metal E_r^i				RISK INDEX
	Mn	Zn	Cu	Co	
ZE- 1	4.5022	1.7154	10.1805	9.806	26.2041
ZE- 2	4.2596	1.6179	9.3305	9.464	24.672
ZE- 3	2.9963	0.8225	4.25	6.1285	14.1973
ZE- 4	5.1941	1.9738	15.521	7.658	30.3469
ZE- 5	2.7566	0.7595	2.903	3.9045	10.3236
ZE- 6	2.5787	0.9088	3.396	4.7235	11.607
ZE- 7	3.0632	0.8091	2.636	3.6545	10.1628
ZE- 8	1.3846	0.8690	3.4	4.2005	9.8541
ZE- 9	1.5574	0.9234	3.6125	5.059	11.1523
ZE- 10	2.0654	0.8784	3.314	4.944	11.2018
ZE- 11	2.7662	0.8303	4.1805	6.6315	14.4085
MEAN	3.0113	1.1007	5.7022	6.0158	

***ZE -** Zuari Estuary

4.4.1 Geo-accumulation index (Igeo)

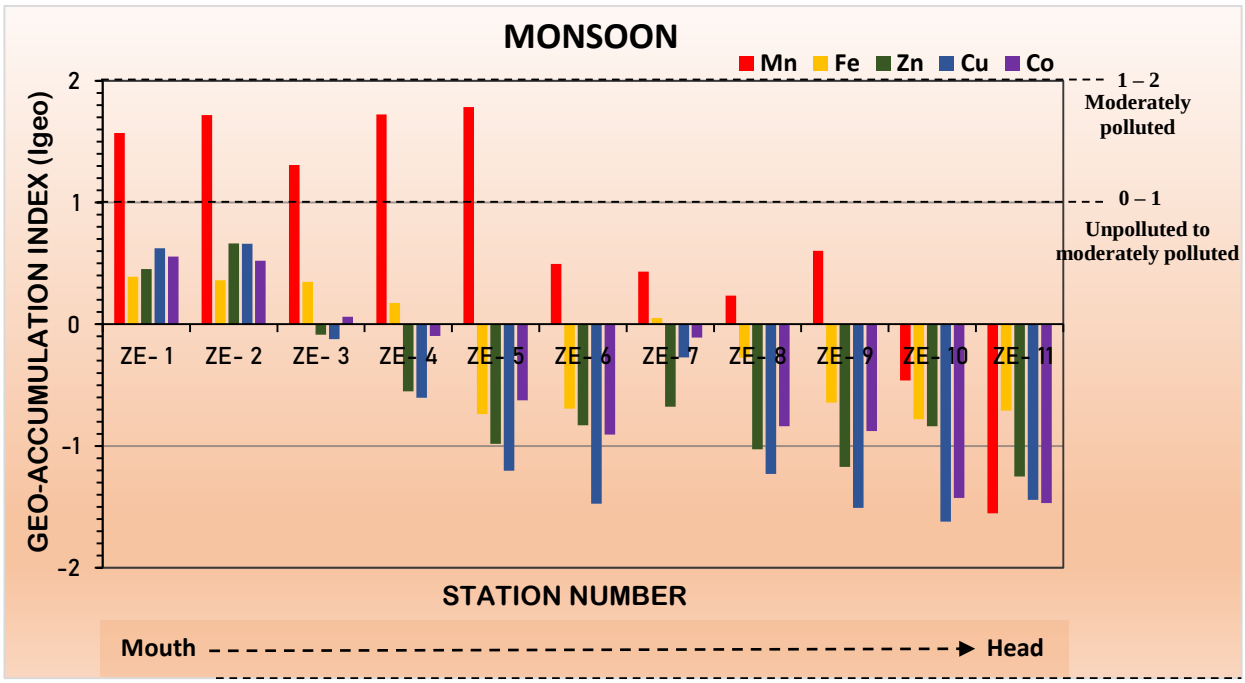

Fig. 33 - Plots showing Igeo values for each metal in the coastal surface sediments of the Zuari estuary during monsoon season.

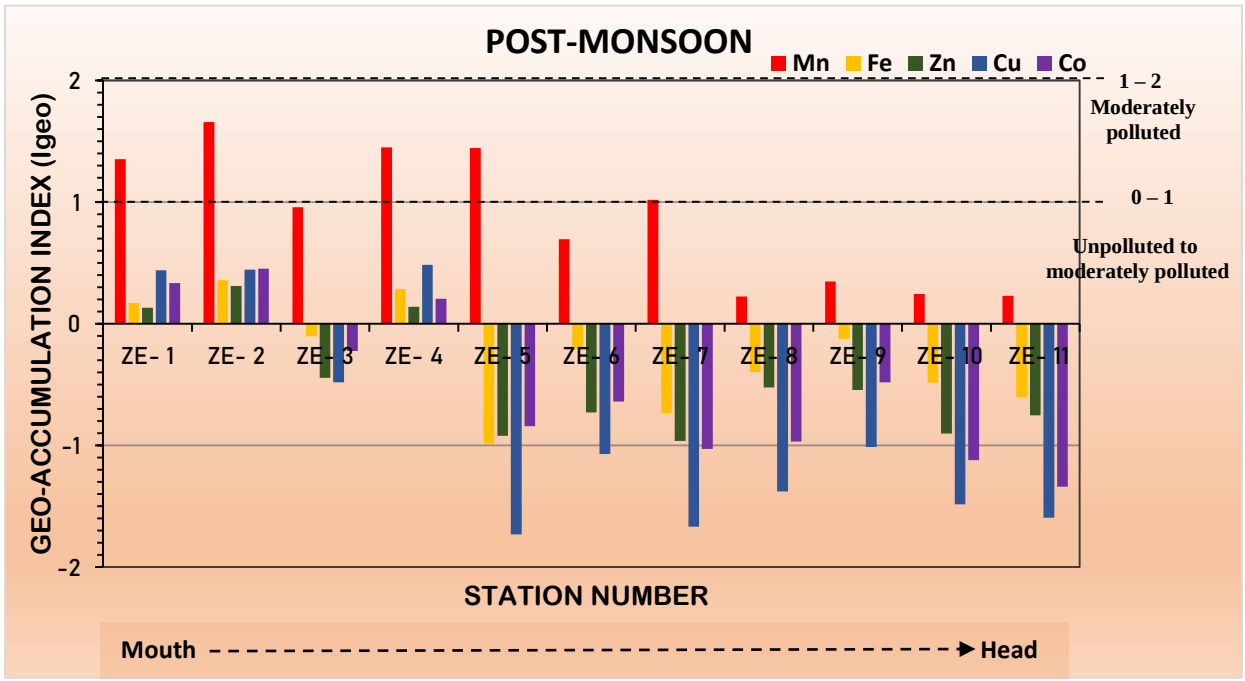

Fig. 34 - Plots showing Igeo values for each metal in the coastal surface sediments of the Zuari estuary during post-monsoon season.

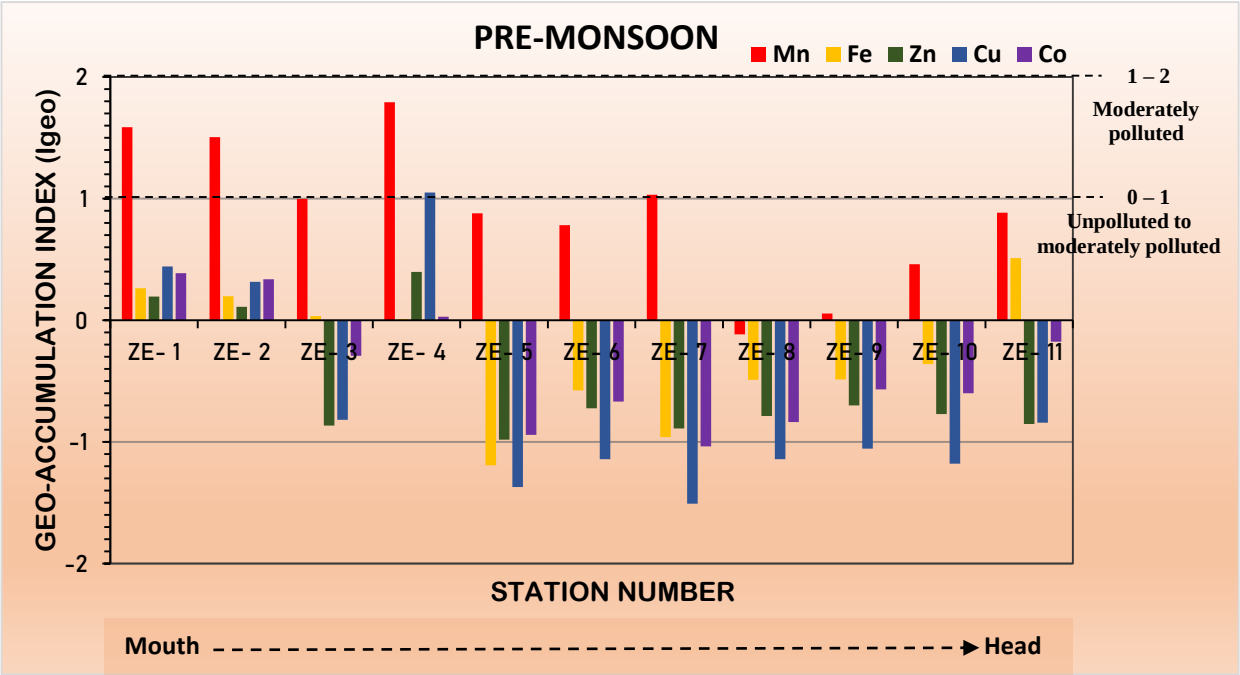

Fig. 35 - Plots showing Igeo values for each metal in the coastal surface sediments of the Zuari estuary during pre-monsoon season.

Geo-accumulation index (Igeo) values for the monsoon, post-monsoon, and pre-monsoon seasons are displayed in **Tables 29, 30** and **31**, respectively. The analysis of geo-accumulation index in the Zuari estuary sediments showed that the surface sediments range from unpolluted to moderately polluted across all seasons **(Figs. 33, 34** and **35)**. Specifically, stations 1, 2, 3, 4, 5 and 7 in the lower and middle estuarine sediments showed moderate pollution with manganese (Mn) across all seasons. Station 3, however, exhibited a range from unpolluted to moderately polluted with Mn during the post-monsoon season. At stations 1 and 2, iron (Fe), zinc (Zn), copper (Cu) and cobalt (Co) ranged from unpolluted to moderately polluted across all seasons. In contrast, at station 4, sediments showed moderate pollution with Cu and a range from unpolluted to moderately polluted with Zn during the pre-monsoon season. In the upper estuarine region, sediments showed a range from unpolluted to moderately polluted with Mn, while they remained unpolluted with the rest of the metals. However, at station 11 during the pre-monsoon season, sediments were unpolluted to moderately polluted with Fe.

In general, the presence of iron-manganese ore deposits and human activities involving the handling and transportation of these ores through the river and estuary have led to moderate pollution of Mn in estuarine sediments.

4.4.2 Contamination factor (CF)

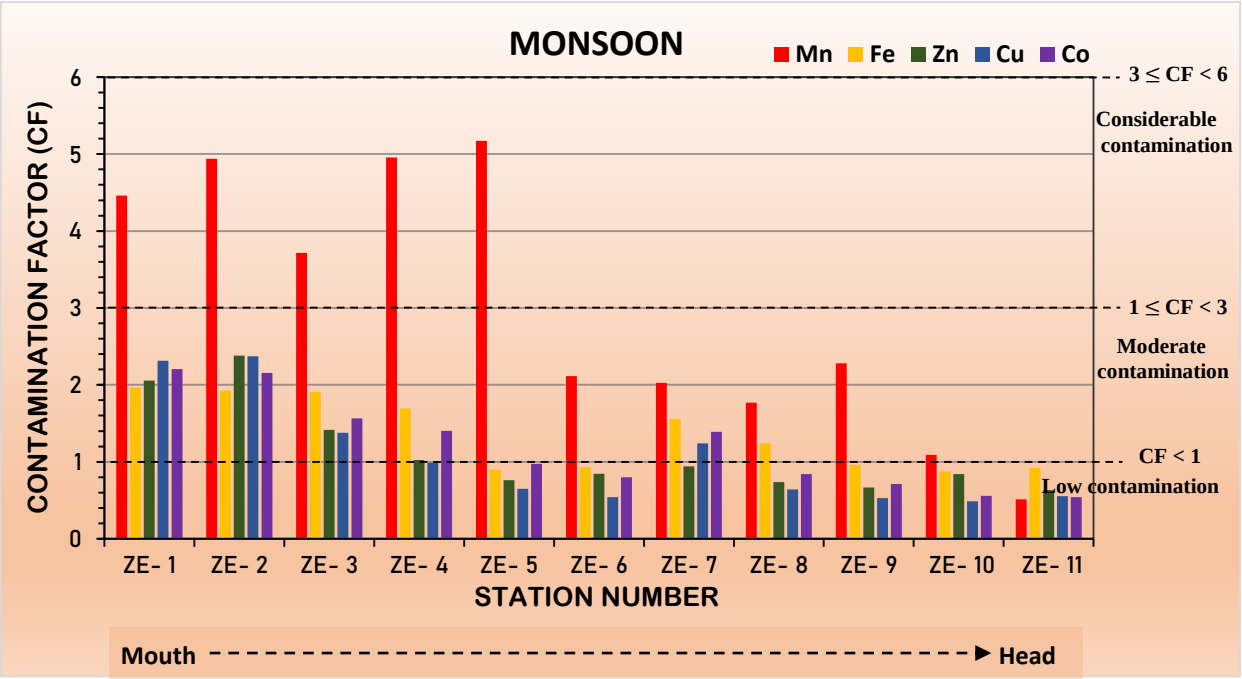

Fig. 36 - Plots showing Contamination factor (CF) values for each metal in the coastal surface sediments of the Zuari estuary during monsoon season.

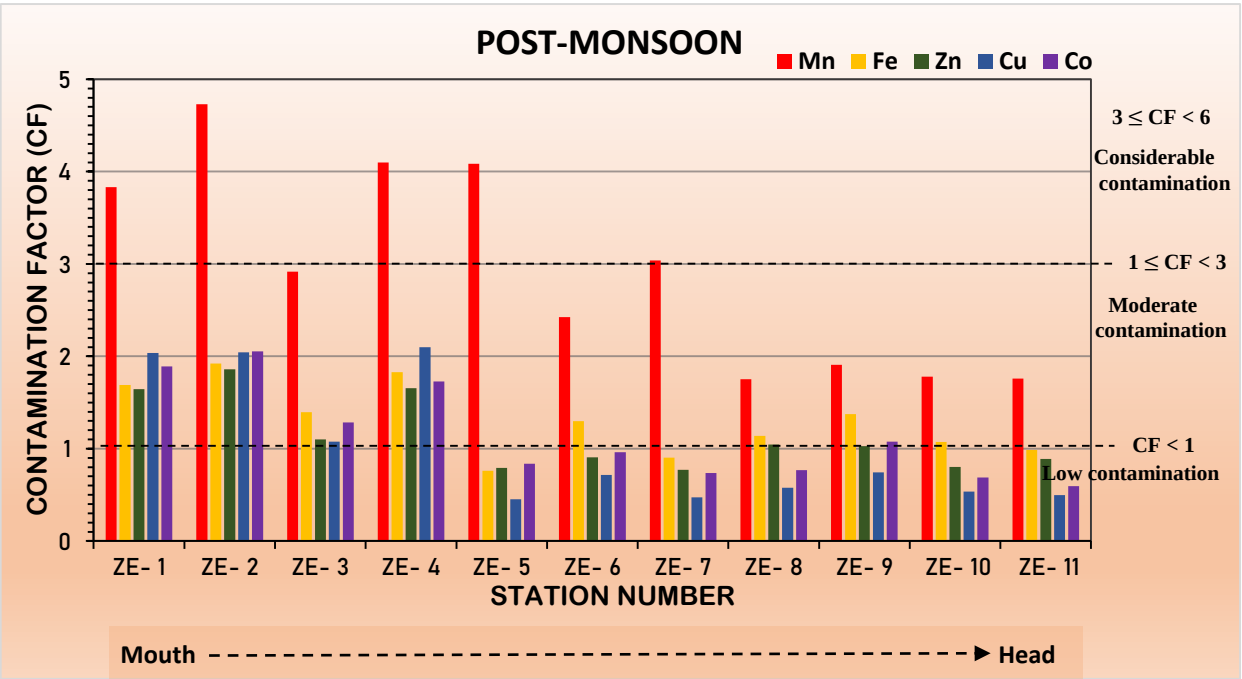

Fig. 37 - Plots showing Contamination factor (CF) values for each metal in the coastal surface sediments of the Zuari estuary during post-monsoon season.

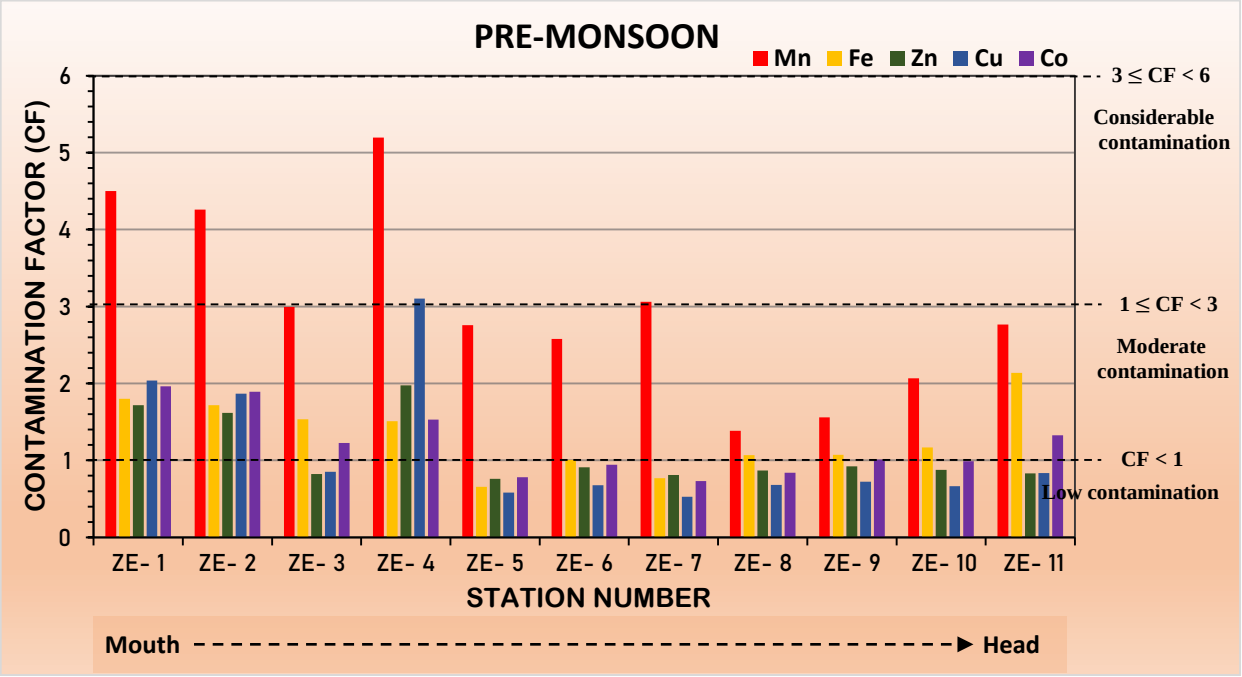

Fig. 38 - Plots showing Contamination factor (CF) values for each metal in the coastal surface sediments of the Zuari estuary during pre-monsoon season.

Contamination factor values for the monsoon, post-monsoon, and pre-monsoon seasons are displayed in **Tables 32, 33** and **34**, respectively. The variation of contamination factor values for each metal during the monsoon, post-monsoon, and pre-monsoon seasons is depicted in **Figs. 36, 37** and **38**, respectively. The Zuari estuarine sediments showed a moderate to considerable contamination level with manganese (Mn) across all seasons and stations, except for station 11 during the monsoon season, which exhibited a low contamination level with Mn. At stations 1 to 4, sediments were moderately contaminated with iron (Fe), zinc (Zn), copper (Cu) and cobalt (Co) across all seasons. However, at station 3, sediments showed a low contamination level with Zn and Cu during the pre-monsoon season. Interestingly, station 4 sediments were considerably contaminated with Cu during the pre-monsoon season. Fe showed a moderate contamination level at stations 7 and 8 during the monsoon season, at stations 6, 8, 9 and 10 during the post-monsoon season, and at stations 8, 9, 10 and 11 during the pre-monsoon season. During the monsoon season, Cu and Co showed moderate contamination levels at station 7. In the post-monsoon season, sediments at stations 8 and 9 were moderately contaminated with Zn. Additionally, during the pre-monsoon season, sediments at stations 9, 10 and 11 exhibited moderate contamination with Co. Considerable contamination of metals in the Zuari estuary can be attributed to anthropogenic input. This includes residential, industrial and atmospheric deposition of fine particles, along with the extensive use of antifouling paints.

4.4.3 Pollution load index (PLI)

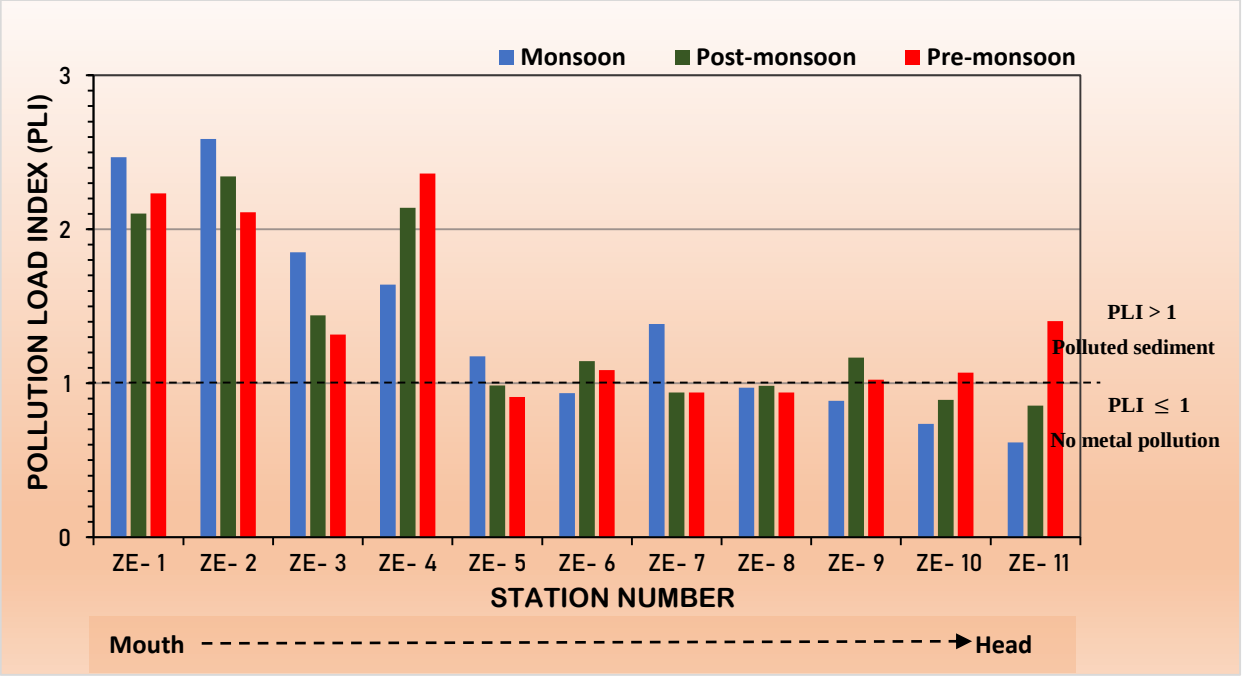

Fig. 39 - Plots showing Pollution load index (PLI) values for each season in the coastal surface sediments of the Zuari estuary.

Pollution load index values are presented in **Table 35** and **Fig. 39** represents the variation of PLI values for each season in the Zuari estuarine sediments. Lower estuarine region sediments are polluted with metals having Pollution Load Index values >1 (from stations 1 to 4). While station 5 sediment showed values >1 during the monsoon season, station 6 sediment was polluted with metals in the pre-monsoon and post-monsoon seasons. Station 9, 10 and 11 sediments had PLI values >1, indicating sediments were polluted with metals during the pre-monsoon season. However, sediment from station 9 also had PLI values >1, indicating sediments are polluted with metals during the post-monsoon season. The sampling stations with PLI values >1 suggest that the sediments are polluted with metals. This could be due to various anthropogenic activities such as industrial discharge, agricultural runoff, urban waste disposal, developmental activities, etc.

.

4.4.4 Contamination degree (Cd)

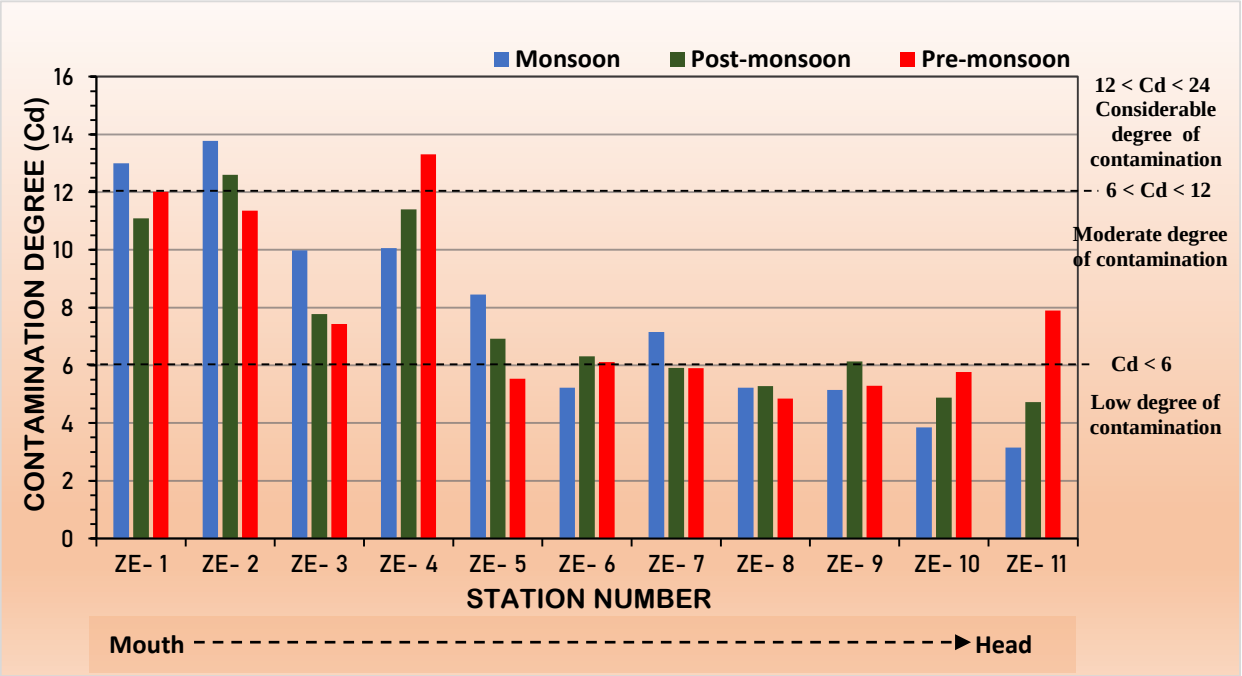

Fig. 40 - Plots showing Contamination degree (Cd) values for each season in the coastal surface sediments of the Zuari estuary.

The results of the contamination degree (Cd) are presented in **Table 36** and **Fig. 40** represents the variation in contamination degree values for each season. In the lower estuarine region (stations 1 to 4), Cd indicated a moderate degree of contamination. However, stations 1 and 2 exhibited a considerable degree of contamination by metals in sediments during the monsoon season, while station 4 showed a considerable degree of contamination during the pre-monsoon season. Station 2 also exhibited a considerable degree of contamination during the post-monsoon season. From stations 5 to 11, sediments generally had low metal contamination levels. However, stations 5 and 7 showed a moderate degree of contamination during the monsoon season; stations 5, 6 and 9 exhibited a moderate degree of contamination during the post-monsoon season; and station 11 had a moderate degree of contamination during the pre-monsoon season. In general, the lower estuarine region exhibited a higher degree of contamination compared to the middle and upper estuarine regions. This observation suggests that contamination levels in the estuarine region vary seasonally, with specific stations experiencing higher contamination levels during particular seasons. Moreover, the increased contamination in the lower estuarine region implies a higher concentration of contaminants in this region.

4.4.5 Modified degree of contamination (mCd)

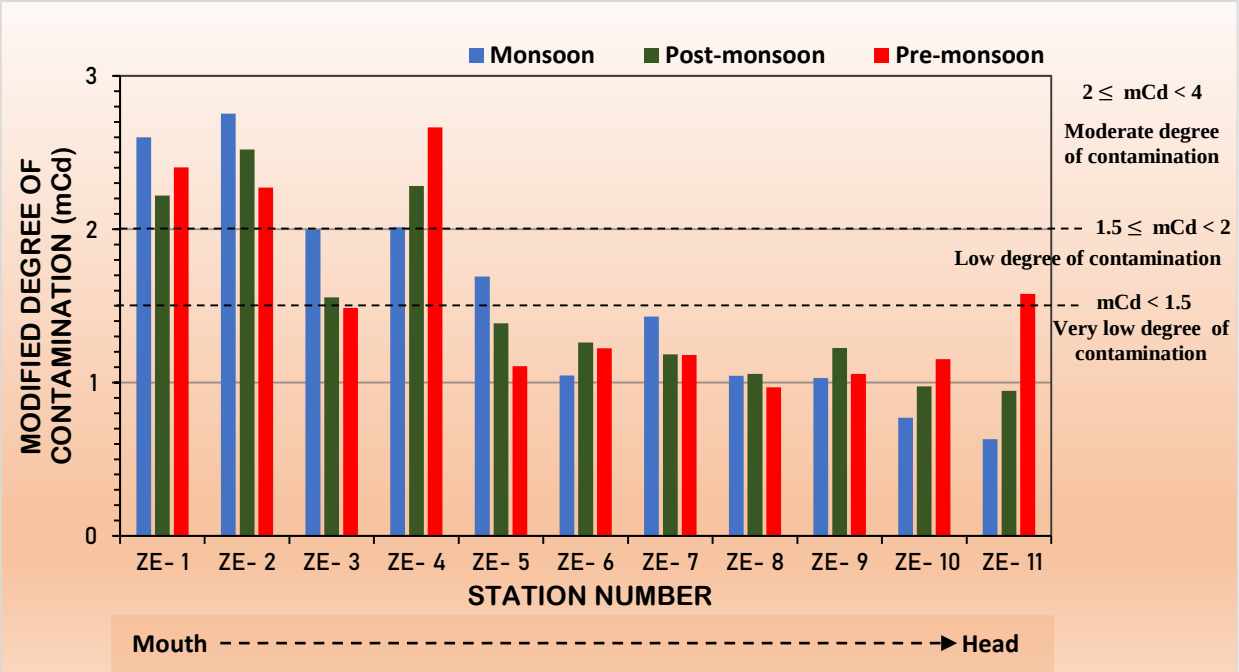

Fig. 41 - Plots showing Modified degree of contamination (mCd) values for each season in the coastal surface sediments of the Zuari estuary.

The contamination levels were calculated using a formula created by **Abrahim and Parker, (2008)**, which was modified from **Hakanson, (1980)**. The mCd ranged from 0.6305 to 2.7540 during the monsoon season, 0.9450 to 2.5206 in the post-monsoon season and 0.9683 to 2.6627 in the pre-monsoon season **(Table 37)**.

Fig. 41 shows how the level of contamination changes across seasons and locations in the Zuari estuary. The mCd values at stations 1, 2 and 4 indicated a moderate level of contamination throughout the year, while station 3 exhibited a moderate contamination level specifically in the monsoon season. Additionally, stations 3, 5 and 11 displayed low contamination levels in the post-monsoon, monsoon and pre-monsoon seasons, respectively. However, station 3 exhibited a very low contamination level during the pre-monsoon season. Subsequently, stations 5 to 11 consistently exhibited very low contamination levels in the sediments throughout all seasons. The lower estuarine region has a higher contamination level than the middle and upper estuarine regions. These results indicate that contamination levels in the estuarine sediments vary considerably based on both the season and the location within the estuary.

4.4.6 Potential contamination index (Cp)

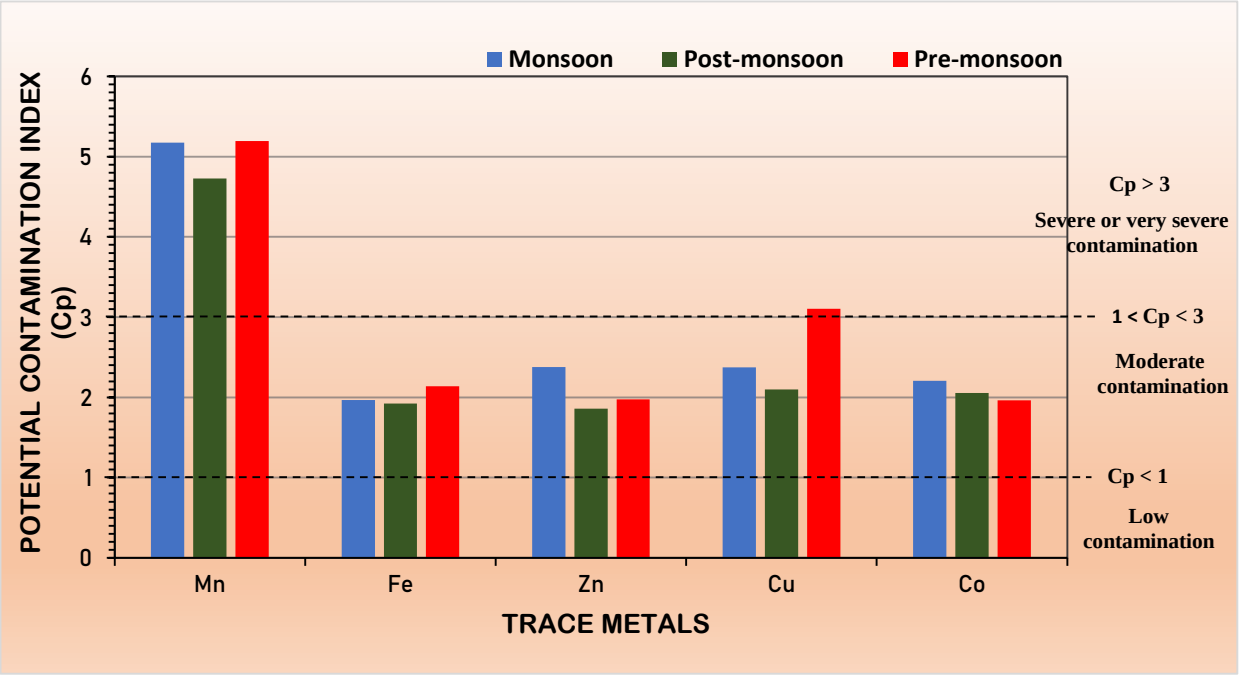

Fig. 42 - Plots showing Potential contamination index (Cp) values for each season in the coastal surface sediments of the Zuari estuary.

The levels of contamination for Mn, Fe, Zn, Cu, and Co were measured during the monsoon, post-monsoon, and pre-monsoon seasons in the Zuari estuarine sediments and the results are reported in **Table 38**. The variations in the contamination index values are provided in **Fig. 42** for the Zuari estuarine sediments. Mn exhibited severe or very severe contamination in all three seasons, whereas Fe, Zn, Cu, and Co displayed a moderate level of contamination. In contrast, Cu exhibited a severe contamination level during the pre-monsoon season. In the monsoon season, the order of element contamination was Mn > Zn > Cu > Co > Fe; in the post-monsoon season, it was Mn > Cu > Co > Fe > Zn; and in the pre-monsoon season, it was Mn > Cu > Fe > Zn > Co. In all three seasons, Mn exhibited a very severe contamination level in the Mandovi estuarine sediments. The high levels of Mn contamination in the Zuari estuarine sediments are alarming, especially considering the consistently very severe contamination levels across all three seasons, indicating a persistent source of Mn in the estuarine sediments.

4.4.7 Potential ecological risk index

Tables 39, 40 and **41** provide the values of the potential ecological risk factor (E_r^i) and the ecological risk index (RI) in the Zuari estuary for the monsoon, post-monsoon and pre-monsoon seasons, respectively. The average E_r^i values of Mn, Zn, Cu and Co were consistently below 40 during all three seasons, indicating a low ecological risk in the Zuari estuary. Across all three seasons, the sequence of potential ecological risk coefficients decreases as follows: Co > Cu > Mn > Zn. The risk index (RI) ranged from 6.6089 to 29.9521 in the monsoon season, 8.0989 to 27.0581 in the post-monsoon season and 9.8541 to 30.3469 in the pre-monsoon season, indicating low risk levels at all sampling stations with RI values below 95.

Based on the potential ecological and risk index data, it is clear that there is no significant environmental risk present in the Zuari estuary. However, the risk assessment showed that the monsoon season has a lower risk than other seasons. This indicates that rainfall and water flow might be contributing to reducing the potential ecological risk in the study area during the monsoon season. The consistently low risk values in all seasons indicate that the overall health of the Zuari estuarine sediments is stable and not highly polluted.

CHAPTER 5

SUMMARY AND CONCLUSION

SUMMARY AND CONCLUSION

In recent years, coastal areas have experienced a notable rise in anthropogenic metal input. This increase is primarily due to urbanization, mining activities, industrial discharge, and enhanced developmental projects. Due to this, the amount of waste entering the estuaries has also increased significantly. This waste contains trace metals that enter the estuary and settle at the estuary's bottom through a series of physiochemical processes. Trace metals below the threshold limit are necessary micronutrients for growth and metabolism in many organisms. However, once these trace metals exceed a specific threshold, they can be detrimental to organisms and ecosystems. As a result, the buildup of these trace metals in estuaries can significantly harm the overall health and biodiversity of the ecosystem. Monitoring and regulating trace metal levels in estuaries is vital to prevent adverse effects on the ecosystem. This study was carried out in the Mandovi and Zuari estuaries, situated on India's west coast. These two significant rivers in Goa are at risk due to mining activities along their banks. Over the last six decades, the transportation of iron and ferromanganese ores to Marmugao harbor via both the Mandovi and Zuari estuaries has contributed to elevated sedimentation and pollution levels, potentially impacting marine life and biodiversity. Therefore, this study aimed to investigate the distribution pattern and spatial and seasonal variations of trace metals in coastal surface sediments of both estuaries. Additionally, it aimed to assess metal enrichment and contamination levels in the coastal sediments of the Mandovi and Zuari estuaries using different pollution indices. The results obtained from the study are summarized below.

Spatial variation of trace metals in the Mandovi etuary showed an almost similar trend of distribution by Mn, Fe, Zn, Cu and Co across all seasons. Simultaneously, Mn, Fe, Zn, Cu and Co showed lower concentrations at station 1 (mouth region). In the upstream region, a sudden increase in the concentration of metals was observed during the pre-monsoon season. The overall trend of metal concentration in the Mandovi estuary is as follows: Fe > Mn > Zn > Cu > Co. In general, a higher concentration of metals was found during the monsoon season. This could be attributed to increased runoff and sediment transport during the monsoon, which can result in a higher input of metals into the estuary. The varying concentrations of these trace metals across different seasons and locations in the Mandovi estuary suggest that different factors are affecting their distribution**.** The spatial distribution of trace metal exhibited significant variation in metal concentration depending on the seasons and station location. And this variation is more clearly observed in the upstream region as compared to the middle and lower estuarine regions, depending on the season. The upstream region appears to be particularly susceptible to fluctuations in metal concentrations, likely due to its proximity to sources of anthropogenic inputs.

Seasonal variation of trace metals in the Mandovi estuarine sediments indicated higher concentrations during non-monsoonal months, particularly in the post-monsoon season, with the exception of Zn and

Cu, which exhibited higher concentrations during the pre-monsoon season. Higher concentrations of metals during non-monsoonal months may be attributed to the mobilization of metals from the over-flooding of metal-rich waste water into the estuary during high rainfall, and reworking the sediments and the geological processes might have facilitated the metal dispersion and mobilization in estuarine sediments.

On the other hand, spatial variation of trace metals in the Zuari estuary found higher concentrations of metals in the lower estuarine region than the upstream region, which might be due to the resuspension of bottom sediments along with the effect of salinity. However, Fe registered a higher concentration in the upper etuarine region during the pre-monsoon season. This could be attributed to the input of Fe-rich sediments from upstream region during the pre-monsoon period. The spatial variation of metal in the Zuari estuary showed an uneven trend from the upper to the lower estuarine regions. Excep Zn and Cu, which showed almost similar concentration across different seasons in the middle and upper estuarine regions. This spatial variation in metal concentrations from head to mouth indicates that different factors may be influencing the distribution of trace metals in the estuary. The overall trend of metal concentrations in the Zuari estuary is as follows: Fe > Mn > Zn > Cu > Co. This suggests that there may be multiple sources of metal inputs within the estuary, as well as variations in the processes controlling their distribution. The higher concentrations of Fe and Mn in the upper regions of the estuary may be attributed to the input of sediments carrying these metals from upstream sources.

Seasonal variation of metals in Zuary estuary showed almost similar concentrations of metal during the monsoon and non-monsoonal months, with slight differences. However, Cu and Co showed a more suignificant seasonal variation.

Overall, the Zuari estuary showed a higher concentration of metal than the Mandovi estuary. However, the seasonal variation of metals showed more variability in the Mandovi estuary across different seasons compared to the Zuari estuary.

In this study, the concentrations of manganese and iron were found to be higher compared to the findings of Gaonkar et al., (2021); however, copper exhibited a lower concentration than the values reported by Gaonkar et al., (2021), and zinc showed similar concentrations during the pre-monsoon season, higher concentrations during the post-monsoon season, and lower concentrations during the monsoon season compared to Gaonkar et al., (2021). In contrast, higher concentrations of Mn, Fe, Zn and Cu were reported in the sediments of the Zuari estuary in this study compared to the findings of Gaonkar and Matta, (2020).

In the Mandovi estuary, the geo-accumulation index (Igeo) value in the sediments indicates moderate to strong pollution with Mn and from unpolluted to moderately polluted with Fe. Additionally, Igeo values in Zuari estuarine sediments showed a moderate pollution level of Mn in the lower estuarine region. Mn contamination levels in the Mandovi estuary varied from considerable to very high, while Fe contamination levels ranged from moderate to considerable. In contrast, the contamination factor for Mn in the Zuari estuary ranged from moderate to considerable levels of contamination.

Moreover, the pollution load index (PLI) in both estuaries shows that the sediments are contaminated with analyzed trace metals. In the Zuari estuary, seasonal PLI variations are observed in the middle and upper estuarine regions. Contamination and modified degree of contamination (mCd) values in the Mandovi estuarine sediments showed a range from very low to considerable contamination and from very low to moderate contamination, respectively. However, at station 11, mCd values indicated a high degree of contamination during non-monsoonal months. The contamination degree in the Zuari estuary showed similar results; however, the modified degree of contamination values ranged from very low to moderate contamination.

Additionally, the potential contamination index (Cp) values in both estuaries revealed severe to very severe contamination with Mn. The other metals showed a moderate contamination level in the sediment, except for Fe, which exhibited severe contamination in the Mandovi estuarine sediment. However, in both estuaries, there was seasonal variation in copper contamination, as observed in the Cp values. At the end, the potential ecological risk index revealed a low level of ecological risk in both estuaries.

Overall, we can conclude that, in recent years, despite bans on mining activities, Goa's industrial expansion, development projects, and urban growth have increased the discharge of anthropogenic waste into the estuarine environment. This may account for the elevated levels of manganese and iron observed in the current study, in contrast to the findings of Gaonkar and Matta (2020) and Gaonkar et al. (2021).

CHAPTER 6

BIBLIOGRAPHY

REFERENCES

- Abrahim GMS, Parker RJ (2008) Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. Environ Monit Assess 136:227–238. https://doi.org/10.1007/s10661-007-9678-2

- Ajani, Gloria & Olatunde, Popoola Samuel & Otolorin, Oyatola. (2020). Evaluation of the Pollution Status of Lagos Coastal Waters and Sediments, Using Physicochemical Characteristics, Contamination Factor, Nemerow Pollution Index, Ecological Risk and Potential Ecological Risk Index. International Journal of Environment and Climate Change. 10.9734/IJECC/2020/XXXXX.

- Ananthan G, Sampathkumar P, Soundarapandian P, Kannan L (2005) Heavy metal concentrations in Ariyankuppam estuary and Verampattinam coast of Pondichery. Indian J Fish 52:501–506

- Ananthan G, Sampathkumar P, Palpandi C, Kannan L (2006) Distribution of heavy metals in Vellar estuary, Southeast coast of India. J Ecotoxicol Environ Monit 16:185–191

- Alagarsamy, R. (2006). Distribution and seasonal variation of trace metals in surface sediments of the Mandovi estuary, west coast of India. Estuarine, coastal and shelf science, 67(1-2), 333-339.

- Alzahrani, Hassan & Qaysi, Saleh & Alshehri, Fahad. (2023). Contamination and Risk Assessment of Potentially Toxic Elements in Coastal Sediments of the Area between Al-Jubail and Al-Khafji, Arabian Gulf, Saudi Arabia. Water. 15. 573. 10.3390/w15030573.

- Arunkumar, K. S.. "Heavy Metal Accumulation in Sediments of a Tropical Estuary: A Case from the Southwest Coast of India." (2020).

- Balachandran KK, Laluraj CM, Martin GD, Srinivas K, Venugopal P (2006) Environmental analysis of heavy metal deposition in a flow-restricted tropical estuary and its adjacent shelf. Environ Foren 7:345–351. https://doi.org/10.1080/15275920600996339

- Balachandran K, Raj CL, Nair M, Joseph T, Sheeba P, Venugopal P (2005) Heavy metal accumulation in a fow restricted, tropical estuary. Estuar Coast Shelf Sci 65(1–2):361–370. https://doi. org/10.1016/j.ecss.2005.06.013

- Berner, R.: Sedimentary pyrite formation, Am. J. Sci., 268, 1–23, 1970.

- Bhattacharya A, Routh J, Jacks G, Bhattacharya P, Morth M (2006) Environmental assessment of abandoned mine tailings in Adak, Vasterbotten district (northern Sweden). Appl Geochem 21(10):1760–1780.

- Bopp RF, Simpson HJ. Contamination of the Hudson River: the sediment record. In: Contaminated marine sediments assessment and remediation. 1989. p. 401–16.

- Boxall ABA, Comber SD, Conrad AU, Howeroft J, Zaman N (2000) Inputs monitoring and fate modelling of antifouling biocides in UK estuaries. Geochim Cosmochim Acta 41:1313–1324. https:// doi.org/10.1016/S0025-326X(00)00021-7

- Bramha, Satyanarayan & Mohanty, Ajit & Satpathy, K.K. & Kv, Kanagasabapathy & Panigrahi, Satya & Samantara, M.K. & Prasad, M.V.R.. (2014). Heavy metal content in the beach sediment with respect to contamination levels and sediment quality guidelines- a study at Kalpakkam coast, southeast coast of India. Environmental earth sciences. 72. 10.1007/s12665-014-3346-y.

- CCREM 1987. Canadian water quality guidelines. Canadian Council of Resource and Environment Ministers, Ontario.

- Chukwujindu, Iwegbue & Lari, Bulouebibo & Osakwe, Stephen & Tesi, Godswill & Nwajei, Godwin & Martincigh, Bice. (2018). Distribution, sources and ecological risks of metals in surficial sediments of the Forcados River and its Estuary, Niger Delta, Nigeria. Environmental Earth Sciences. 77. 10.1007/s12665-018-7344-3.

- Dauvalter V, Rognerud S (2001) Heavy metal pollution in sediments of the Pasvik River drainage. Chemosphere 42:9–18. https://doi.org/ 10.1016/S0045-6535(00)00094-1

- Dean RJ, Shimmield TM, Black KD (2007) Copper, zinc and cadmium in marine cage fish farm sediments:an extensive survey. Environ Pollut 145: 84−95

- Dehadrai, Padmakar V.. "Changes in the environmental features of the Zuari and Mandovi estuaries in relation to tides." *Proceedings of the Indian Academy of Sciences - Section B* 72 (1970): 68-80.

- Dessai, D. V., & Nayak, G. N. (2009). Distribution and speciation of selected metals in surface sediments, from the tropical Zuari estuary, central west coast of India. Environmental monitoring and assessment, 158, 117-137.

- Devanesan, E. et al. "Heavy metal and potential ecological risk assessment in sedimentscollected from Poombuhar to Karaikal Coast of Tamilnadu using Energy dispersive X-ray fluorescence (EDXRF) technique." *Beni-Suef University Journal of Basic and Applied Sciences* 6 (2017): 285-292.

- Dill, H G., (2010). The "Chessboard" Classification Scheme of Mineral Deposits Mineralogy and Geology from Aluminum toZirconium. Earth Science Review 100: 1-420

- Duruibe, J., Ogwuegbu, M. and Egwurugwe, J., (2007). Heavy Metals Pollution and Human Biotoxic Effect. International Journal of Physical Science 2:112-118.

- Emelina, G., (2011). Assessment of the Effect on Acid Mine Drainage on Mugpog River Ecosystem, Marinduque and Possible Impact on Human Communities Philippines, Investor Relation, Technology Business. Pp 1-5.

- EPA., (2007). Lead: Human Exposure and Health Risks Assessment for Selected Case Studies, Volume I. Human Exposure and Health Risk Assessments- Full-Scale, EPA452/R-07-014a.

- Eugenia JO, Sanchez G, Marcado G (2004) Cleaner production and environmental sound biotechnology for the prevention of upstream nutrient pollution in the Mexican coast of the Gulf of Mexico. Oceno Coast Mang 47:641–670. https://doi.org/10.1016/j.oceco aman.2004.12.006

- Feng H, Han X, Zhang W, Yu L (2004) A preliminary study of heavy metal contamination in Yangtze River intertidal zone due to urbanization. Mar Pollut Bull 49(11–12):910–915. https://doi. org/10.1016/j.marpolbul.2004.06.014

- Feng H, Zhang W, Zhang L, Wang X-C, Yu L, Yu D. Heavy metal contamination in selected urban coastal regions in US and China. Hauppauge: Nova Science Publishers, Inc; 2008. p. 265–86

- Fernandes L., Nayak G.N., Ilangovan D., Borole D. (2011). Accumulation of sediment, organic matter and trace metals with space and time, in creek along Mumbai coast, India. Estuarine Coastal and shelf Science, 91 (3), 388-399.

- Gaonkar CV, Matta VM (2019) Impact of mining on metal concentration in waters of the Zuari estuary, India. Environ Monit Assess 191(6):368. https://doi.org/10.1007/s10661-019-7506-0

- Gaonkar C, Matta VM (2020) Assessment of metal contamination in a tropical estuary, West Coast of India. Environ Earth Sci 79:1–17. https://doi.org/10.1007/s12665-019-8745-7

- Gaonkar, C. V., Nasnodkar, M. R., & Matta, V. M. (2021). Assessment of metal enrichment and contamination in surface sediment of Mandovi estuary, Goa, West coast of India. Environmental Science and pollution Research, 28, 57872-57887.

- Gayathri, S., Krishnan, K.A., Krishnakumar, A. *et al.* Monitoring of heavy metal contamination in Netravati river basin: overview of pollution indices and risk assessment. *Sustain. Water Resour. Manag.* **7**, 20 (2021). https://doi.org/10.1007/s40899-021-00502-2

- Gopal V, Krishnakumar S, Peter TS, Nethaji S, Kumar KS, Jayaprakash M, Magesh NS (2017) Assessment of trace element accumulation in surface sediments off Chennai coast after a major flood event. Mar Pollut Bull 114:1063–1071. https://doi.org/10.1016/j.marpolbul. 2016.10.019

- Hakanson L (1980) An ecological risk index for aquatic pollution control. A sedimentological approach. Water Res 14(8):975–1001

- Håkanson, Lars & Ervik, A. & Mäkinen, Timo & Møller, B.. (1988). Basic Concepts Concerning Assessments of Environmental Effects of Marine Fish Farms. Nordic Council of Ministers, NORD. 90.

- Haris, Hazzeman & Looi, Ley Juen & Aris, Ahmad Zaharin & Mokhtar, Farhana & Ayob, Nur & Yusoff, Fatimah & Salleh, Abu & Praveena, Sarva. (2017). Geo-accumulation index and contamination factors of heavy metals (Zn and Pb) in urban river sediment. Environmental geochemistry and health. 39. 10.1007/s10653-017-9971-0.

- Hill MK. Understanding environmental pollution. 3rd ed. New York: Cambridge University Press; 2010.

- Hirchberg, D. J., & amp; Schubel, J. R. (1979). Recent geochemical history of flood deposits in the northern Chesapeake Bay. Estuarine and coastal Marine science, 9(6), 771-IN7.

- Holliman, A. F. and Wilbur, E., (2001). Inorganic Chemistry. An Organischen Chemic. Walter De Grugter paper 1085-1095.

- Huang et al., 2012, J. Huang, X. Ge, D. Wang. Distribution of heavy metals in the water column, suspended particulate matters and the sediment under hydrodynamic conditions using an annular flume J. Environ. Sci., 24 (12) (2012), pp. 2051-2059.

- IBM (2002) Mineral taxation regime in India. Mineral Economics Division, Indian Bureau of Mines (IBM), Ministry of Steel and Mines, Government of India, Nagpur.

- Jarvis, I.J. and K.E. Jarvis, 1985. Rare earth element geochemistry of standard sediments: A study using inductively coupled plasma spectrometry. Chem. Geol., 53(3-4): 335-344.

- Jilbert, T. and Slomp, C. P.: Iron and manganese shuttles control the formation of authigenic phosphorus minerals in the euxinic basins of the Baltic Sea, Geochim. Cosmochim. Acta, 107, 155–169, 10.1016/j.gca.2013.01.005, 2013.

- Joseph PV, Chacko J (2006) Distribution of trace metals in the surface sediments of Chitrapuzha, tropical tidal river on south west coast of India and implications to industrial pollution. Indian J Environ Prot 26:892–904

- Karthikeyan R, Vijayalakshmi S, Balasubramanian T (2007) Monthly variations of heavy metals and metal resistant bacteria from the Uppanar estuary (Southeast coast of India). Res J Microbiol 2(1):50–57. https://doi.org/10.3923/jm.2007.50.57

- Kalnejais LH, Martin WR, Bothner MH (2010) The release of dissolved nutrients and metals from coastal sediments due to resuspension. Mar Chem 121:224–235. https://doi.org/10.1016/j.marchem.2010.05.002

- Kerdijk HN, Salomons W (1981) Heavy metal cycling in the Scheldt estuary. Delft Hydraulics Report M1640/M1736 (in Dutch).

- Kraal, P., Burton, E. D., Rose, A. L., Kocar, B. D., Lockhart, R. S., Grice, K., Bush, R. T., Tan, E. and Webb, S. M.: Sedimentary iron-phosphorus cycling under contrasting redox conditions in a eutrophic estuary, Chem. Geol., 392, 19–31, 10.1016/j.chemgeo.2014.11.006, 2015.

- Kumar S, Barath & Mohanty, Ajit & Satpathy, K.K. & Padhi, Ranjib. (2020). Distribution and ecological- and health-risk assessment of heavy metals in the seawater of the southeast coast of India. Marine Pollution Bulletin. 16. 111712. 10.1016/j.marpolbul.2020.111712.

- Liss, P. S., & Burton, J. D. (Eds.). (1976). Estuarine chemistry. Academic press.

- Maanan, Mohamed & Saddik, Mohammed & Maanan, Mehdi & Chaibi, Mohamed & Assobhei, Omar & Zourarah, Bendahhou. (2014). Environmental and ecological risk assessment of heavy metals in sediments of Nador lagoon, Morocco.

- Mance, G. and Yates, J. (1984). Proposed Environmental Quality Standards for List III-or ganisms, Ocassional Publication No.2 In:T.R Crompton, Marine Biology Association, Plymouth, USA, 495p. PMid:6748931 PubMed/NCBI

- Manta DS, Bellanca A, Angelone M (2002) Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy. Sci Total Environ 300(1–3):229–243. https://doi.org/10.1016/S0048 - 9697(02)00273-5

- Manoj NT, Unnikrishnan AS, Sundar D (2009) Tidal asymmetry in the Mandovi and Zuari estuaries, the west coast of India. J Coast Res 25(6):1187–1197. https://doi.org/10.2112/08-1056.1

- Martin J-M, Whitfield M. The significance of the river input of chemical elements to the ocean. In: Trace metals in sea water. Springer; 1983. p. 265–96

- Magesh, N. S., Chandrasekar, N., & Roy, D. V. (2011). Spatial analysis of trace element contamination in sediments of Tamiraparani estuary, southeast coast of India. Estuarine, Coastal and shelf Science, 92(4), 618-628.

- Mascarenhas, Antonio and G. Kalavampara. "Natural resources of Goa: A geological perspective." (2009).

- Mohaihsh, A.S., Al-Swailem, M.S., Mahjoub, M., (2004). Heavy Metals Content of Commercial Inorganic Fertilizer Used in the Kingdom of Saudi Arebia. A Journal of Agricultural and Marine Science. 1: 21-25.
- Müller J, Ruppert H, Muramatsu Y, Schneider J. Reservoir sediments—a witness of mining and industrial development (Malter Reservoir, eastern Erzgebirge, Germany). Environ Geol. 2000;39: 1341–51.

- Muller G (1979) Heavy-metals in sediment of the Rhine-changes since 1971. Umschau in Wissenschaft und Technik 79(24):778–783

- National Institute of Oceanography (NIO), Goa (1979) Master Plan for Pollution control of the Rivers Zuari and Mandovi. Technical Report No. 02/79

- Nishitha, D., Amrish, V.N., Arun, K. *et al.* Study of trace metal contamination and ecological risk assessment in the sediments of a tropical river estuary, Southwestern India. *Environ Monit Assess* **194**, 94 (2022). https://doi.org/10.1007/s10661-021-09728-1

- Lalonde, K., Mucci, A., Ouellet, A. and Gélinas, Y.: Preservation of organic matter in sediments promoted by iron, Nature, 483, 198–200, 2012.

- Lee PK, Kang MJ, Yu S, Ko KS, Ha K, Shin SC, Park JH (2017) Enrichment and geochemical mobility of heavy metals in bottom sediment of the Hoedong reservoir, Korea and their source apportionment. Chemosphere 184:74–85. https://doi.org/10.1016/j. chemosphere.2017.05.124

- Liu Y, Guo HC, Yu YJ, Huang K, Wang Z (2007) Sediment chemistry and the variation of three altiplano lakes to recent anthropogenic impacts in south-western China. Water SA 33:305–310

- Luptakova A, Ubaldini S, Macingova E, Fornari P, Giuliano V (2012) Application of physical–chemical and biological–chemical methods for heavy metals removal from acid mine drainage. Proce-Biochem 47(11):1633–1639. https://doi.org/10.1016/j.jbiot ec.2010.09.133

- Parvez Al-Usmani SM (2018) Impact of mining activities on estuarine hydrological regime and benthic life in Goa India. Oceanogr Fish Open Access J 8(3):555–737. https://doi.org/10.19080/OFOAJ.2018.08.555737

- Pathak, M. C., Kotnala, K. L., & Prabaharan, N. (1988). Effects of bridge piers on a tropical estuary in Goa, India. Journal of Coastal Research, 4, 475-481.

- Pradhan U, Shirodkar PV (2011) Assessment of the impact of developmental activities on the estuarine environments of Mandovi and Zuari Rivers of Goa along the West Coast of India. In: Proceedings of international conference in ocean engineering, 1–5 Feb. 2009. IIT Madras, Chennai, India, pp 1145–1156.

- Praveena, S.M., Ahmed, A., Radojevic, M. *et al.* Multivariate and Geoaccumulation Index Evaluation in Mangrove Surface Sediment of Mengkabong Lagoon, Sabah. *Bull Environ Contam Toxicol* **81**, 52–56 (2008). https://doi.org/10.1007/s00128-008-9460-3

- Prichard, D. W. (1967). What is an estuary: physical viewpoint. American Association for the Advancement of Science.

- Quasim, S. Z., Sengupta, R., & Reddy, C. V. G. (1979). Master plan for pollution control of the rivers Zuari and Mandovi (No. 2). NIO Technical Report.

- Rane, Nitin and Vishnu Murty Matta. "Assessment of metal contamination in sediment cores of Zuari and Kushavati rivers with reference to past mining in Goa, west-coast of India." (2019).

- Ren, J., Hao, J. & Tao, L. Concentrations, spatial distribution, and pollution assessment of heavy metals in surficial sediments from upstream of Yellow River, China. *Environ Sci Pollut Res* **28**, 2904–2913 (2021). https://doi.org/10.1007/s11356-020-10349-3

- Robertson, E. K., Roberts, K. L., Burdorf, L. D. W., Cook, P., and Thamdrup, B.: Dissimilatory nitrate reduction to ammonium coupled to Fe (II) oxidation in sediments of a periodically hypoxic estuary. Limnol. Oceanogr. 61, 365–381, 2016

- R, Shynu & purnachandra Rao, Venigalla & Kessarkar, Pratima & Rao, T.. (2012). Temporal and spatial variability of trace metals in suspended matter of the Mandovi estuary, central west coast of India. Environmental Earth Sciences. 65. 725-739. 10.1007/s12665-011-1119-4.

- Rubio B, Nombela MA, Vilas F (2000) Geochemistry of major trace elements in sediments of the Ria de vigo (NW Spain) an assessment of metal pollution. Mar Pollut Bull 40:968–980. https://doi.org/10.1016/S0025-326X(00)00039-4.

- Lovley, D., Holmes, D. and Nevin, K.: Dissimilatory Fe(III) and Mn(IV) reduction, Advances in Microbial Physiology, 49, 219–286, 10.1016/S0065–2911(04)49005–5, 2004.
- Obasohan, E. E. and Osayanmo I. Eguavoen. "Seasonal variations of bioaccumulation of heavy metals in a freshwater fish (Erpetoichthys calabaricus) from Ogba river, Benin city, Nigeria." *Indian Journal of Animal Research* 42 (2008): 171-179.

- Senthilnathan, S. and Balasubramanian, T. (1999) Distribution of Heavy Metals in Estuaries of Southeast Coast of India. Indian Journal of Marine Science, 26, 95-97. http://nopr.niscair.res.in/handle/123456789/36157

- Shetye. S. R., Dileep Kumar, M., & Shankar, D. (2007). The Mandovi and Zuari Estuaries.

- Shetye, S. R., Gouveia, A. D., Singbal, S. Y., Naik, C. G., Sundar, D., Michael, G. S., & Nampoothiri, G. (1995). Propagation of tides in the Mandovi-Zuari estuarine network. Proceedings of the Indian Academy of Sciences-Earth and Planetary Sciences, 104, 667-682.

- Shetye, S.R., Kumar, M.D., & Shankar, D. (2007). The Mandovi and Zuari estuaries.

- Shields, M. R., Bianchi, T. S., Gelinas, Y., Allison, M. A. and Twilley, R. R.: Enhanced terrestrial carbon preservation promoted by reactive iron in deltaic sediments, Geophys. Res. Lett., 43, 1149–1157, 10.1002/2015GL067388, 2016.

- Sholkovitz ER (1987) Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater. Geochim Cosmo Acta 40(7):831–84

- Singh, K. K., Matta, V. M., Sharma, B.M., & Usha, K. H. (2009). Trace metals in sediments of the Zuari river Goa, west coast of India.

- Silambarasan K, Senthilkumaar P, Velmurugan K (2012) Studies on the distribution of heavy metal concentrations in River Adyar, Chennai, Tamil Nadu. Eur J Exp Biol 2(6):2192–2198

- Sivakumar, S., Chandrasekaran, A., Balaji, G., Ravisankar, R., 2016. Assessment of heavy metal enrichment and the degree of contamination in coastal sediment from south east coast of tamilnadu, India. Journal of Heavy Metal Toxicity and Disease 1, 1–8

- Slomp, C. P., Epping, E. H. G., Helder, W. and Van Raaphorst, W.: A key role for iron-bound phosphorus in authigenic apatite formation in North Atlantic continental platform sediments, J. Mar. Res., 54, 1179–1205, 1996.

- Tomlinson DL, Wilson JG, Harris CR, et al. Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. Helgoländer Meeresuntersuchungen. 1980;33(1–4):566–575

- Trifuoggi, ., Ferrara, L., Toscanesi, M. *et al.* Spatial distribution of trace elements in surface sediments of Hooghly (Ganges) river estuary in West Bengal, India. *Environ Sci Pollut Res* **29**, 6929–6942 (2022). https://doi.org/10.1007/s11356-021-15918-8

- Turekian KK, Wedepohl KH (1961) Distribution of the elements in some major units of the earth's crust. Geol Soci Am Bull 72(2):175–192
- Udayakumar, P., Chandran, A., Jean Jose, J., Rajesh, B. R., Narendra Babu, K., & Ouseph, P. P. (2011). Seasonal dynamics of dissolved metals in surface coastal waters of southwest India. Bulletin of environmental contamination and toxicology, 87, 662-668.

- USEPA 1986. Quality criteria for water. US Department of commerce, National Technical Information Service, US Environmental Protection Agency, Springfield, Virginia. PB87-226759, EPA 440/5 65-001.

- Veerasingam, S., Mugilarasan, M., Venkatachalapathy, R., & Vetamony, P.(2016). Influence of 2015 flood on the distribution and occurrence of microplastic pellets along the Chennai coast, India. Marine pollution bulletin, 109(1), 196-204.

- Vineethkumar, V. et al. "Estimation of pollution indices and hazard evaluation from trace elements concentration in coastal sediments of Kerala, Southwest Coast of India." *Bulletin of the National Research Centre* 44 (2020): 1-16.

- Wasike Peter Wekesa, analysis of selected heavy metals in water from river Kuywa and adjacent wells in Bungoma central sub county- Kenya, I56/CE/11203/2007

- WHO., (1998) Copper: Environmental Health criteria Monograph 200. International Program on Chemical Safety (IPCS)

- WHO., (2004). Guideline for Drinking Water Quality 4th ed Geneva, Switzerland World Health Organization. Xiii, 541

- WHO., (2008). Guideline for Drinking Water Quality, World Health Organization. Guideline for Drinking water quality (WHO), Geneva, 130p.