Studies on Distribution of Trace Metals along the beaches of Goa-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

KRUTIKA KASHINATH DEVASHETTI

Roll Number: **22P0400012**

ABC ID: **313024413635**

PR Number: **20190251**

Under the Supervision of

DR. 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 Distribution of Trace Metals along the beaches of Goa-West Coast of India**" is based on the results of investigations carried out by me in the Discipline of Marine Sciences at the School of Earth, Ocean and Atmospheric Sciences, Goa University under the Supervision of Dr. Vishnu Murty Matta and the same has not been submitted elsewhere for the award of a degree or diploma by me. Further, I understand that Goa University or its authorities will not be responsible for the correctness of observations/experimental or other findings given in 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.

Date 30/04/2024

Krutika Kashinath Devashetti
Seat No. 22P0400012

Place: Goa University, Taleigão Plateau, Goa

COMPLETION CERTIFICATE

This is to certify that the dissertation report "**Studies on distribution of Trace Metals along beaches of Goa-West Coast of India**" is a bonafide work carried out by Ms. Krutika Kashinath Devashetti under my supervision in partial fulfilment of the requirements for the award of the degree of Master of Science in the Discipline of Marine Sciences at the School of Earth, Ocean and Atmospheric Sciences, Goa University.

Date 30/04/2024

30/04/2024
Dr. Vishnu Murty Matta
Discipline of Marine Sciences,
School of Earth, Ocean and Atmosphereic Sciences

21/5/24
Sr. Prof. Sanjeev C. Ghadi,
Senior Professor and Dean
Marine Sciences
School of Earth, Ocean and Atmospheric Sciences.
Date:
Place: Goa University, Taleigão Plateau, Goa.

PREFACE

In an era marked by rapid development and urban expansion, coastal ecosystems are increasingly vulnerable to pollution and contamination. Goa, celebrated for its pristine beaches, faces the challenge of safeguarding its coastal environments amidst growing human activity. To effectively manage these areas and advance conservation efforts, it's crucial to understand the dynamics of organic carbon levels and metal pollution in beach sediments. This research aims to assess pollution indicators, metal distribution, and organic carbon content in the surface sediments of North and South Goa beaches. By examining various pollution indices, this study seeks to illuminate the current contamination levels and potential ecological risks to these coastal habitats.

ACKNOWLEDGEMENT

I would like to express my heartfelt gratitude to the Almighty for granting me the strength throughout the journey of completing this dissertation and also extend my deepest appreciation to my family for their support.

It gives me pleasure and honour to express my deep gratitude and heartiest thanks to my guide Dr. Vishnu Matta, Vice-Dean (Research) and Professor of Marine Sciences at the School of Earth, Ocean and Atmospheric Sciences, Goa University, for his valuable advice, time, patience and constant support throughout this year.

I would like to thank Sr. Prof. Sanjeev C. Ghadi, Dean of School of Earth, Ocean and Atmospheric Sciences, Goa University and Sr. Prof. C. U. Rivonker, Former Dean of School of Earth, Ocean and Atmospheric Sciences, for providing with the necessary facilities that aided in the completion of my dissertation work. I extend my sincere thanks to Mrs. Utkarsha, Ms. Sitam, Mrs. Mahima and Mrs Gayatri and all the other non-teaching and laboratory staff members.

I would like to express my sincere thanks to my friends K. M. Dharani, Mayuresh Pednekar, Varsha Kumari, Cristopher Fernandes, Glennis Da Costa, Tirtha Bagi and Gaurav Gawas for helping me and supporting me throughout my dissertation work.

LIST OF ABBREVIATIONS

Abbreviations	**Entity**
B	Baina
BM	Bogmalo
H	Hollanth
J	Japanese
TOC	Total Organic Carbon
Fe	Iron
Mn	Manganese
Zn	Zinc
Cu	Copper
Co	Cobalt
AAS	Atomic Absorption Spectrophotometer
CF	Contamination Factor
PL1	Pollution Load Index
n	Number
%	Percentage
B_n	Concentration of the same metal in the upper crust
I_{geo}	Geo-Accumulation Index
GPS	Global Positioning System
°C	Degree Celsius
cm	Centimeter
F 1	Fraction 1
F 2	Fraction 2
F 3	Fraction 3
F 4	Fraction 4
F 5	Fraction 5

LIST OF EQUATIONS

1. $\% \text{ of TOC} = 10 (1 - T/S) \times F$
2. $I_{geo} = \log_2 (C_n / 1.5 * B_n)$
3. $CF = C_{metal}/C_{background}$
4. $PLI = n\sqrt{} (CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n)$

ABSTRACT

The research examines the organic carbon content, metal distribution, and pollution indices of surface beach sediments of Vasco beaches. Four main beaches from Vasco, representing urbanized, rural, and fishing zones, were selected for investigation. Sediment samples underwent geochemical and sedimentological analyses to quantify metals and total organic carbon. Various pollution indices, including Geo-accumulation Index (Igeo), Contamination Factor (CF), Pollution Load Index (PLI). Results indicated variations in organic carbon content and metal pollution levels among the studied beaches. Rural and fishing zones displayed consistent organic carbon levels, while urban areas showed lower levels. Pollution indices generally indicated low to moderate contamination and reduced ecological risks, although some regions exhibited moderate contamination levels. This study emphasizes the importance of monitoring and conservation efforts in Goa's coastal ecosystems and provides valuable insights for coastal management strategies.

1.1 BACKGROUND

Coastal environment is a complex ecosystem, and it is subjected to continuous changes by the natural as well as human interposes. Different varieties of flora and fauna, such as seaweeds, mangroves, marine algae, corals, sponges and fishes, survive in this environment. In addition, it is viable for various economic activities such as shipping, fishing, aquaculture, etc. Apart from the geogenic sources, the increasing population and developmental activities in the coastal regions induce the generation of huge amounts of solid waste containing different metals and their disposal into the seawater poses serious environmental risks. The coastal aquifers are affected by seawater intrusion due to over-extraction of groundwater. Thus, the groundwater along the coast is also vulnerable to heavy metals released from the beach sediments into the sea.

The term beach is defined as a landform along the shoreline of an ocean, sea, lake, or river consisting of loose particles such as sand, gravel, shingle, pebbles, or cobblestones. Beaches are dynamic environments that are shaped by the action of waves, currents, tides, and wind. They play a crucial role in coastal ecosystems and provide habitats for various species of plants and animals.

The landward limit of the beach is considered to be the maximum reach of storm waves in front of coastal dunes. For the seaward limit, four options have long been debated: the “low water line”, the external limit of oscillatory waves, the outer limit of the breaker zone and a fixed selected water depth of 10 m. Out of which, the external limit of oscillatory waves, where the interaction between waves and sediments begin is the widely accepted one (Stanica and Ungureanu 2010). However, the depth of such a limit will vary in response to changing wave characteristics and catastrophic events viz., tsunamis or extremely strong storms and would shift the limit further seaward to deeper waters. The length of a beach varies greatly; some stretch for hundreds of kilometers whereas, others called pocket beaches, which are restricted by headlands and are only a few tens of meters long.

Metal and trace element in sediments are assessed using the geochemical criteria, in which the total concentrations are evaluated with respect to the background values. These criteria include the geo accumulation index **(Igeo, Muller, 1969; Zahra et al., 2014)** and the pollution load index **(PLI, Wilson et al., 2008).** Trace elements are the most common contaminants of coastal environment because of their toxicity, as well as their ubiquitous and persistent nature **(e.g. Diagomanolin et al., 2004).** For example, the anthropogenic activities contribute to the contamination of As, Cd, Cr, Pb and Hg in both sediment and water. These systematic toxicants induce adverse health effects in humans including cardiovascular diseases, developmental abnormalities, neurologic disorders, diabetes, hearing loss immunologic disorders as well as different types of cancer **(e.g. Tchounwou et al., 2012).** Exposure to high concentrations of Cr is related to pulmonary cancer **(e.g. Cefalu and Hu, 2004),** chronic ulcers and pneumonia **(e.g. Dayan and Paine, 2001)**. The consumption of water with more As and Cr is also carcinogenic **(e.g. Nordstrom, 2002; Kumar et al., 2020).**

In general, the distribution of metals and trace elements is controlled by nature of the parent materials and climatic conditions affecting their relative mobility. (**Singh et al. 2005)** and (**Jain et al. 2007)** have identified the influence of mineralogy on the concentration of metals. The anthropogenic activities also play vital roles in their enrichment in beach sediments **(Milenkovic et al., 2005; Venkatramana et al., 2014).** Trace elements sourced from weathering of surrounding rock formations and generated from the anthropogenic activities are deposited in beach sediments by adsorption, hydrolysis and co-precipitation **(Bartoli et al., 2012; Song et al., 2014).** Sediments in marine environment, however, are considered as the ultimate sink for these elements as most of them enter into the ocean along with the suspended sediments **(e.g. Gaur et al., 2005; Santos et al., 2005; Aa et al., 2016).**

Coastal region is a dynamic ecosystem where the changes in the variables viz., suspended particulate matter, pH, Eh, salinity, and ionic composition are most common which cause periodic remobilization of metals from the contaminated sediment surfaces and thereby making the sediments a potential source of metals **(Osakwe et al. 2014).** Distribution and mobility of metals within the water column depends strongly on their chemical forms **(Dessai and Nayak 2009).** The metals may be present in the bioavailable fraction or in the residual fraction. The bio-available fraction, as the name suggests, can be consumed by organisms living in the ecosystem. It consists of labile forms of metals which may be altered due to change in chemical properties like pH, redox potential, salinity or temperature and play an important role in the geochemical cycle **(Yuan et al. 2004).**

To prevent the damage caused by heavy metals in the sand, it is necessary to investigate the harmful metal content of coastal sand and the degree of contamination. Metals are transported naturally from their source areas **(Nagarajan et al., 2019)** to beaches through stream runoffs and also by washouts at some point of heavy rainfall **(Sheela et al., 2012).** Other contributions are atmospheric fallouts and offshore sediments transported by waves and currents. But continuous stresses on beaches through anthropogenic activities inclusive of rapid urbanization, industrialization and tourism **(Feng et al., 2004; Qiao et al., 2013; Bray et al., 2022; Nagarajan et al., 2023; Dessai, 2023)** account for more mobile litters (which carries metals) and accumulated in beaches, which leads to elevating selective metal concentrations in soils and sediments eventually **(Buzzi et al., 2022)**.

1.2 AIM AND OBJECTIVES:

The aim of this dissertation work is to comparatively study concentration and distribution of metals along the coast of Vasco.

The objectives of the dissertation work are:

- To determine the grain size of the sediments collected from various stations.
- To calculate the Organic carbon content.
- To analyse the distribution of metals.
- To analyse the metal toxicity along the coast of Goa.

1.3 SCOPE

Goa could provide valuable insights into environmental health, pollution sources, and potential impacts on marine ecosystems. It could also inform management strategies for preserving the coastal environment. It will also encourage more people of that area to conduct more and more research work as no specific work has been carried out in these stations.

(Bramha et al. 2014) The study examined heavy metal levels along the southeast coast of India, from Kalpakkam to Mamallapuram. Using different indices, contamination levels in beach sediment were evaluated. Results showed moderate to severe enrichment of Cr, Cu, Pb, and Cd, particularly in Mamallapuram. However, the sediment was generally deemed unpolluted, with Ni and Cr values surpassing the probable effect limit, indicating potential adverse effects, but overall toxicity remained low.

(Sundar et al. 2021) The study analyzed 18 different metals and trace elements in 64 bulk sediment samples collected from Kanyakumari beach in southern India, covering a distance of 71km. Its goal was to create a baseline dataset for the region and determine the degree of enrichment compared to the upper continental crust. Various environmental indices, including enrichment factor, contamination factor, and geo-accumulation index, were used to assess the contamination level.

(Krishnakumar et al. 2013) The study highlights sediment contamination due to coastal urbanization in developing countries. High-positive correlations between elemental concentrations of Cr, Pb, Ni, Mn, and Zn with Fe suggest the presence of Fe oxides in sediments. Pollution indicators such as EF, Igeo, CF, and PLI showed significant differences depending on background values. Comparison with NOAA-SQUIRTs and CSG guidelines revealed serious Cd and Cr contamination impacting organisms and coastal habitat along the Nagapattinam coast.

(Abdel Ghani, 2015) The study aimed to evaluate the pollution levels of trace metals (V, Al, Sn, As, and Se) in sediments, seawater, and fish samples from Marsa Matrouh Beaches. Results showed high EF values for Sn in sediments, indicating anthropogenic sources, supported by CF > 6, mCd, and Igeo. According to PLI, most sites were found to be polluted (PLI > 1), suggesting contributions from anthropogenic sources.

(Sadanandan et al. 2021) Nineteen sediment samples were collected from the southwest Bay of Bengal in five transects linking Cuddalore and Nagapattinam districts in Tamil Nadu, India. The samples were analyzed for organic matter, sediment texture, and trace metals (Fe, Cu, Co, Mn, Pb, Zn, Cr, and Ni). Except for transect 3, sandy fractions predominated due to the influence of the Pichavaram estuary, fed by the Vellar and Coleroon rivers. Fe was the most abundant trace element. Elevated background levels of Co, Pb, Cr, and Ni suggest human-induced pollution effects.

(Nagarajan et al. 2013) Sediment samples from six beaches in Miri City, Sarawak, Malaysia, were analyzed for trace metal enrichment. Fe, Mn, Cr, Co, Cu, Ni, Pb, Sr, and Zn concentrations were measured. Eco-toxicological assessments revealed that Pb exceeded safe levels, Ni surpassed both Lowest Effect Level (LEL) and Effects Range Low (ERL), and Cr exceeded Severe Effect Level (SEL) and LEL. However, Cu concentrations remained within safe limits.

(Wong et al. 2006) This study examined trace metal contamination in sediments from Guiyu, China, known for crude electronic waste processing. Analysis detected Cd, Cu, Ni, Pb, and Zn in river sediments, with varying concentrations. Comparing Pb-contaminated sediments from different sources revealed lower 206 Pb/207 Pb and 208 Pb/207 Pb ratios, indicating non-indigenous Pb contributions. Moreover, non-residual fractions of Cu, Pb, and Zn in contaminated sediments were notably higher compared to uncontaminated samples.

(Liu et al. 2005) Sewage irrigation in Beijing's agricultural soils leads to heavy metal contamination, posing risks to human health. Analysis of plant and soil samples revealed significant pollution, particularly with Cd, Cu, Zn, and Pb showing worsening trends. Metal enrichment factors indicate a rise in toxic metal accumulation during sewage irrigation. Transfer of these metals from soil to plants increases human exposure risks. As Beijing expands, inhalation and ingestion of contaminated soil may become major exposure routes for the population.

(Venkatramanan et al. 2011) Beach sediments along an 11-kilometer stretch between Karikal and Nagore, near the Tirumalairajanar River mouth, show a gradual decrease in mean grain size. They are mainly medium to coarse grained, somewhat sorted, and bimodal, with sand and silt dominating. Sediment transport is primarily northward due to littoral currents and wave sorting, with the Tirumalairajanar River being the main sediment source. Wave agitation significantly influences sediment sorting. Short-term studies on sediment dynamics during the summer monsoon and grain size variations near Nagore and Karaikal support these findings.

(Gopal et al. 2023) The study investigated heavy metal pollution in marine sediments along the Vedaranyam coast, attributing it to both human and natural factors. Sediment analysis detected chromium, copper, manganese, iron, nickel, zinc, and cobalt. Despite variations, all individual toxic risk indices were below 5, indicating no major threat to aquatic life. Various indicators were employed to assess contamination levels and sediment quality, pointing to human activities as the main source of heavy metal contamination. Additionally, a strong positive correlation among metals suggests a common origin.

(Gandhi et al. 2020) The study investigates acid leachable trace metals (ALTMs) and their ecological risk in beach sediments along Southern India's Coromandel Coast. Thirty-six samples, half from low tide and half from high tide, were collected. Results suggest significant anthropogenic influences on sediment enrichment processes, with Fe, Cr, Mn, Pb, Ni, Cu, Co, and Zn detected in declining order of distribution. Natural processes like weathering, river action, and leaching contribute to metal concentrations. Additionally, factors such as calcium carbonate content, organic matter, and sediment texture influence metal distribution.

(Alagarsamy et al. 2008) The study analyzed 35 surface sediment samples from the Indian continental shelf, focusing on major and trace elements. Elements were analyzed using inductively coupled plasma atomic emission spectroscopy. Goals included identifying natural and manmade sources, establishing regional baseline values, and understanding processes influencing major and trace elements in sediments. Enrichments of Cu and Co near major urban districts on both east and west coasts were linked to industrialized activity zones. After normalizing metals to Al, enrichment factors showed high levels of Ca, Ti, Fe, Na, Mg, Co, Cu, Ga, V, and Ba. This indicated higher estuary silt levels on the west coast, reflecting riverine material origins.

(Santhiya et al. 2011) The study surveyed the concentration of Partially Extracted Trace Metals (PETMs) in beach sediments from 57 locations in Chennai Metropolitan City, India. Results revealed higher concentrations of PETMs, including Pb and Ni, in industrialized areas compared to tourist beaches. Sediments in the northern part of the city, near industrial regions, showed greater organic matter content. This suggests a potential impact of industrial activities on metal contamination levels in beach sediments.

(Kumar et al. 2016) In a study conducted along the southeast coast of India, researchers analyzed surface sediment from eight different ecosystems to assess the distribution of trace metals and their potential ecological impact. They used energy dispersive X-ray fluorescence to determine concentrations of key elements and trace metals. Various metrics were employed to evaluate pollution levels, including contamination factor, geo-accumulation index, potential effect level, enrichment factor, and pollution load index. Results showed considerable metal contamination along the shore, except for cadmium. The toxicity probability indicated low risk. There were significant positive correlations between clay and Fe, Cu, Zn, and Co, while chromium showed a significant negative correlation with clay and a positive correlation with sand content.

(Bhutia et al. 2023) In Goa, India, sediments from three different water bodies were studied to understand metal bioavailability and bioaccumulation in two types of edible bivalves. Sediment dynamics varied due to hydrodynamics and anthropogenic stress. Changes in metal levels, particularly Mn and Zn, were observed in November and December. Moderately contaminated sediments contained significant zinc levels at Chapora and zinc, copper, and cobalt at Zuari stations. Bivalves showed high adaptability to zinc. Metal concentrations in bivalves exceeded allowable limits at certain stations, indicating potential toxicity concerns.

(Bhatkhande et al. 2022) The study analyzed sediment cores from different depths in Chapora Estuary to assess metal contamination. It found variations in metal concentrations due to factors like hydrodynamics and sand mining. Iron oxides and organic carbon were identified as key factors influencing metal distribution. Core C-3 showed moderate to high contamination, especially with manganese. Saccostrea cucullata, a local species, accumulated high levels of manganese, nickel, and zinc, suggesting toxicity and unsuitability for human consumption.

(Ramkumar et al. 2023) The study focused on metal contamination in tourist beaches in Kerala, Southern India. Sediment analysis revealed differences between ilmenite-rich (IRS) and quartz-rich (QRS) samples, with varying mineral compositions. Kovalam beach showed enrichment in W, Th, and U, while IRS had higher concentrations of W, U, and Th compared to QRS. Both sediment groups posed moderate ecological risks, with concerns about Pb, As, and Cu levels. Further research is required to understand the impact and bioavailability of these metals from both natural and human-induced sources.

(Solai et al. 2013) Surface sediment samples off the southeast coast of Pondicherry, India, were analyzed for grain size, carbonates (CaCO3), and organic matter (OM) content. Additionally, heavy metal buildup (Mn, Cr, Cu, Cd, Ni, Pb, Zn) was examined using atomic absorption spectrophotometry. Sediment elements were found in the order: Cr > Mn > Pb > Zn > Cu > Ni > Cd. The high sand concentration in surface sediments is attributed to the Virampattinam tidal effect. Fine sediments at the river mouth are suspended by seawater, carried into the water column, and removed by tidal currents. OM values showed no significant depth variation.

(Singh et al. 2008) Bottom sediment samples were collected from 10 stations along the Zuari River in Goa, India, spanning three seasons: pre-monsoon, monsoon, and post-monsoon. The concentrations of zinc, manganese, cobalt, copper, and chromium in the sediments peaked during the monsoon season, attributed to increased river runoff and mining/shipping activity. Iron and cadmium concentrations were somewhat higher during the post-monsoon season, likely due to similar factors.

(Ladislao et al. 2015) The study investigated trace metal levels in surface sediments from 15 sites covering the Sundarban Mangrove Wetland and Hugli River Estuary in eastern coastal India. Metal concentrations showed a general decline trend, with significant pollution by Ag, Cd, and Pb in Nurpur of HRE based on contamination factor and geo-accumulation index values. The Potential Ecological Risk Index indicated varying degrees of ecological risk, with metals showing a positive association with organic carbon in sediments. Trace metal contamination in sediment negatively affected organisms living in the silt, as per the research findings.

(Usmani et al. 2015) The study examined trace metal pollution in water, sediment, and three bivalve species in the Mandovi and Chapora estuaries of Goa. Mandovi showed higher trace metal levels in water and sediment compared to Chapora. Bivalve species in Mandovi, namely Paphia malabarica, Perna viridis, and Saccostrea cucullata, exhibited concentrations ranging from 1205.2 to 2506.7 ppm, 1906.2 to 2802.6 ppm, and 778.7 to 1607.5 ppm, respectively. In Chapora, concentrations ranged from 199.4 to 625.8 ppm for P. malabarica, 812.6 to 1220.2 ppm for P. viridis, and 392.5 to 418.6 ppm for S. cucullata. The high trace metal levels in Mandovi are primarily attributed to human activities.

3.1 Introduction

A sample taken from a specific quantity is indicative of the biogeochemical activities occurring in the environment during collection. These samples are collected, sealed, and stored for later analysis in a laboratory. To ensure precise results reflecting the environment and its associated challenges, analyses must adhere to established protocols. Therefore, the materials, techniques, and procedures utilized should align with globally accepted standards.

3.2 Sampling.

Four distinct beaches were chosen based on the amount of anthropogenic input and the number of visitors, a total of twelve locations from which surface sediment samples were taken. Three samples were gathered from each beach: one from the far left, one from the far right, and one from the middle. To gather the sediments, a plastic scoop was used. The sediment samples were kept in an ice box after being packaged in polythene bags with labels. After being oven dried at 60 degrees to eliminate moisture, the samples were utilized for geochemical and sedimentological examination.

3.3 Study Area

The study is conducted over the coastal lines of Vasco that is in the west coast of India. Vasco is a small city located in the state of Goa, this place is not at all studied by any of the scientist, the reason being that it was not known or not very popular as rest other tourism attracted cities of Goa are, but in recent years there are lot of developments that have been done in this city and which has attracted the tourist not only from India but the entire world.

Four major beaches were selected on the basis of different anthropogenic activities. Some of the beaches are not much subjected to any such activities but some have become a major tourist spot. The human activities have significantly interfered with natural conditions and processes of the beach, mainly during the last few decades. The environmental pollution caused by uncontrolled human induced activities is occurring on a vast and unprecedented scale around the globe. The four beaches that were selected to carry out the study are: (a) Baina Beach, (b) Hollanth Beach, (c) Bogmalo Beach and (d) Japanese Beach.

Baina beach initially was not at all known by any of the tourist, the locals here also never much visited it as there was nothing that might attract the people in large amounts, but now in recent years there is a huge bridge that has been constructed over the beach which has been a major attraction, apart from this there are lot of water activities or water sports that have been started so people here come for the activities which in turn results water pollution. This is one of the sources through which the metals can enter the water through sediments.

On the other hand Hollanth and Bogmalo beaches are the one where people usually visit, especially during vacations, there are many groups of who come for picnic and have fun by bathing in the water which eventually pollutes the water, also there are lot of fishing boats that go in the water for the catch of fishes so this can also account for pollution.

The last station that is the Japanese beach is not as polluted as the other beaches as there are no much people who come here, this is due to the roughness of the beach or in other words there are usually high tide region and locals say that it is very risky to go there. So on the basis of different sources of metal pollution and also keeping in consideration that these station are not studied by anyone till date the stations were chosen and after all the analyses were done the data was compared as to see which is the most polluted beach of all. The samples were analysed using AAS (Atomic Absorption Spectrometer).

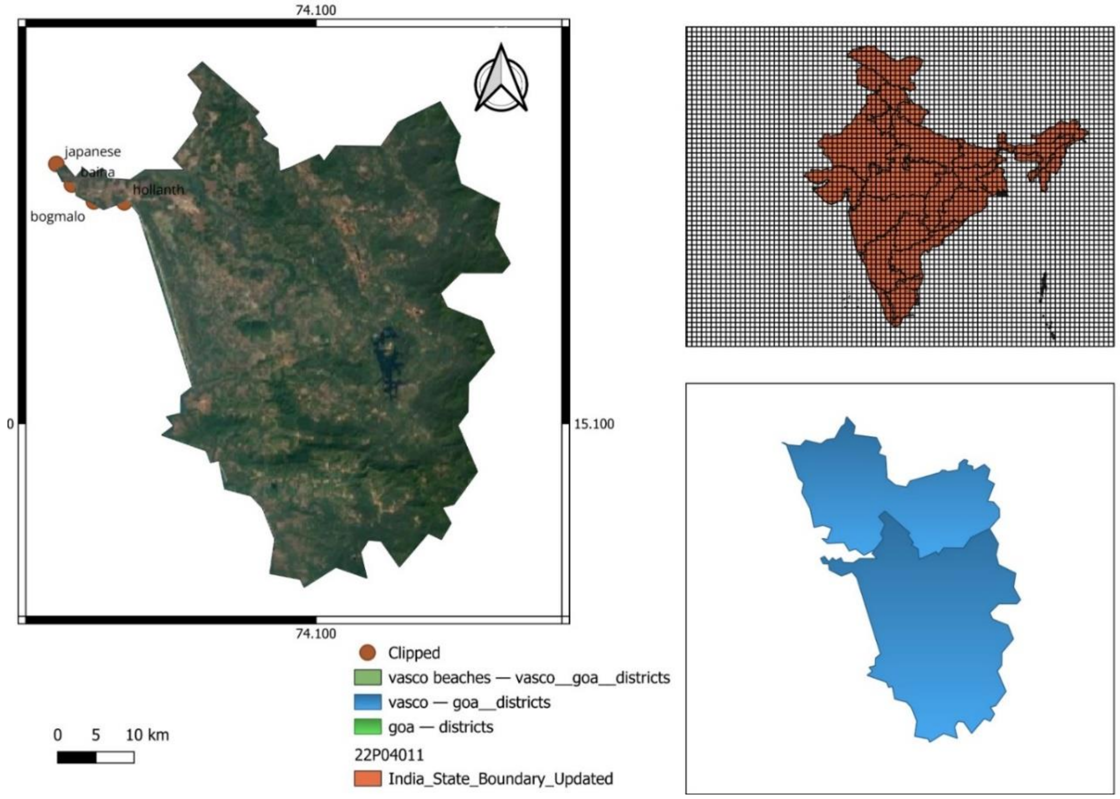

Fig 3.1 Map showing sampling locations

Table 3.1 The location of sampling site across the beaches of Vasco.

Sampling Station	Baina Beach		Bogmalo Beach	
	Latitude	Longitude	Latitude	Longitude
Station 1	15° 23’ 30” N	73° 48’ 24” E	15° 23’ 29” N	73° 50’ 7” E
Station 2	15° 23’ 18” N	73° 48’ 53” E	15° 23’ 13” N	73° 50’ 18” E
Station 3	15° 23’ 52” N	73° 48’ 17” E	15° 23’ 40” N	73° 50’ 45” E

Table 3.2 The location of sampling site across the beaches of Vasco.

Sampling Station	Hollanth Beach		Japanese Beach	
	Latitude	Longitude	Latitude	Longitude
Station 1	15° 22’ 12” N	73° 51’ 43” E	15° 24’ 18” N	73° 47’ 12” E
Station 2	15° 22’ 30” N	73° 51’ 17” E	15° 24’ 8” N	73° 47’ 23” E
Station 3	15° 22’ 10” N	73° 51’ 32” E	15° 24’ 31” N	73° 47’ 41” E

3.4 Sedimentological Analysis

3.4.1 Grain Size

The size of the sediment particles changes depending on the hydrodynamics and the environment where the sediment deposits. The pipette method involving the setting velocity principle based on the Stoke’s law was used to determine the sand:silt:clay ratio **(Folk 1968).**

In this method, 10 g of oven dried sediment sub-sample was weighed and was transferred into a 1000 ml beaker. The distilled water was added to the beaker containing sediment and was left for overnight. On the next day, the water from the beaker was decanted using a decanting pipe without disturbing the sediment in the beaker. This was repeated for 4-5 times in order to remove the salinity of the sediment sample. After 5th day, the salinity was checked by adding $AgNO_3$, in the decanted water. Upon the removal of the salinity, 10 ml of 10% sodium hexametaphosphate was added to the sediment sample in order to dissociate the clay particles and it was left overnight. The next day, the sample was treated with 5 ml of 30% hydrogen peroxide solution to completely oxidize the organic matter and was left undisturbed for a day. On the next day, the treated sample was sieved through a 63micron (230 mesh size) sieve and the filter was collected in a 1000 ml measuring cylinder. The beaker was washed thoroughly until clear solution was attained. The sand particles retained on the sieve were washed with the distilled water and transferred into a pre-weighed clean 100 ml beaker. It was kept in the oven to dry at 60°C. The solution in the measuring cylinder was made up to 1000 ml using the distilled water and was homogenised for 2 minutes using a stirrer. The solution was allowed to settle and the stirring time was noted. The room temperature was noted with the help of a thermometer and the extraction time was calculated for size 8 using the Table 2.3.

Table 3.3 Time schedule to be used for the pipette analysis.

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

% Sand = (Weight of sand / Total weight of sediments) ×100.

X = (Weight of clay × 1000/25) – 1.

% Clay = (X / Total weight of sediment) ×100.

% Silt = 100 - (% of Sand + % of Clay).

3.5 Geochemical Analysis

3.5.1. Total Organic Carbon (TOC)

The estimation of TOC was carried out to understand the role of organic components of the sediment in transport, deposition and mobility of trace metals. The TOC was estimated using the Wallkey-Black (1974) method. The method involves exothermic heating using potassium dichromate (KCr_2O) and oxidation with the concentrated sulphuric acid (H:SO). The chromic acid was used to clean all the glassware. 0.5 g of powdered sediment sample was weighed and taken in a 500 ml conical flask. To it, 10 ml of 1 N standard potassium dichromate solution, and 20 ml of sulphuric acid and silver sulphate mixture was added. The conical flask was gently swirled and was allowed to stand for 30 minutes. Thereafter, 200 ml of the MilliQ water was added to it followed by 10 ml of 85% orthophosphoric acid and 0.2 g of sodium fluoride. The conical flask was gently swirled to thoroughly mix the reagents with the sediment sample. Also, few drops of diphenylamine indicator were added to the flask. The solution was treated against 0.5 N ferrous ammonium sulphate till an end point (one drop end point) was attained showing brilliant green. The addition of silver sulphate prevented the oxidation of chlorine ions. The standardization blank was performed using the same procedure without the sediment sample.

The percentage of TOC was calculated using the following formula:

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

Where,

S = Standardization blank titration, ml of ferrous solution

T = Sample titration, ml of ferrous solution

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

3.5.2. Total Metals Analysis

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

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

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

3.5.3. Metal Speciation

The quantification of species of metals is known as metal speciation. Ure et al. (1993) defined speciation as either as the process of identifying and quantifying the different defined species, forms or phases present in a material or the description of the amounts and the kinds of the species, forms or phases. The speciation determines the transport and biogeochemical cycling processes of a metal. It is useful in determining the concentration of a metal in different forms or species present in the sediment depending on the factors viz., temperature, salinity, pH, redox potential, etc. Therefore, metal speciation is very specific with respect to these factors and with respect to the storage of the treated samples. Tessier et al. (1979) proposed a 5-steps sequential extraction method that classifies metal associated with sediments as exchangeable. carbonate, iron-manganese oxide, organic matter/sulphide and residual fractions. Though, the method is time consuming, it gives precise detailed information about the origin, mode of occurrence, biological and physiochemical availability, mobilization and the transport of trace metals. A 5-steps sequential extraction procedure (Tessier et al. 1979) modified by Dessai and Nayak (2009) was adopted in the present study.

The 5-steps sequential extraction procedure was carried out as follows:

3.5.3.1. Exchangeable fraction (F1)

It is the most loosely bound or liable fraction of metals. The metals adsorbed on the sediment surface in the exchangeable form are highly mobile and can be desorbed by changes in the iconic composition of the sea water. The metals in the exchangeable fraction were extracted as follow: 1 g of the powdered sediment sample was weighed and taken in a centrifuge tube. 8 ml of 1 N $MgCl2$, adjusted to pH 7, was added to the sediment sample. The sediment sample solution was continuously agitated for 1 hour at room temperature. Thereafter, the sample was centrifuged at 8000 rpm for 10 minutes. The supernatant was then transferred into a 25 ml volumetric flask and the volume was made up to 25 ml using the MilliQ water. The sample was stored in a pre-cleaned polyethylene bottle. The sediment residue (1) was washed with the MilliQ water and was used for the next step.

3.5.3.2 Carbonate fraction (F2)

The metals are readily bound to the carbonate fraction in sediments and can be leached out by treating the sediment with sodium acetate at pH 5, 8 ml of 1 N sodium acetate adjusted to pH 5 was added to the residue I. The mixture was continuously agitated at room temperature for 5 hours. Thereafter, the mixture was centrifuged at 8000 rpm for 10 minutes. The supernatant was collected in a 25 ml volumetric flask and the volume was made up to 25 ml with the MilliQ water. It was then transferred into a pre-cleaned polyethylene bottle. The residue (II) was washed with the MilliQ water and was used for the next step.

3.5.3.3. Iron-Manganese oxide fraction (F3)

In the marine environment, the iron-manganese oxides are known as the scavengers of trace metals as they hold high amounts of trace metals such as Zn, Cu, Co, Ni, etc.

20 ml of 0.04 M hydroxylamine hydrochloride in 25% acetic acid was added to the residue II and the mixture was heated at 96 ±3°C in a water bath for 6 hours. The sample was gently swirled at regular intervals. Later, the sample was centrifuged at 8000 rpm for 10 minutes. The supernatant was collected in a 25 ml volumetric flask and the volume was made up to 25 ml using the MilliQ water. It was then transferred

into a pre-cleaned polyethylene bottle. The residue (III) was washed with the MilliQ water and was used for the next step.

3.5.3.4. Organic matter/ Sulphide fraction (F4)

This fraction includes the metals bound to organic matter and sulphides in sediments. The detritus has inert properties that hold the metals in this fraction.

3 ml of 0.02 M HNO, and 5 ml of 30% H:O: (adjusted to pH 2 with HNO3) was added to the residue III. The mixture was heated in a water bath at 85°C for 2 hours. Thereafter, additional 3 ml of 30% H:O; was added to it and was kept in a water bath at 85°C for 3 hours. Later, 5 ml of 3.2 M ammonium acetate in 20% HNOy was added to the mixture and was kept for agitation for 30 minutes. The mixture was then centrifuged at 8000 rpm for 10 minutes. The supernatant was collected in a 25 ml volumetric flask and the volume was made up to 25 ml with the MilliQ water. It was then transferred into a pre-cleaned polyethylene bottle. The residue (IV) was washed with the MilliQ water and was used for the next step.

3.5.3.5. Residual Fraction (F5)

The metals in the residual fraction are present in the lattice structure of the minerals in sediments and are considered to be a cohesive part of the sediment. The metals in this fraction are extracted by an intense acidic treatment. The residue IV was transferred into a pre-cleaned Teflon beaker. 10 ml of acid mixture of HF, HNO3 and HCIO, in the ratio 7:3:1 was added to the sample in a Teflon beaker and was dried on a hot plate at 150°C. After complete drying, additional 5 ml of the acid mixture was added and was kept for drying. Once the sample had dried completely, 2 ml of concentrated HCI was added to it and was dried on a hot plate. The dried sample was extracted with 10 ml of 1:1 HNO3:MilliQ water and was heated for few minutes. The digested sediment sample was then cooled and was transferred into a 25 ml volumetric flask. The volume was made up to 25 ml with the MilliQ water. It was then transferred into a pre-cleaned polyethylene bottle and stored for the chemical analysis.

The sediment fractions were analysed through the flame AAS to determine the concentration of metals viz., Fe, Mn, Zn, Cu, Co and Ni.

3.6 Pollution Indices

3.6.1 Geo-accumulation Index (I_{geo})

The geo-accumulation index (I_{geo}) was calculated according to the below given formula by **(Muller 1969).**

$$I_{geo} = \log_2 (C_n/1.5*B_n)$$

Where, C_n is the concentration of a metal in the sediment sample and B_n is the concentration of the metal under consideration of average shale value **(Turkian and Wedepohl 1961). Muller (1969)** proposed seven grades or classes for the I_{geo} along with the associated sediment quality which are presented in the table 3.3

Table 3.4 Classes with respect to sediment quality and pollution intensity **(Muller 1969).**

Pollution intensity	**Sediment accumulation**	**I_{geo} class**
Very strongly polluted	>5	6
Strongly to very strongly polluted	4-5	5
Strongly polluted	3-4	4
Moderately to strongly polluted	2-3	3
Moderately polluted	1-2	2
Unpolluted to moderately polluted	0-1	1
Practically unpolluted	<0	0

3.6.2 Contamination factor (CF)

The contamination of metal in the selected stations were calculated by computing CF

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

Where, C_{metal} is the metal content in the sediment and $C_{background}$ is the background value of that metal in the metal in reference sediment (average shale value **Turkian and Wedepohl 1961**). The CF is classified into four categories (Pekey et al. 2004); CF < 1 refers to low contamination; 1<CF<3, 3<CF<6, 6<CF, 1-3 refers to moderate contamination, considerable contamination, and very high contamination respectively.

3.6.3 Pollution load index (PLI)

The PLI is used for the determination of entire pollution level of a specific area. It is also explained as the assessment of overall sediment toxicity. The PLI was proposed by **Tomlinson et al. (1980)** and can be calculated using the following formula:

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

where CFn is the contamination factor of n^{th} metal, and n is the number of metals assessed.

The PLI value of > 1 suggests pollution, whereas PLI value < 1 indicates no pollution **(Harikumar et al. 2009)**.

The shale value was considered as the background value **(Turekian and Wedepohl 1961).**

4.1 Sedimentological Analysis

4.1.1 Grain size and TOC

The concentration of sand varied from 68.46 – 234.84 % in the surface sediments of the beaches of Vasco. (Table 4.1). The Clay showed the variations from 1.7 – 9.6 %, while silt was in the range of 0.97 – 15.6 %. The TOC varied from 0.02 – 1.03 % in the sediments of Vasco.

Table 4.1. Range of average of sand, silt, clay and TOC in sediments of Vasco Beaches.

Stations	Sand %	Clay %	Silt %	TOC %
B1	89.18	3.6	7.22	0.23
B2	94.5	7.2	1.7	0.59
B3	92.794	2.36	4.8	1.03
BM1	102.53	1.7	4.23	0.05
BM2	87.79	4.6	7.61	0.11
BM3	89.43	9.6	0.97	0.06
H1	68.46	8.5	2.04	0.02
H2	99.15	2.4	2.07	0.14
H3	89.82	9.4	0.78	0.2
J1	114.66	2.6	2.36	0.43
J2	234.84	3.5	15.6	0.46
J3	97.44	5.4	2.84	0.38
Range	68.46 -234.84	1.7 – 9.6	0.97 – 15.6	0.02 – 1.03
Average	105.049	5.071	4.351	0.308

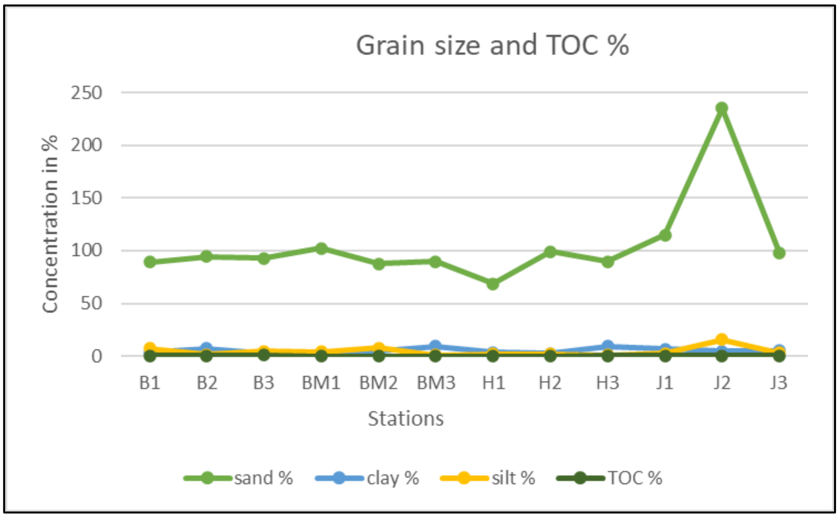

Fig 4.1. The grain size and TOC distribution in surface sediments of Vasco Beaches.

The concentration of sand was almost 100% in stations BM1, J1, and J2. In other stations it has decreased in few percent and the range varied from (99 – 80 %) in stations H2, J3, H3, B2, B3, BM3, B1, BM2, and in one station that is in H1, the sand % was less than 70 %. In most of the observations the sand was found to be medium to coarse in nature. This characteristic of the intertidal sediment can be attributed to the higher wave energy regime due to local topography that prevents sedimentation of fine-grained particles **(Bramha et al. 2014).** The sediments are mainly of fine to medium grained sand. The high energy of waves and tides facilitates the retention of the sand size particles **(Nasnodkar and Nayak 2015).** The % of Clay and Silt in all the stations was very low**.** The Total Organic Carbon content ranged from 0.02 – 1.03. the TOC was highest in B3. The variation of TOC were governed by the distribution of finer sediments hence the Total Organic Carbon in all the stations were mostly low.

4.2. Geochemical Analysis

4.2.1. Total Metal Analysis

The concentrations of total metals (Fe, Mn, Zn, Cu and Ni) in all the beaches of Vasco are presented in the (Table 4.2). The Fe concentration varied from (2.83 – 7.81 %) while Mn ranged from (253.97 – 716.42 ppm). The metals viz, Zn, Cu and Co ranged from (59.75 – 171.95), (122.27 – 228.57) and (6.45 – 14.35) ppm respectively.

Table 4.2. Range and average of total metals in sediments of Vasco Beaches.

Stations	**Fe (%)**	**Mn (ppm)**	**Zn (ppm)**	**Cu (ppm)**	**Co (ppm)**
B1	2.93	253.97	70.4	177.37	9.425
B2	3.20	285.87	59.75	156.12	7.3
B3	3.05	308.75	65.525	144.8	8.675
BM1	7.34	439.37	73.22	173.2	6.525
BM3	2.89	439.67	63.8	122.27	7.925
BM3	7.38	452.65	67.37	178.37	6.45
H1	4.8	317.27	70.85	158.47	11.2
H2	4.3	377.25	73.4	148.75	9.475
H3	6.40	515.1	73.25	145.97	7.275
J1	3.91	347.27	74.52	154.4	6.575
J2	7.81	716.42	112.15	228.57	8.7
J3	5.91	279	171.95	217.35	14.35
Range	2.83 – 7.81	253.97 – 716.42	59.75 – 171.95	122.27 – 228.57	6.45 – 14.35
Average	4.998	394.385	81.35	167.139	8.656
Average Shale Value ((Turekian And Wedepohl 1961).	4.72 %	850	95	45	19

The Fe concentration in the beaches was more than 2%, while Mn was above 250 ppm. Fe was greater than the shale value but Mn did not exceed the shale value limit. The enrichment of these metals showed their enrichment in the beach's indication their anthropogenic sources, but due to less concentrations in some stations it can be said that the contamination is in control. The several researchers have indicated open caste iron ore mining as the major contributor of Fe and Mn **(Dessai and Nayak 2009).**

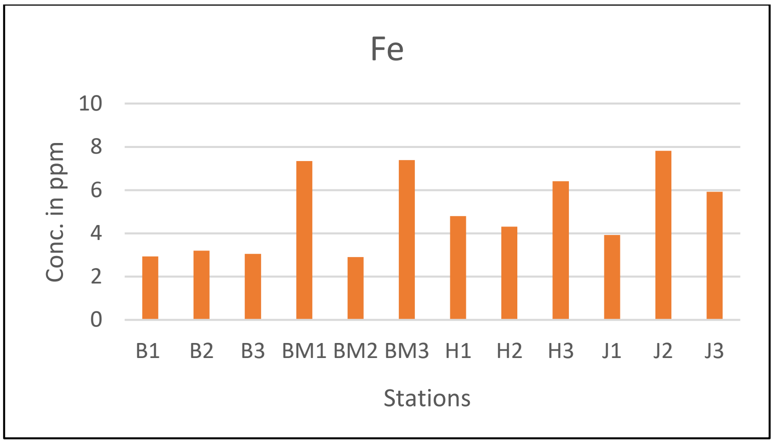

Fig 4.2. The concentration of Fe in the surface sediments of the Vasco beaches.

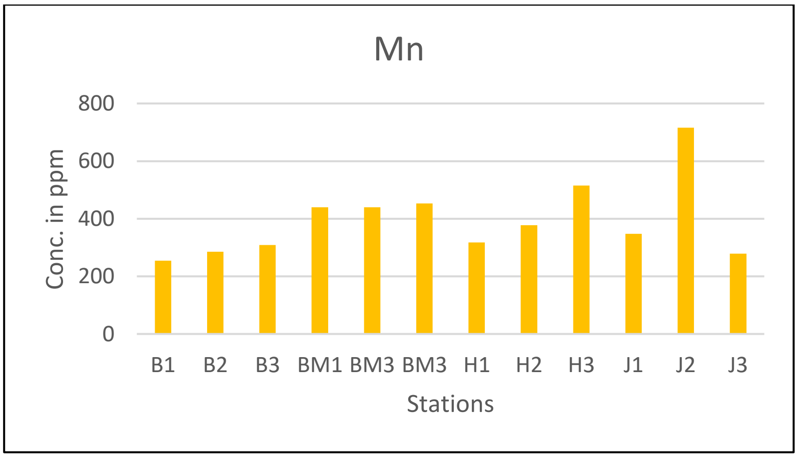

Fig 4.3. The concentration of Mn in the surface sediments in the Vasco Beaches.

The transportation of mining ore in an open system caused the spillage of ore into the water bodies which eventually travels through the high wave currents and comes into the beaches. Even the barges which usually go for fishing purposes act as a source of metallic waste.

Further increasing urbanisation and development in those stations have resulted in discharge of lot of domestic waste, these are additional anthropogenic sources of Fe and Mn. Fe in % and Mn in ppm was much high as compared to all the other metals in stations J1, J2 and J3 which is the entire stretch of Japanese Beach which might be the result of a huge dump yard which is just a few km away in the proximity to these stations, the seavage or the waste disposal is too high and has to be treated. It travels through the water into the beaches. The Mn was the highest (716.42 ppm) in J2 which was attributed to its adsorption onto the highly enriched finer sediments.

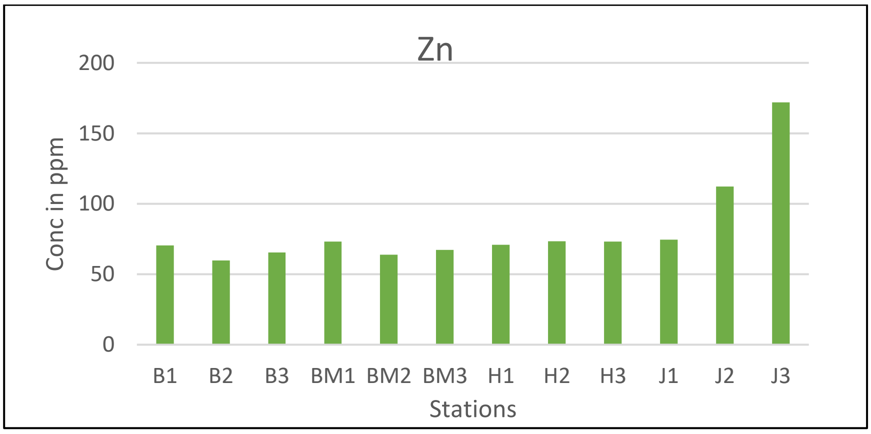

Fig 4.4. The concentration of Zn in the surface sediments in the Vasco Beaches.

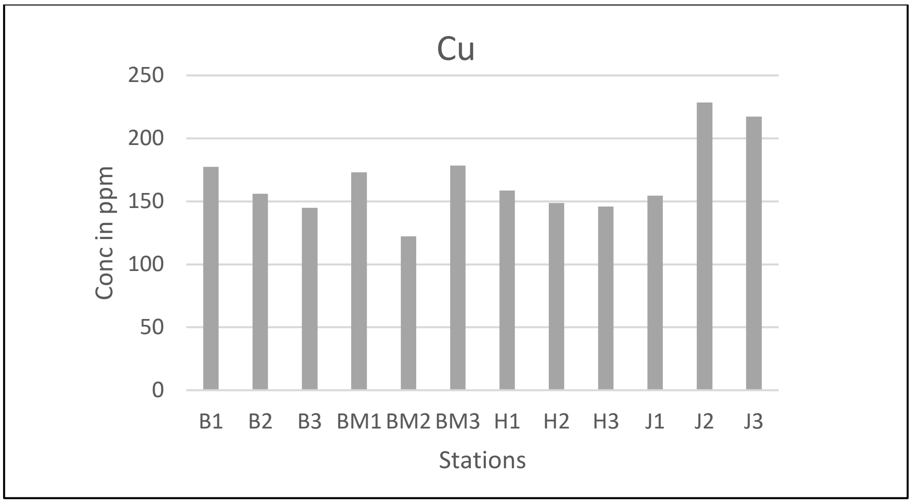

Fig 4.5. The concentration of Cu in the surface sediments in the Vasco Beaches.

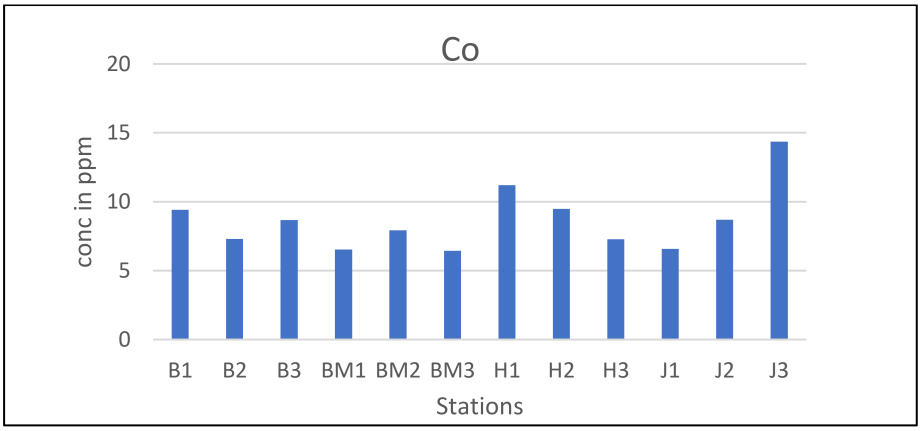

Fig 4.6. The concentration of Co in the surface sediments in the surface sediments of the Vasco Beaches.

The trace metals viz., Zn, Cu and Cu were more than their average shale value and therefore suggested their anthropogenic sources in the stations selected. The anthropogenic sources are mining of ore, domestic, agricultural waste, tourism, barges, urbanization and fishery activities **(Noronha-D’Mello and Nayak 2016; Gardade and Khandeparker 2017).** Among the above metals Cu and Zn was highly abundant in the sediments of the beaches that were collected with the concentrations above (100-200 ppm). Copper and Zinc is not typically found in significant quantities on beaches naturally, however there are a few potential sources. As mentioned earlier Marine pollution that is pollution due to industrial discharge, urban runoff and agricultural runoff can find their way into coastal waters and ultimately deposit on beaches. Other than this, shipwrecks or discarded metal objects or debris that washes ashore may corrode over time releasing copper into the surroundings. Zn is commonly used in antifouling paints applied to the hulls to prevent the growth of marine organisms, over time as these ships sail, some of the paint may wear off and releases Zn into the water which could potentially end up on beaches near shipping routes.

4.2.2. Speciation of Metals

The range and the average concentration of different geochemical forms of metals (Fe, Mn, Zn, Cu and Co) in the sediments of the Beaches of Vasco is presented in Table and Fig

Table 4.3**.** Range and average of metals in different sediment fraction in the beaches of Vasco.

Metal Stations	**Exchangeable (%)**	**Carbonate (%)**	**Fe-Mn (%)**	**Organic/Sulphide (%)**	**Residual (%)**
B1- Fe	1.935	2.307	20.997	2.359	72.400
B2- Fe	3.066	3.740	22.691	3.911	66.590
B3- Fe	2.824	3.485	19.666	3.577	70.446
BM1- Fe	1.727	2.057	11.045	2.189	82.979
BM2- Fe	2.750	2.968	11.929	3.168	79.183
BM3- Fe	2.097	2.335	9.176	2.518	83.872
H1- Fe	1.759	1.845	6.725	1.955	87.713
H2- Fe	1.923	1.953	7.915	1.971	86.236
H3- Fe	1.934	1.896	8.634	1.259	86.274
J1- Fe	1.648	1.808	5.486	1.838	89.217
J2- Fe	1.614	1.761	5.239	1.911	89.472
J3- Fe	1.896	1.983	7.208	2.125	86.785
Metal Stations	**Exchangeable (%)**	**Carbonate (%)**	**Fe-Mn (%)**	**Organic/Sulphide (%)**	**Residual (%)**
B1- Mn	0.478	27.725	4.479	5.583	61.732
B2- Mn	2.812	33.045	4.132	6.164	53.845
B3-Mn	2.351	20.362	3.857	6.995	66.433
BM1- Mn	1.410	12.105	3.662	8.747	74.073
BM2- Mn	1.790	36.992	2.145	6.178	52.893
BM3- Mn	1.626	23.757	1.810	7.031	65.774
H1- Mn	1.829	25.368	1.476	6.177	65.147
H2- Mn	1.220	12.535	0.944	2.637	82.662
H3- Mn	0.836	11.743	0.704	2.670	84.044
J1- Mn	0.962	11.977	0.872	3.087	83.100
J2- Mn	0.463	4.679	0.339	1.793	92.723
J3- Mn	0.257	0.535	0.300	2.392	96.514
Metal Station	**Exchangeable (%)**	**Carbonate (%)**	**Fe-Mn (%)**	**Organic/Sulphide (%)**	**Residual (%)**
B1- Cu	68.278	6.775	8.315	8.315	8.315
B2- Cu	70.112	4.607	10.848	10.848	3.583
B3- Cu	33.883	5.547	25.637	25.637	9.295
BM1- Cu	12.798	13.333	29.099	29.099	15.669

BM2- Cu	8.283	11.464	30.389	30.389	19.473
BM3- Cu	17.205	6.301	29.369	29.369	17.753
H1- Cu	4.325	16.426	33.676	33.676	11.894
H2- Cu	15.181	13.110	29.672	29.672	12.363
H3- Cu	9.367	15.801	33.690	33.690	7.449
J1- Cu	11.899	15.483	15.483	33.400	23.732
J2- Cu	18.653	16.486	16.486	38.544	9.829
J3- Cu	5.606	14.993	14.993	46.153	18.252
Metal Stations	**Exchangeable (%)**	**Carbonate (%)**	**Fe-Mn (%)**	**Organic/Sulphide (%)**	**Residual (%)**
B1- Zn	11.760	8.809	22.968	15.964	40.496
B2- Zn	7.593	10.713	25.592	19.090	37.009
B3- Zn	8.912	10.906	20.356	18.468	41.357
BM1- Zn	5.830	8.294	21.340	16.940	47.593
BM2- Zn	6.306	7.945	28.285	17.256	40.458
BM3- Zn	5.683	6.164	23.199	17.565	47.385
H1- Zn	5.801	8.614	19.378	16.021	50.184
H2- Zn	5.391	8.327	21.296	15.034	49.950
H3- Zn	4.918	6.539	21.367	15.683	51.490
J1- Zn	5.605	7.565	19.986	12.579	54.262
J2- Zn	4.251	4.897	11.715	9.658	69.477
J3- Zn	0.638	0.813	2.441	1.457	94.648
Metal Stations	**Exchangeable (%)**	**Carbonate (%)**	**Fe-Mn (%)**	**Organic/Sulphide (%)**	**Residual (%)**
B1- Co	12.002	1.249	25.123	21.150	40.473
B2- Co	10.194	1.873	23.892	29.589	34.449
B3- Co	12.577	1.725	17.883	26.954	40.859
BM1- Co	1.799	1.968	15.113	32.908	48.210
BM2- Co	1.688	1.295	19.832	30.266	46.917
BM3- Co	1.889	1.682	17.944	24.864	53.618
H1- Co	3.584	1.891	12.559	7.703	74.260
H2- Co	3.443	2.071	13.501	4.885	76.099
H3- Co	2.782	2.347	8.539	4.995	81.334
J1- Co	1.624	1.219	12.979	25.743	58.432
J2- Co	1.950	1.419	14.212	28.666	53.750
J3- Co	1.886	1.062	8.554	14.730	73.766

In the sediments of the Vasco beaches, Fe was abundant and was more than 50% in the residual fraction. (Table 4.3) Among the bioavailable fractions, the concentration of Fe was more than 10% in the Fe-Mn oxide fraction at stations B1, B2, B3, BM1 and BM2. It was less than 10% in the Organic/Sulphide fractions in all the stations. The Mn was more than 50% in the residual fraction in all the stations, whereas it was more than 10% in the Carbonate fraction in all the stations except in J2 and J3. The exchangeable fraction and Fe-Mn was very less that is >5% for Mn in all the stations while the Organic/Sulphide fractions had concentrations of more than 5% but less than 10%. Cu was more than 50% in B1 and B2, while in the other six stations that is in B3, BM1, BM3, H2, J1 and J2 the concentration % was less than 50 but more than 10 and remaining stations that is in BM2, H1, H3 and J3 the % of Cu was >10 %. The concentration of Zn was in considerable amount that is >10% in all the stations of the Vasco beaches except in the first station that is in B1, here in this this station the % was slightly high in concentration. In the carbonate fraction the concentration of Zn was less than 10% in stations B1, BM, BM2, BM3, H1, H2, H3, J1, J2 and J3, while it was 10% in B2 and B3. In the Fe-Mn fraction the concentration was more than 10% in all the stations except the last station that is in J3. The residual fraction was the highest among all the fractions for Zn, it was more than 50% in 5 stations that is in H1, J1, J2 and very high in J3 that 94%, rest of the station it was >50% but more than 10%. Cobalt was highest and was above 40% in the residual fraction in stations B1, B3, BM1, BM2, BM3, H1, H2, H3, J1, J2 and J3 except B2, in B2 the concentration % was slightly lower than the other stations. The Co concentration was more than 10% in Fe-Mn oxides in B1, B2, B3, BM1, BM2, BM3, H1, H2, J1 and J2 except J3, in J3 it was less than 10%. In carbonate fraction we can see a decrease in the % concentration where it was less than 10% in all the stations studied. In exchangeable fraction we can see the Co concentration to be higher than 10% in the first 3 stations which is in one Beach, the beach was Baina where high % of exchangeable fraction was observed. In rest of the stations was in a very considerable amount that is less than 10%. In Organic/Sulphide fraction the concentration was observed to be more than 10% in most of the stations except three stations that is in H1, H2 and H3.

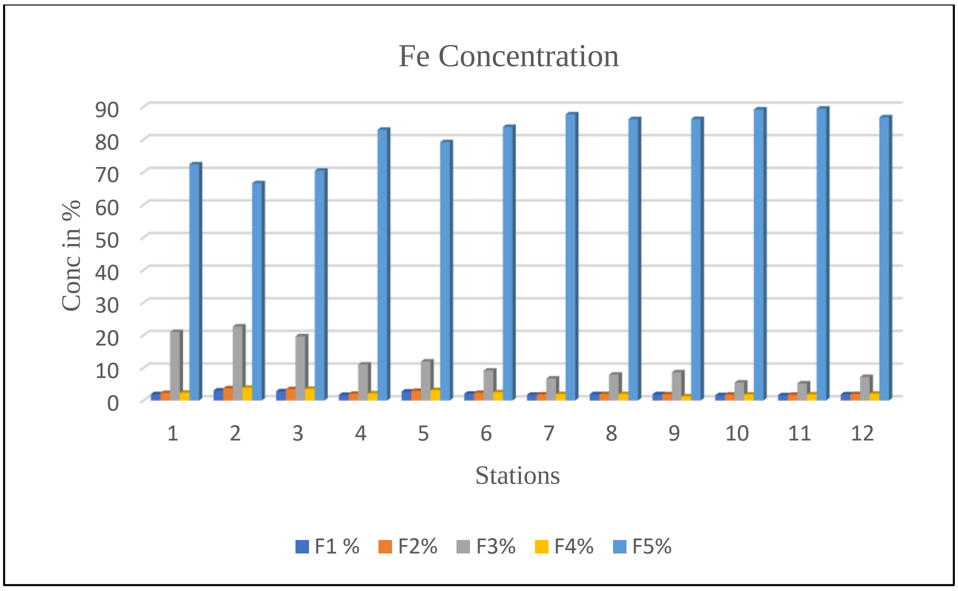

Fig 4.7. Concentration of Fe in different Fractions.

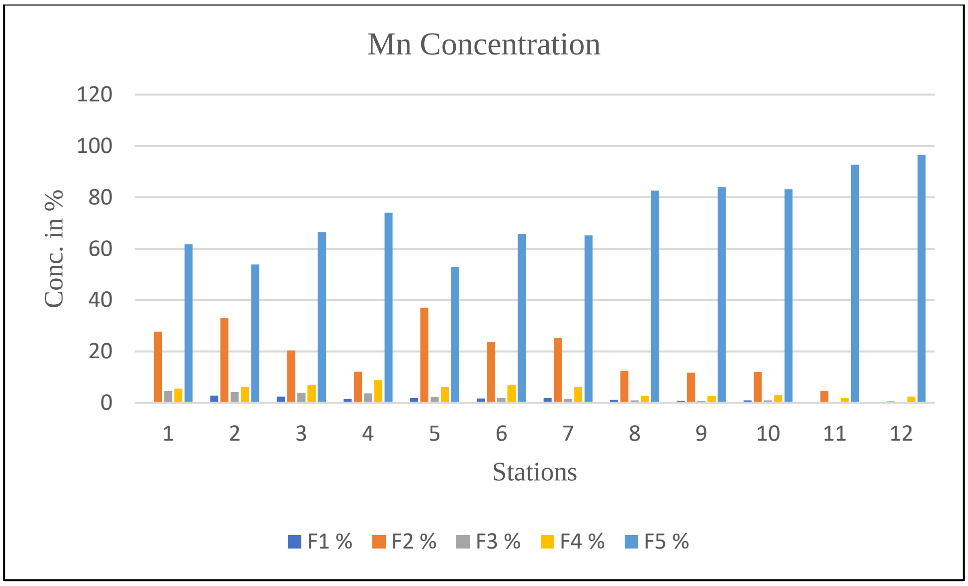

Fig 4.8. Concentration of Mn in different Fractions.

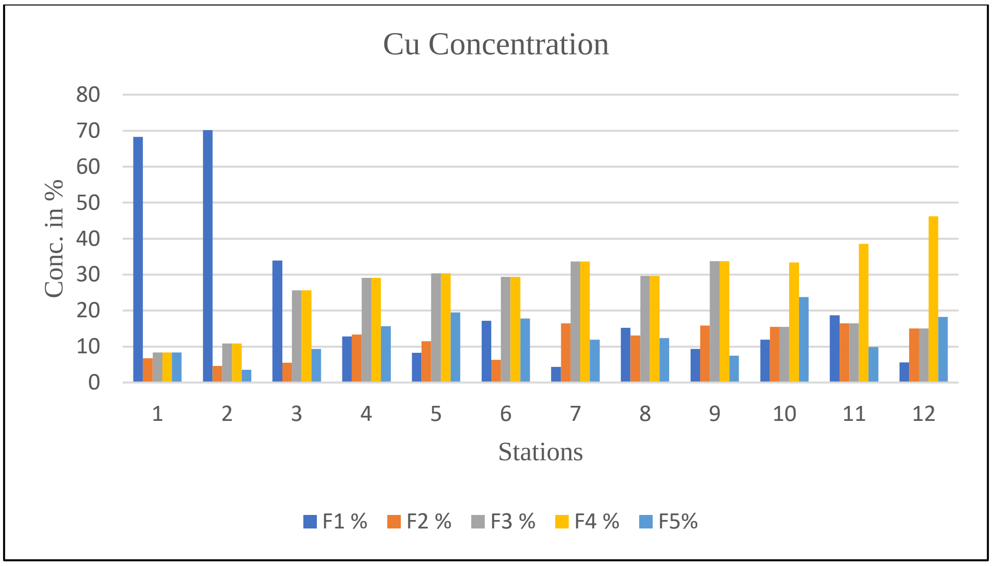

Fig 4.9. Concentration of Cu in different Fractions.

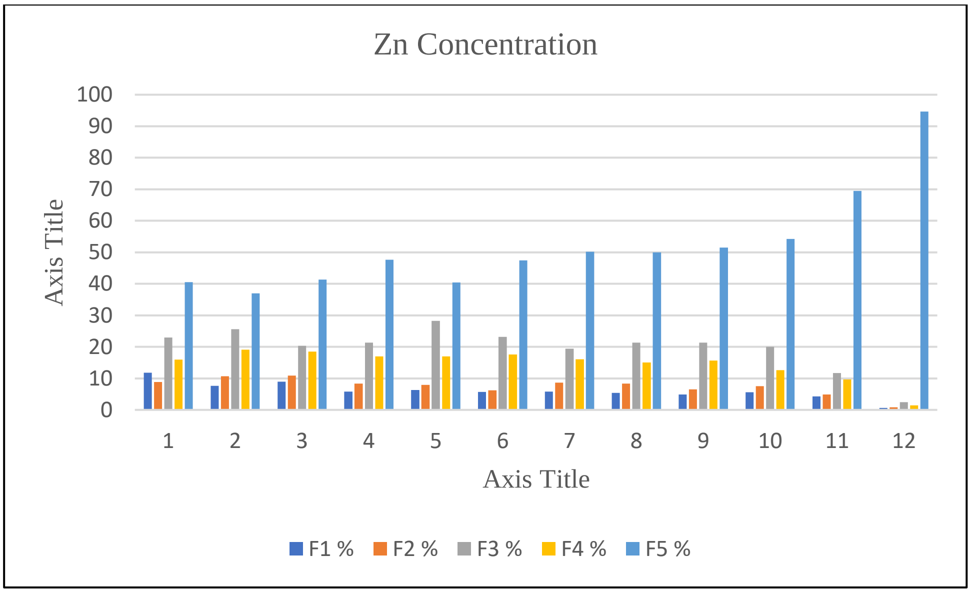

Fig 4.10. Concentration of Zn in different Frcations.

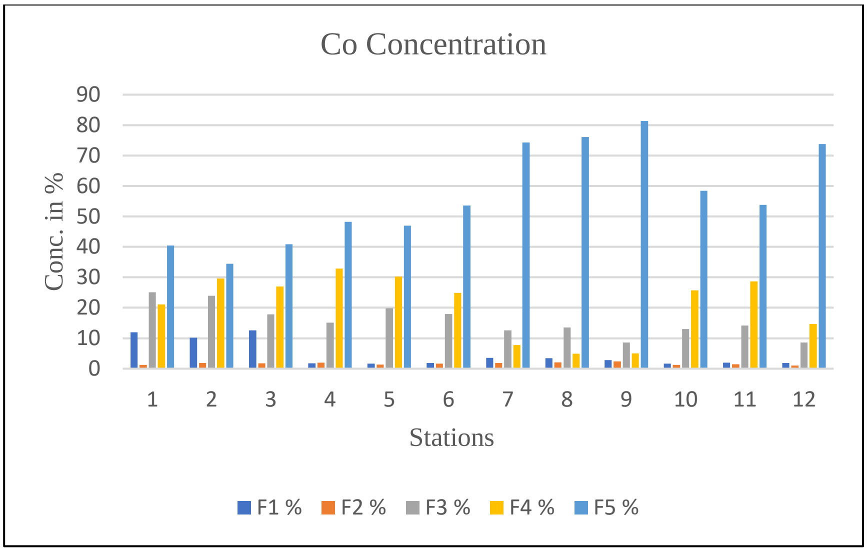

Fig 4.11. Concentration of Co in different Frcations.

The speciation of metals in the sediments of the Beaches of Vasco revealed significant that is high as well as considerable that is (>10%) concentration of Fe in all the stations. The residual fraction in Mn, Zn and Co was highest in all the stations that is in B1, B2, B3 BM1, BM2, BM3, H1, H2, H3, J1, J2 and J3, whereas the concentration % of Cu was high in BM1, BM2, BM3, H1, H2, J2 and J3 and low that is (>10%) in B1, B2, B3, H3 and J2. The residual fraction is also referred as environmentally unreactive, inert or immobile fraction in sediments **(Ratuzny et al. 2009).** The metals in this fraction are of natural origin and are derived from the weathering of the rocks from the catchment area **(Kanetkar et al. 2022).** The metals are strongly held in the lattice structure of minerals in sediments and are not involved in geochemical and biological processes **(Zimmerman Amanda et al. 2010).** Among the bioavailable fraction, the metals were mainly associated with the Fe-Mn oxide fraction. The Fe and Mn are redox sensitive element and are effective scavengers of trace metals in the marine environments **(Venkatramanan et al. 2014).** The trace metals get readily adsorbed on the surface of the precipitated Fe-Mn oxides/hydroxides and are removed from the water column. Thus, metals are generally associated with Fe – Mn oxides in sediments. Adding to it, metals were also associated in considerable that is (>10 %) proportion in one or more other bioavailable fractions like in exchangeable, carbonate and organic/sulphide bound fractions. The metals in the bioavailable fractions are mainly derived from the anthropogenic sources and are loosely bound (adsorbed) on the surface of the sediment particles **(Nasnodkar et al. 2021).** Therefore, the metals in the bioavailable fractions indicated their bioavailability to sediment associated biota. The bioavailable metals are weakly bound and can be mobilised from sediment to water column as they are highly susceptible to change in physico – chemical properties of the water **(Cruz et al. 2020).** The variations in the Ph, Eh, salinity, ionic composition, organic matter, etc., are frequent in the dynamic marine ecosystem. A slight variation in these properties of the water column can trigger the desorption of the metals from the sediments to water from the bioavailable fractions in the Beaches of Vasco.

4.3. Metal Pollution Indices.

4.3.1. Geo-accumulation Index.

The I_{geo} was determined to understand the pollution status of metals in the sediments of Vasco beaches.

Table 4.3 a Geo – accumulation index (I_{geo}) considering shale values as background value.

Stations	Igeo				
	Fe	**Mn**	**Cu**	**Co**	**Zn**
B1	1.272	2.327	1.393	-1.596	-1.017
B2	1.143	2.157	1.209	-1.964	-1.253
B3	1.212	-0.199	1.101	2.345	-1.120
BM1	0.052	-0.610	1.359	2.603	-0.960
BM2	1.288	-1.329	0.857	2.101	-1.159
BM3	0.061	0.626	1.401	2.645	-1.080
H1	0.561	1.830	1.231	2.475	-1.008
H2	0.717	-2.072	1.139	2.383	-0.957
H3	0.144	-1.307	1.112	-1.969	-0.960
J1	1.852	1.876	1.193	2.115	0.935
J2	2.142	0.831	1.759	1.711	0.345
J3	1.259	2.192	1.687	0.989	0.271

The Fe at stations B1, B2, B3, BM2, J1 and J3 was moderately polluted in the sediments while the stations BM1, BM3, H1, H2 and H3 felt under the category of unpolluted to moderately polluted. Among all the stations the Fe concentration was the most in J2 categorized as moderately to strongly polluted, this might be because there is a dump yard next to this beach from where lot of untreated sewage might enter the water column. Mn in the sediments strongly polluted to unpolluted in the beaches of Vasco. Zn was not strongly polluted hence it came in the category of unpolluted. The pollution intensity of Cu varied from moderately polluted to unpolluted and Co in some station showed least pollution while in some stations it was strongly polluted.

The sediments of the Vasco beaches are unpolluted to strongly polluted. The reason being the anthropogenic input.

4.3.2. Contamination Factor

Table 4.4 b The Contamination Factor (CF) and the Pollution Load Index (PLI).

Stations	**CF**					
	Fe	**Mn**	**Cu**	**Co**	**Zn**	**PLI**
B1	0.620	0.073	3.941	0.496	0.741	0.128
B2	0.679	0.000799	3.469	0.384	0.628	0.106
B3	0.647	0.000762	3.217	7.621	0.689	0.45
BM1	1.555	0.00183	3.848	9.115	0.770	4.38
BM2	0.613	0.000722	2.717	6.435	0.671	0.36
BM3	1.565	0.001841	3.963	9.388	0.709	1.378
H1	1.016	0.001196	3.521	8.340	0.745	2.58
H2	0.912	0.001073	3.305	7.828	0.772	2.21
H3	1.357	0.001597	3.243	0.382	0.771	0.228
J1	0.830	0.000977	3.431	0.346	0.784	0.137
J2	1.656	0.001948	5.079	0.457	1.180	0.47
J3	1.253	0.001474	4.83	0.755	1.81	0.552

According to CF, Cu was strongly polluted in most of the stations and it was the highest in J2, reason is because of the dump yard which is situated next to the beach, all the waste travels through the water making the beach polluted. The Fe concentrations were comparatively low in B1, B2, B3, BM2, H2 and J1 categorized under least polluted, while in stations BM1, BM3, H1, H3, J2 and J3 it showed moderately polluted. Mn concentrations in all the stations were very low indicating that it was very least polluted. Zn was also very least polluted in most of the stations but it was moderately polluted in J2 and J3. Cu on the other hand was very strongly polluted in B3, BM1, BM2, BM3, H1 and H2 the concentration was more then 5. Thus, the computation of CF revealed unpolluted to moderate to strongly polluted or very high contamination of metals in the beaches of Vasco attributing to human –

induced activities. The pollution of the metals (Fe, Mn, Zn, Cu and Co) was alsp supported by PLI that is Pollution Load Index.

The present study was conducted in the coastal region of Goa. Vasco da Gama often shortened to Vasco, is a city in the state of Goa on the west coast of India. The city lies on the western tip of the Mormugao peninsula, at the mouth of the Zuari River, about 30 kilometres (19 mi) from Panaji, Goa's capital, 28 kilometres (17 mi) from Margao, the district headquarters and about 5 kilometres (3.1 mi) from Dabolim Airport. The study is conducted on 4 major beaches of Vasco. Viz,. Baina beach, Bhogmalo beach, Hollanth beach and Japanese beach also locally called as Japanese Garden. The objective of the study was to understand the distribution of trace metals and to check the metal contamination levels in the beaches. The main motive to select these stations was because no study had been done in these areas and as a local resident it made me keen to know about the pollution and the toxicity levels the beaches hold.

Four major beaches were selected and from each beach 3 samples were taken one from extreme right of the beach one from exactly middle and one from extreme left so that equal distribution can be studied. The samples were analysed for four different parameters that to check the Total Organic Carbon, Grain Size, Total Metals and Speciation of metals in each fraction. The samples collected were taken to the laboratory in an ice box and performed to check the concentrations for each metal (Fe, Mn, Zn, Cu and Co). The final concentrations were analysed using the Atomic Absorption Spectrophotometer (AAS). Since these locations are thought of as sandy beaches, the investigation found that there was a significant percentage of sand in each one. On the other hand, lower levels of the proportion of silt and clay were reported. Since finer sediments have a larger surface area by volume ratio than coarser sediments, the distribution of finer sediments determined the TOC. Regarding the total metal concentrations, it is noted that Fe and Mn concentrations are high in the majority of the stations. This is mostly due to open-pit mining activity in Goa. A role is also played by other anthropogenic activities, such as urbanization, tourism, and the release of raw sewage. The paint coatings used on recreational boats and fishing trawlers contain components of Zn and Cu which was also reported in minimal amount in some of the stations. The pollution indices computed for the metals (Fe, Mn, Zn, Cu, Co) revealed various levels of contamination. The Geo-accumulation index (Igeo) indicated unpolluted to moderately polluted contamination, while Contamination Factor (CF) showed low, moderate, considerable and severe contamination levels. The Pollution Load Index (PLI) for stations (B1, B2, B3, BM2, H3, J1, J2 and J3) showed no metal contamination in sediments, however for stations (BM1, BM3, H1, H2) indicated polluted metal sediments.

1. Abdel Ghani, S. A. (2015). Trace metals in seawater, sediments and some fish species from Marsa Matrouh Beaches in north-western Mediterranean coast, Egypt. Egyptian Journal of Aquatic Research, 41(2), 145–154. https://doi.org/10.1016/j.ejar.2015.02.006
2. Alagarsamy, R. (2006, March). 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. https://doi.org/10.1016/j.ecss.2005.11.023
3. Alagarsamy, R., & Zhang, J. (2009, March 18). Geochemical characterisation of major and trace elements in the coastal sediments of India. *Environmental Monitoring and Assessment*, *161*(1–4), 161–176. https://doi.org/10.1007/s10661-008-0735-2
4. Antizar-Ladislao, B., Mondal, P., Mitra, S., & Sarkar, S. K. (2015, December). Assessment of trace metal contamination level and toxicity in sediments from coastal regions of West Bengal, eastern part of India. *Marine Pollution Bulletin*, *101*(2), 886–894. https://doi.org/10.1016/j.marpolbul.2015.11.014
5. Badr, N. B. E., El-Fiky, A. A., Mostafa, A. R., & Al-Mur, B. A. (2008, August 12). Metal pollution records in core sediments of some Red Sea coastal areas, 58 Kingdom of Saudi Arabia. Environmental Monitoring and Assessment, 155(1–4), 509–526. https://doi.org/10.1007/s10661-008-0452-x
6. Ben Amor, R., Yahyaoui, A., Abidi, M., Chouba, L., & Gueddari, M. (2019, April 15). Bioavailability and Assessment of Metal Contamination in Surface Sediments of Rades-Hamam Lif Coast, around Meliane River (Gulf of

Tunis,Tunisia, Mediterranean Sea). Journal of Chemistry, 2019, 1–11. https://doi.org/10.1155/2019/4284987

7. Bhatkhande, A. D., & Nasnodkar, M. R. (2022). Metal enrichment in sediments and bioaccumulation in edible bivalve saccostrea cucullata from mudflats of a tropical estuary, India: A study to investigate toxicity and consumption suitability. *Environmental Science and Pollution Research*, *29*(39), 59885–59902. https://doi.org/10.1007/s11356-022-19999-x

8. Bhutia, T., Nasnodkar, M. R., & Nayak, G. N. (2023, May 25). Speciation of metals in sediments and their bioaccumulation by edible bivalves (Cassosstrea spp. and Polymesoda spp.) in the aquatic bodies of Goa, west coast of India. *Arabian Journal of Geosciences*, *16*(6). https://doi.org/10.1007/s12517-023-11488-w

9. Bhuyan, M. S., Haider, S. M. B., Meraj, G., Bakar, M. A., Islam, M. T., Kunda, M., Siddique, M. A. B., Ali, M. M., Mustary, S., Mojumder, I. A., & Bhat, M. A. (2023, July 7). Assessment of Heavy Metal Contamination in Beach Sediments of Eastern St. Martin's Island, Bangladesh: Implications for Environmental and Human Health Risks. Water, 15(13), 2494. https://doi.org/10.3390/w15132494

10. Bramha, S. N., Mohanty, A. K., Satpathy, K. K., Kanagasabapathy, K. V., Panigrahi, S., Samantara, M. K., & Prasad, M. V. R. (2014, May 30). 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*(11), 4463–4472. https://doi.org/10.1007/s12665-014-3346-y

11. Carman CMI, Xiang Dong L, Gan Z, Onyx Wai WH, Sheung Y (2007) Trace metal distribution in sediments of the Pearl River Estuary and the surrounding coastal area, South China. J Environ Pollut 147:311–323
12. Chatterjee, M., Massolo, S., Sarkar, S. K., Bhattacharya, A. K., Bhattacharya, B. D., Satpathy, K. K., & Saha, S. (2008, May 7). An assessment of trace element contamination in intertidal sediment cores of Sunderban mangrove wetland, India for evaluating sediment quality guidelines. Environmental Monitoring and Assessment, 150(1–4). https://doi.org/10.1007/s10661-008-0232-7
13. Dessai, D. V. G., & Nayak, G. N. (2008, October 23). Distribution and speciation of selected metals in surface sediments, from the tropical Zuari estuary, central west coast of India. Environmental Monitoring and Assessment, 158(1–4), 117–137. https://doi.org/10.1007/s10661-008-0575-
14. Fernandes, L. L., & Nayak, G. (2014, February). Characterizing metal levels and their speciation in intertidal sediments along Mumbai coast, India. Marine Pollution Bulletin, 79(1–2), 371–378. https://doi.org/10.1016/j.marpolbul.2013.11.013
15. Fernandes, L., Nayak, G., Ilangovan, D., & Borole, D. (2011, February). Accumulation of sediment, organic matter and trace metals with space and time, in a creek along Mumbai coast, India. Estuarine, Coastal and Shelf Science, 91(3), 388–399. https://doi.org/10.1016/j.ecss.2010.11.002 60
16. Fernandes, M. C., & Nayak, G. N. (2015, December 10). Role of sediment size in the distribution and abundance of metals in a tropical (Sharavati) estuary, west coast of India. Arabian Journal of Geosciences, 9(1). https://doi.org/10.1007/s12517-015-2127-6

17. Folk RL (1974) Petrology of sedimentary rocks. Hemphill, Austin, Texas.
18. 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(41), 57872–57887. https://doi.org/10.1007/s11356-021-14610-1
19. Gaudette HE, Flight WR, Toner L (1974) An inexpensive titration method for the determination of organic carbon in recent sediment. J Sediment Petrol 44(1):249–253
20. Gomez Parra A, Forja JM, Del Valls TA, Saenz I, Riba I (2000) Early contamination by heavy metals of the Guadalquivir estuary after the Aznalco´llar mining Spill (SW Spain). Mar Pollut Bull 40:1115–1123
21. Gopal, V., Krishnamurthy, R. R., Vignesh, R., Sabari Nathan, C., Anshu, R., Kalaivanan, R., Mohana, P., Magesh, N. S., Manikanda Bharath, K., Ekoa Bessa, A. Z., Abdelrahman, K., & Abioui, M. (2023, December). Assessment of heavy metal contamination in the surface sediments of the Vedaranyam coast, Southern India. *Regional Studies in Marine Science, 65,* 103081.https://doi.org/10.1016/j.rsma.2023.103081
22. Huh CA, Finney BP, Stull JK (1992) Anthropogenic inputs of several heavy metals to near shore basins off Los Angeles. Prog Oceanogr 30:335–35
23. Jain, C., & Sharma, M. (2001, November). Distribution of trace metals in the Hindon River system, India. Journal of Hydrology, 253(1–4), 81–90. https://doi.org/10.1016/s0022-1694(01)00484-x

24. Jarvis IJ, Jarvis K(1985). Rare earth element geochemistry of standard s sediments: a study using inductively coupled plasma spectromrtry. Chemica Geology 53:335 – 253.
25. Karlonienė, D., Pupienis, D., Jarmalavičius, D., Dubikaltinienė, A., & Žilinskas, G. (2021, January 25). The Impact of Coastal Geodynamic Processes on the Distribution of Trace Metal Content in Sandy Beach Sediments, South-Eastern Baltic Sea Coast (Lithuania). Applied Sciences, 11(3), 1106. https://doi.org/10.3390/app11031106
26. Krishnakumar, P., Lakshumanan, C., Jonathan, M. P., Sundararajan, M., & Navarrete-Lopez, M. (2013, May 11). Trace metal in beach sediments of Velanganni Coast, South India: application of autoclave leach method. *Arabian Journal of Geosciences*, *7*(7), 2655–2665. https://doi.org/10.1007/s12517-013-0956-8
27. Kumar, S. B., Padhi, R., Mohanty, A., & Satpathy, K. (2017, January). Elemental distribution and trace metal contamination in the surface sediment of south east coast of India. *Marine Pollution Bulletin*, *114*(2), 1164–1170. https://doi.org/10.1016/j.marpolbul.2016.10.038
28. Lameed, G. (2011, September). Environmental sensitivity mapping of the coastal areas in the south-western zone of Nigeria: anthropogenic influences on fauna. Biodiversity, 12(3), 165 180. https://doi.org/10.1080/14888386.2011.605345
29. Largeau, C., & De Leeuw, J. (1995, October). Sedimentary organic matter: Organic facies and palynofacies. Organic Geochemistry, 23(10), 995–996. https://doi.org/10.1016/0146-6380(95)90073-x

30. Liu, W. H., Zhao, J. Z., Ouyang, Z. Y., Söderlund, L., & Liu, G. H. (2005, August). Impacts of sewage irrigation on heavy metal distribution and contamination in Beijing, China. *Environment International*, *31*(6), 805–812. https://doi.org/10.1016/j.envint.2005.05.042
31. Lopez, G. R. (1983, March). The Ecology of Marine Sediments. An Introduction to the Structure and Function of Benthic Communities.John S. Gray. The Quarterly Review of Biology, 58(1), 107–107. https://doi.org/10.1086/413143
32. Loveson, V. J., Gujar, A. R., Iyer, S. D., Udayaganesan, P., Luis, R. A. A., Gaonkar, S. S., Chithrabhanu, P., Tirodkar, G. M., & Singhvi, A. K. (2014, April 24). Beach dynamics and oscillations of shoreline position in recent years at Miramar Beach, Goa, India: a study from a GPR survey. Natural Hazards, 73(3), 2089–2106. https://doi.org/10.1007/s11069-014-1175-7
33. Manaf LA, Samah MAA, Zukki NIM (2009) Municipal solid waste management in Malaysia; practices and challenges. Waste Manage 29:2902–2906 Martin CW (2000) Heavy me
34. Mikulic, N., Orescanin, V., Elez, L., Pavicic, L., Pezelj, D., Lovrencic, I., & Lulic, S. (2007, April 26). Distribution of trace elements in the coastal sea sediments of Maslinica Bay, Croatia. Environmental Geology, 53(7), 1413–1419. https://doi.org/10.1007/s00254-007-0750-6
35. Nagarajan, R., Jonathan, M., Roy, P. D., Wai-Hwa, L., Prasanna, M., Sarkar, S., & Navarrete-López, M. (2013, August). Metal concentrations in sediments from tourist beaches of Miri City, Sarawak, Malaysia (Borneo Island). Marine Pollution Bulletin, 73(1), 369–373. https://doi.org/10.1016/j.marpolbul.2013.05.036

36. Nasnodkar, M. R., & Nayak, G. N. (2015, March 25). Processes and factors regulating the distribution of metals in mudflat sedimentary environment within tropical estuaries, India. Arabian Journal of Geosciences, 8(11), 9389–9405.https://doi.org/10.1007/s12517-015-1823-6

37. Parvez Al-Usmani, S., Jagtap, T., & Patil, D. (2015, October). Trace metals in water, sediment and bivalves of a tropical estuary, west coast of India. *Marine Pollution Bulletin*, *99*(1–2), 328–331. https://doi.org/10.1016/j.marpolbul.2015.07.036

38. Pekey, H., Karakaş, D., Ayberk, S., Tolun, L., & Bakoğlu, M. (2004, May). Ecological risk assessment using trace elements from surface sediments of İzmit Bay (Northeastern Marmara Sea) Turkey. Marine Pollution Bulletin, 48(9–10), 946–953. https://doi.org/10.1016/j.marpolbul.2003.11.023

39. Raj, S. M., & Jayaprakash, M. (2007, December 15). Distribution and enrichment of trace metals in marine sediments of Bay of Bengal, off Ennore, south-east coast of India. *Environmental Geology*, *56*(1), 207–217. https://doi.org/10.1007/s00254-007-1156-1

40. Ramkumar, M., Nagarajan, R., Athira, P., Sharma, A., Gopika, P., Fathima, A., Sugavanam, G., Manobalaji, A., & Mohanraj, R. (2024, February). Assessment of heavy metal contamination of sediments in popular tourist beaches of the Kerala State, southern India: Implications on textural and mineralogical affinities and mitigation. *Geosystems and Geoenvironment*, *3*(1), 100244. https://doi.org/10.1016/j.geogeo.2023.100244

41. Sadanandan, H., Dharmalingam, S. N., Sridharan, M., Agarwal, N., & Anbuselvan, N. (2023, March 9). Assessment of Trace Metal Pollution in Surface Sediments from Southwestern Part of Bay of Bengal, India. *Journal*

of the Geological Society of India, *99*(3), 383–389. https://doi.org/10.1007/s12594-023-2321-1

42. Sanjai Gandhi, K., Pradhap, D., Saravanan, P., Krishnakumar, S., Kasilingam, K., Sukanta Patel, H., Prakash, P., Muthukumaran, S., & Magesh, N. (2020, November). Metal concentration and its ecological risk assessment in the beach sediments of Coromandel Coast, Southern India. *Marine Pollution Bulletin*, *160*, 111565. https://doi.org/10.1016/j.marpolbul.2020.111565
43. Santhiya, G., Lakshumanan, C., Jonathan, M., Roy, P., Navarrete-Lopez, M., Srinivasalu, S., Uma-Maheswari, B., & Krishnakumar, P. (2011, November). Metal enrichment in beach sediments from Chennai Metropolis, SE coast of India. *Marine Pollution Bulletin*, *62*(11), 2537–2542. https://doi.org/10.1016/j.marpolbul.2011.08.019
44. Sundar, D., & Shetye, S. R. (2005, October). Tides in the Mandovi and Zuari estuaries, Goa, west coast of India. *Journal of Earth System Science*, *114*(5), 493–503. https://doi.org/10.1007/bf02702025
45. Sundar, S., Roy, P., Chokkalingam, L., & Ramasamy, N. (2021). Evaluation of metals and trace elements in sediments of Kanyakumari Beach (southernmost India) and their possible impact on coastal aquifers. *Marine Pollution Bulletin*, *169*, 112527. https://doi.org/10.1016/j.marpolbul.2021.112527
46. Tessier, A., Campbell, P. G., & Bisson, M. (1979). Sequential extraction procedure for the speciation of Particulate Trace Metals. *Analytical Chemistry*, *51*(7), 844–851. https://doi.org/10.1021/ac50043a017
47. Venkatramanan, S., Ramkumar, T., Anithamary, I., & Ramesh, G. (2011, December). Variations in texture of beach sediments in the vicinity of the

Tirumalairajanar river mouth of India. *International Journal of Sediment Research*, *26*(4), 460–470. https://doi.org/10.1016/s1001-6279(12)60005-5

48. Wong, C. S., Wu, S., Duzgoren-Aydin, N. S., Aydin, A., & Wong, M. H. (2007, January). Trace metal contamination of sediments in an e-waste processing village in China. *Environmental Pollution*, *145*(2), 434–442. https://doi.org/10.1016/j.envpol.2006.05.017
49. Yalcin, M. G., Simsek, G., Ocak, S. B., Yalcin, F., Kalayci, Y., & Karaman, M. E. (2013). Multivariate statistics and heavy metals contamination in beach sediments from the Sakarya Canyon, Turkey. *Asian Journal of Chemistry*, *25*(4), 2059–2066. https://doi.org/10.14233/ajchem.2013.13309
50. Yalcin, M. G., Simsek, G., Ocak, S. B., Yalcin, F., Kalayci, Y., & Karaman, M. E. (2013). Multivariate Statistics and Heavy Metals Contamination in Beach Sediments from The Sakarya Canyon, Turkey. *Asian Journal of Chemistry*, *25*(4), 2059–2066. https://doi.org/10.14233/ajchem.2013.13309
51. Zimmerman, A. J., & Weindorf, D. C. (2010). Heavy Metal and trace metal analysis in soil by Sequential Extraction: A review of procedures. *International Journal of Analytical Chemistry*, *2010*, 1–7. https://doi.org/10.1155/2010/387803
52. Zimmerman, A. J., & Weindorf, D. C. (2010). Heavy Metal and Trace Metal Analysis in Soil by Sequential Extraction: A Review of Procedures. *International Journal of Analytical Chemistry*, *2010*, 1–7. https://doi.org/10.1155/2010/387803