Metals in sediments and fish from coastal region of Caranzalem, Goa

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To My Parents

DECLARATION BY STUDENT

I hereby declare that the data presented in this dissertation report entitled "Metals in sediments and fish from coastal region of Caranzalem, Goa" 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. M. R. Nasnodkar 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.

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COMPLETION CERTIFICATE

This is to certify that the dissertation report "Metals in sediments and fish from coastal region of Caranzalem, Goa" is a bonafide work carried out by Mr. Abhay Mahesh Patil under my supervision in partial fulfilment of the requirements for the award of the degree of Master of Sciences in the Discipline of Marine Sciences at the School of Earth, Ocean and Atmospheric Sciences, Goa University.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

The marine environment is the most significant ecosystem on the planet and has a variety of habitats with a high potential for biodiversity, including mangroves, sandy beaches, mudflats, coral reefs etc., **(Job et al. 2023)**. According to **Kennedy et al. (2002)**, the coastal zone is a dynamic region where the atmosphere, land and water systems interact, leading to abundant productivity and valuable resources from a commercial perspective. It is a broad transitional area in which the terrestrial environment influences the marine environment and in which the marine environment influences the terrestrial environment. The coastal zone extends upstream as far as tidal influence is felt, which can vary overtime in response to tidal or river flow characteristics.

The coasts are among the most dynamic part of the earth's surface; they act as an interface between the land and the sea containing abundant natural resources. It is broader and includes areas below and above the waterline viz., shoals, dunes and cliffs. It is important to explain the geomorphological changes occurring on the coast in order to sustainably use or manage the coastal resources. The geomorphology of the coast can be examined in planform (also called shore-parallel or long-shore) or in profile (also called cross-section, cross-shore, shore-normal or orthogonal). In planform, a coastal embayment can be divided into relatively distinct landforms based on factors such as topography and lithology, or sediment texture and resistance. The most resistant are rocky coasts, characterised by cliffs. The shoreline migrates daily with the tide; it can change seasonally and varies over longer time scales as the coast erodes or deposits, or as sea level changes. When the coastal land rises or sea level falls, the coastline is described as emergent. A submergent coastline is found when the land is sinking relative to sea level, or sea level is rising **(Johnson 1919; Valentin 1952)**.

Another basic group of classifications uses structural controls to distinguish between various types of coastal landforms. (i) Bold coasts are developed in resistant rocks whereas low coasts are developed on alluvial coastal plains and are also associated with recent sea-level variations (**Bloom 1978**). (ii) **Inman and Nordstrom (1971)** developed a tectonic classification based on plate tectonic theory, recognizing four distinct coastal types which are: divergent coasts (e.g. Red Sea coasts), convergent coasts (e.g. the island arc systems of Japan), transform coasts (e.g. the coast of southern California) and stable coasts (e.g. coasts of India and Australia). (iii) **Shepard's (1963)** divided coasts into primary and secondary coasts. Primary coasts are those which are unaffected by marine processes whereas, secondary coasts have been altered considerably by marine processes such as erosion, accretion and organic deposition. The coastal sediment deposits are shaped and reshaped by wave and current processes, that in turn vary through time **(Woodroffe 2002)**. Sand and gravel are more mobile in the coastal zone and form coastal barriers in which there are beaches and associated landforms.

A beach is a gently sloping shore covered by silt, sand, or gravel that is washed by waves and tides. Most beaches are sandy and vary in detail, but certain features are commonly observed. They can both adapt their shape very quickly to changes in wave energy and also dissipate this energy in minor adjustments of the position of each sand grain. On any beach, the rush of water up the beach face after waves have broken (swash) tends to push the sediment upslope toward the land and after specific time interval, gravity and the retreating backwash together carry it down again. The process begins with erosion. The waves deposit sediment onto the land and result in beach growth. Marine animals, including fish indirectly contribute to erosion. For instance, those living near coral reefs feed on algae growing on the coral. As they nibble on the algae, they cause the coral to break off into smaller pieces. Some of these smaller coral fragments end up in the waves adding to the suspended sediment. The river deltas also contribute to beach expansion as rivers carry eroded sediments to the ocean **(Montgomery 1993).**

The coastal region is highly vulnerable to input of pollutants from terrestrial region. The majority of the world's population lives in close proximity to sea in coastal zone. Thus, often contribute to pollution at coastal regions. Also, estuaries are known to discharge significant quantity of metals to adjacent coastal water. Among the pollutants, metal is one of the highly persistent chemical constituents adding to the deterioration of coastal environment. The metals can be derived from rocks as a part of the weathering process and are recycled through various environmental compartment by biotic and abiotic processes and ultimately find their way in the coastal region. The weathering of the catchment area rocks is an important process of release of metals in the marine environment. It is the breakdown of rocks, soil and minerals as well as wood and artificial materials through contact with the atmosphere, water and biological organisms. Past few years, there has been a worldwide concern about the deterioration of the coastal region due to continuous introduction of metals from various uncontrolled human activities viz., industrial waste, municipal waste, untreated sewage dumping, dredging and mining activities, agricultural and household discharge **(Saiful Islam et al. 2021)**. Trace metals are considered as harmful substances for the environment since they are highly toxic, they remain in the environment for a long time and they can easily be accumulated by the organisms present in the surrounding water bodies **(Islam 2021; Swarnalatha et al. 2013)**.

The metals when introduced in the marine environment in the dissolved form try to settle onto the suitable substratum into the water column viz., suspended sediment particles. Further, physical, chemical and biological processes, groundwater discharge, continuous mixing of waters causes diffusion of metals from sediments into the water column **(Silva Filho et al. 2010; Sanders et al. 2012)**. The metal generally exists in numerous chemical forms in sediments viz., exchangeable ions, metal carbonates, oxides, sulphides, organometallic compounds, ions in the crystal lattices of minerals (**Baeyens et al. 2003**). Each chemical form of a particular metal has considerable impact on the ecosystem **(Tessier et al. 1979)**. The total metal concentration in an environment does not represent metal bioavailability. On the other hand, metal speciation study enables to segregate the bioavailable forms of metal and the residual form of metal in the sediment sample. It is important to know that it is the bioavailable form of metal that is highly susceptible to mobilization due to physico-chemical factors/processes and is responsible for the biological activity of metal. Trace metals released from the sediment into the environment may have adverse impacts on living organisms **(Delgado et al. 2011)**.

Trace metals get access into body tissues of marine organisms through variety of pathways including seawater, particulate matter as well as ingestion of contaminated food. The bioaccumulation is the uptake and retention of bioavailable metal from one or all possible external sources. For it to occur, the rate of uptake from all possible sources must be greater than the rate of loss of the metal from the tissues of the organism. The nature of the contaminant, itself either organic or inorganic is a crucial factor affecting the tissue uptake, as well as the capacity of the organism to metabolize and excrete it.

The continuous exposure in aquatic environments leads to the accumulation of metals in various tissues of fish and sessile organisms, making them valuable bioindicators for assessing pollution levels and ecological conditions **(Krishnakumar et al. 1994).** Several factors viz., seasonal changes, age, sex, habitat and exposure duration affect the accumulation of metals in fish species; and due to these reasons, they tend to have high metallic content in their tissues. Fish absorb trace elements both directly from water, in minor and larger quantities through the consumption of prey **(Handy 1996)**. The essential elements viz., Cu, Fe, Co and Zn play vital role in fish growth and metabolic functions **(WHO 1989)**, whereas metals like Cd, As, Hg and Pb, being non-essential, pose toxicity risks even at low concentrations to biota and their consumers **(Rejomon et al. 2010; El Moselhy et al. 2014)**. Conversely, humans are exposed to these elements through the food chain, leading to both acute and chronic effects **(Rejomon et al. 2010)**.

1.2 Study area

Caranzalem is a scenic coastal region in North Goa, India. It has a beach which acts as a transitional zone between terrestrial region and the Arabian Sea on west. The Caranzalem beach is located between Miramar and Dona Paula region, and has a length of 3.5 Km. It has stretches of white sand and clear water. The Caranzalem beach is well known for the traditional ‘Rapon’ fishing activity and supports the livelihood of local fishermen communities. The coastal water near the Caranzalem beach is a suitable environment for edible fishes viz., *R. kanagurta*, *S. longiceps*, *M. cephalus*, etc. They have a high commercial value due to rich nutritional content. There is a continuous movement of boats and cruises including water sports and other tourism related activities along the stretch of water parallel to the beach. There are several hotels and restaurants in proximity to Caranzalem beach that dump their waste into the Arabian Sea. Such activities have enhanced metal input in the coastal regions of Caranzalem. Also, the Mandovi Estuary is reported to have enriched level of metals due to the practice of open-cast ore mining in the catchment area and its transportation through estuary (Kanetkar et al. 2022). The high precipitation during the monsoon season and the tidal action have facilitated the discharge of metals from the Mandovi Estuary to nearby coastal water, including Caranzalem. Therefore, the coastal fauna near Caranzalem is prone to high bioavailable forms of metals.

1.3 Objectives

- To study total metals and their speciation in coastal sediments at Caranzalem, Goa.

- To understand bioaccumulation of metals in soft tissues of edible fish.

1.4 Literature review

Nasnodkar and Nayak (2017)	Studied the speciation and mobility of trace metals (Fe, Mn, Ni, Co and Cr) in the core sediments of Mandovi and Sharavathi estuarine ecosystems. The speciation showed high concentration of Mn and Co in the bioavailable fractions; and RAC indicated slight risk from Mn and Co to the sediment associated biota in both the estuaries.
Satapathy et al. (2019)	Established a general perception about the bioavailability, sources and distribution of metals in Mahanadi and Hooghly estuaries to estimate the threat with regards to consumption of oysters (*Saccostrea cucullata)*; and suggested guidelines to deal with estuarine safety and awareness. Both the estuaries were moderate to strongly contaminated to Cd and Pb due to nearby industrial and sewage pollution. THQ values suggested Mn, Ni, Cd, Fe, Pb and Cu of Mahanadi and Cu, Ni, Pb, Cd and Fe of Hooghly might result in non-carcinogenic health risks for the oyster consuming population.
Nasnodkar and Nayak (2015)	Investigated sediment cores from Mandovi, Sharavathi, and Gurupur estuarine ecosystems for geochemical and sedimentological characterization. The Gurupur estuary had a high concentration of coarser sediments whereas Mandovi and Sharavathi estuaries had a high concentration of finer sediments. Thus, a low metal concentration was observed in the sediments of Gurupur estuary due to the coarser particles, whereas, high metal concentration was observed in Mandovi and Sharavathi estuaries due to finer sediment particles.
Fernandes et al. (2014)	The study investigated the depositional environment of mudflats, mangroves and analyzed four sediment

	cores from the middle part of the Shastri estuary for grain size, total organic carbon (TOC) and total metal concentration. The TOC and total metal concentrations were found to be enhanced due to tributary input. The sediments in the upper middle estuary were deposited under highly varying hydrodynamic energy conditions, while the lower middle estuary experienced relatively stable hydrodynamic energy conditions over time.
Fernandes et al. (2010)	Two sediment cores were collected from the intertidal regions of Manori Creek, a tidally influenced creek near Mumbai to understand the distribution as well as the variations of selected elements (Fe, Mn, Cu, Ni, Pb, Co, Zn, Cr, Al, Ca and V) from the head to the mouth of the creek. The sediments from inner region of the creek were found to be enriched with metal and organic matter due to direct discharge of industrial and domestic waste into the creek whereas, on the other hand sediments from the mouth region of the creek had lower concentrations of metal and organic matter.
Gadkar et al. (2019)	The study was done to examine the metal enrichment and their bioavailability in mudflat and mangrove sediment cores obtained from the juncture of the Zuari river and Cumburjua canal contaminated with open-cast mining waste. The mudflat sediments were contaminated with Fe, Mn and Co, whereas the mangrove sediments were moderately contaminated with Fe, Mn, Cu and Co. The bioavailability of Fe in mangrove sediments and Mn in both mangrove and mudflat sediments was reported. The sediment quality values suggested toxicity to sediment-associated biota.
Vieira et al. (2021)	The study aimed to quantify metals and microplastics in oysters (*Crassostrea gasar*) from Parangua

	Estuarine System (PES). The results showed potential risk to human health from consumption of these oysters due to elevated concentrations of As and Zn. Similarly, bioaccumulation of microplastics was reported in the oysters.
Al-Musharafi et al. (2013)	Studied the metals in sediments and fish species *(Cephalopholis hemistiktos Diodon liturosus, Lutjanus ehrenbergi,* and *Stephanolepis diaspros)* collected from the dumping site near a treated sewage effluent (TSE) in Muscat, Gulf of Oman. The most significant aspect in this investigation was that the fish samples were contaminated with metals which were found in higher concentration in TSE and sediment.
Gu et al. (2017)	Investigated the metal concentration in four edible fishes (*Thunnus obesus, Decapterus lajang, Cubiceps squamiceps* and *Priacanthus macracanthus)* collected from the western continental shelf of south China Sea. The concentration of metals was below the acceptable daily upper limit. Thus, indicated no adverse health effects on humans.
Shalini et al. (2021)	The study was done to determine distribution of trace metals in gills, bone, liver and muscle of eight edible fishes (*Sardinella gibbosa, Caranx sexfaciatus, Lethrinus lentjan, Siganus canaliculatus, Sphyraena jello, Strongylura strongylura, Euthynnus affinis* and *Scomberomorus commerson*) collected from the southeast coast of India. The concentration of As, Cd, Hg and Pb was found to be lower than International Legislation limits.
Job et al. (2023)	The physicochemical parameters of coastal seawater and metal concentration in muscle tissues of *Leiognathus equulus, Lates calcarifer, Sil-lago sihama, Scolopsis bimaculatus* and *Lutjanus*

	fulvifamma along the Thondi coast were studied. The average metal concentration in fish samples was below the FAO/WHO/EU recommended limits. The THQ value for As was more than one indicating possible risk to the consumers.
Bawuro et al. (2018)	The study was done considering the health risk of metals in animals and people within the environment from the consumption of fishes (*Clarias anguilaris, Heterotis niloticus and Tilapia zilli*) in lake Geriyo, Adamawa State, Nigeria. Health risk analysis of metals in edible fish parts indicated safe levels for human consumption. But Pb in Clarias and Tilapia during wet season and Heterotis in both wet and dry season exceeded maximum permissible limit, hence unsafe for consumption.
Aljohani et al. (2023)	The study was carried out to assess the level of metals (As, Cu, Cr, Pb and Cd) in the water and fish samples (*Cephalopholis hemistiktos, Thalassoma lunar, Aethaloperca rogaa* and *Odonus nigar*) collected from proximity of Ras Al Khair desalination plant and to determine the potential risk related to consumption of these fishes. The health risk assessment proved safe conditions for consumption of the fishes but there were alarming situations with regards to As and Cr.
Anandkumar et al. (2018)	The fish species (*Carcharhinus leucas, Scomberomorus lineolatus, Sphyraena qenie, Setipinna tenuifilis, Psettodes erumei, Trichiurus lepturus* and *Otolithes ruber*) were collected from the Miri coast, Sarawak, Borneo to investigate the bioaccumulation of trace metals and to determine the possible human health related risks from the consumption of these fishes. Based on human health risk assessment none of the elements possess any

	adverse health effects to humans for ingestion rates proposed by USEPA, except for Pb and Cd in certain species for habitual consumers.
Patchaiyappan et al. (2023)	The study was carried out to determine the metal and non-metal contaminations (As, Cr, Cd, Pb, Cu and Zn) in the muscle tissues of twenty-eight marine organisms from the Pondicherry coast, Southeast coast of India. The health hazard index values for all the organisms studied were below the threshold value of 1 implying that there would be no health risk at ingestion rates.

CHAPTER 2

MATERIALS

AND

METHODS

2.1 Introduction

A sample of a specific quantity represents the biogeochemical processes prevailing in the environment. The samples are collected from a desired site(s), stored and later analysed for several parameters, upon reaching the laboratory. The analysis must be done by using the standard analytical procedure to obtain accurate results which represent not only the environment but also the issues pertaining in the environment. Thus, the materials, methods and the techniques used must be of internationally accepted standards. To meet the objectives of the study, the following methodology was adopted:

2.2 Sampling

The field sampling was carried out at Caranzalem site, west coast of Goa for the months of August, October, November, December and January 2023-2024 (Fig 2.1). The fish samples were collected from the fisherman at the time of fishing (Rapon) activity at the Caranzalem beach. Three fish samples per species were collected for analysis. The surface sediment samples were retrieved from intertidal region with the help of a plastic scoop at the vicinity of the sampling station. Location of the sampling site was marked using the Global Positioning System (GPS).

The biota and sediment samples were collected in pre-labelled cloth and polyethylene bags respectively. The sediment and biota samples were transported to the laboratory in an ice box. Upon reaching the laboratory, the sediment samples were stored at 4°C in a refrigerator and the biota samples were stored at -20°C in the deep freezer until further analysis. The biota samples were identified which are listed in Table 2.1.

Fig 2.1: Sampling location of sediment and fish samples at the Caranzalem beach.

Table 2.1: The fish species collected from the Caranzalem beach.

Months	Fish species
August	• *Sardinella longiceps* • *Sardinella fimbriata* • *Terapon jarbua* • *Johnius belangerii*
October	• *Nematolosa nasus* • *Mugil cephalus* • *Lactarius lactarius* • *Otolithes ruber* • *Polynemus indicus* • *Gerrus filamentous*
November	• *Rastreliger kanagurta* • *Nematolosa nasus* • *Gerrus filamentous* • *Alepes djedeba*
December	• *Mugil cephalus* • *Rastreliger kanagurta* • *Nematolosa nasus* • *Gerrus filamentous*
January	• *Rastreliger kanagurta* • *Sardinella longiceps* • *Sphyraena barracuda* • *Mugil cephalus*

2.3 Sedimentological and geo-chemical analysis

The surface sediment samples were oven dried at 60°C for 96 hours. A portion of the dried bulk sediment sample was used for the grain size analysis, while the remaining dried sediment sample was powdered using an agate mortar and pestle, and was utilized for the estimation of Total Organic Carbon (TOC), total metals and their speciation study.

2.3.1 Grain size analysis

To understand the composition of sand:silt:clay in sediment the pipette technique proposed by **Folk (1974)** was adopted. This method involves the separation of silt and clay based on the settling velocity principle of the particles following the Stoke's law. The settling velocity of a sediment particle depend on its size and density, and the viscosity of the liquid.

In this method, 10 g of the dried bulk sediment sub-sample was weighed and transferred into the 1000 mL glass beaker. Then the glass beaker was filled with distilled water and was mixed well. Later, the sediments were allowed to settle at the bottom of the beaker for almost 24 hours. Once all the sediment particles were settled at the bottom of the beaker, water was decanted using a decanting pipe without disturbing the settled sediments. This step was repeated 4 to 5 times until there were no traces of salinity observed which was verified with $AgNO_3$ solution. Later, the sediment sample was treated with 10 mL of 10 % sodium hexametaphosphate and was kept overnight to dis-integrate the grain particles. On the next day, the sediment sample was treated with 5 mL of 30 % H_2O_2 and was kept overnight to oxidize the organic matter. The treated sediment sample was wash-sieved through 63 µm mesh size sieve using distilled water to separate sand component from silt and clay. The sand retained on sieve was transferred into the 100 mL pre-weighed beaker and was kept for oven drying. The filtrate containing silt and clay was collected in the 1000 mL measuring glass cylinder. The volume of filtrate in glass cylinder was made to 1000 mL with distilled water and the solution was homogenised using stirrer for 2 minutes. The homogenised solution in the measuring cylinder was allowed to settle. After measuring the room temperature using thermometer the extraction time (from stirring to pipetting) was calculated at 8 phi size following the Table 2.2.

According to the extraction time, 25 mL clay solution was pipetted out from the depths of 10 cm and was transferred into 100 mL pre-weighed beaker. The beaker was kept in an oven for drying. The weight of dried sand and clay particles in the beakers was measured and used for calculation of the percentage of sand, silt and clay using the following formulae:

$$\%Sand = (\text{Weight of sand} / \text{Total weight of sediments}) \times 100$$

$$X = (\text{Weight of clay} \times 1000/25) - 1$$

$$\%\ Clay = (X / \text{Total weight of sediment}) \times 100$$

$$\%\ Silt = 100 - (\%\ \text{of Sand} + \%\ \text{of Clay})$$

Table 2.2: Time schedule to be used for 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				
		28ºC	29ºC	30ºC	31ºC	32ºC
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	-	-	-

2.3.2 TOC analysis

The organic matter has the ability to adsorb metals in the estuarine environment. The microbial degradation of organic matter can desorb or release metals in the interstitial pore water and water column. The analysis of TOC enables to understand the role of organic matter in retention and bioavailability of metal in sediments. A modified Walkey-Black method **(Gaudette et al. 1974)** was followed to estimate the concentration of TOC in sediments. It involves exothermic heating and oxidation of organic carbon in the sediment with $K_2Cr_2O_7$ and concentrated H_2SO_4 respectively. The excess of $K_2Cr_2O_7$ which does not participate in the reaction is titrated against 0.5 N ferrous ammonium sulphate solution to a sharp one drop brilliant green end point.

All the glass-wares were cleaned with chromic acid prior to use. The 0.5 g of powdered sediment sub-sample was transferred into 500 mL conical flask. To this 10 mL of 1 N $K_2Cr_2O_7$ solution was added, followed by 20 mL of H_2SO_4 and $AgSO_4$ mixture. The conical flask was gently swirled and was kept for 30 minutes reaction time. After 30 minutes, 200 mL of MillQ water, 10 mL of 85 % of ortho-phosphoric acid and 0.2 g of NaF was added, and was mixed well. After adding few drops of diphenylamine indicator, the solution was titrated against 0.5 N ferrous ammonium sulphate solution till one drop brilliant green end point was observed. The same procedure was followed for standardization of blank without sediment sample.

The percentage of TOC was calculated using the following formula:

$$\% \text{ of TOC} = 10\ (1 - T/S) \times F$$

Where,

S = Standardization blank titration, ml of ferrous solution

T = Sample titration, ml of ferrous solution

F = (Normality of $K_2Cr_2O_7$ × milliequivalent weight of carbon× 100)/Sample weight

Milliequivalent weight of carbon= 12/4000

F is equal to 0.6, when the sample weight is exactly equal to 0.5 g

2.3.3 Total metal

The total metal in the bulk sediment is the concentration of the metal present in residual fraction as well as in the bioavailable fraction. To determine the total metal concentration in the sediment, the acid digestion method proposed by **Jarvis and Jarvis (1985)** which was later modified by **Sholkovitz (1990)** was adopted.

The apparatus was cleaned with chromic acid prior to use. 0.2 g of the powdered sediment sample was taken in a Teflon beaker, to which 10 mL of acid mixture of HF, HNO_3, $HClO_4$ in the ratio of 7:3:1 was added, respectively. Later, the Teflon beaker was kept on a hot plate at 150℃ and the mixture was dried completely. Additional, 5 mL of the same acid mixture was added to the Teflon beaker and further dried for 1 hour. It was followed by complete digestion of sample with 2 mL of concentrated HCl. Further, the digested sample was extracted with 10 mL of 1:1 HNO_3. The solution was then filtered through Whatman filter paper in 50 mL volumetric flask. The volume of filtrate (extracted sample) was made to 50 mL using MilliQ water and was transferred into the pre-cleaned polyethylene bottle.

The concentration of metals viz., Fe, Mn, Zn, Cu, Co and Ni in the digested sediment sample was determined using the flame Atomic Absorption Spectrophotometer (AAS) Thermo Fischer, iCE 3000 Series.

2.3.4 Metal speciation

The speciation of metals enables to segregate bioavailable forms of metal and residual form of metal in the sediment sample. To determine the different forms of metal (exchangeable, carbonate, Fe-Mn oxide, organic matter/sulphide, and residual fractions) in the sediment sample, the 5-steps sequential extraction procedure proposed by **Tessier et al. (1979)** which was later modified by **Dessai and Nayak (2009)** was adopted. The first four fractions in this method are considered as bioavailable forms of metal. It is the bioavailable form of metal which is environmentally reactive, whereas the residual form of metal is environmentally unreactive as the metal is firmly held in the lattice structure of the mineral. The speciation study provides valuable information on source, mobilisation and bioavailability of metal in the sediment and its possible toxicity to the sediment associated biota **(Nasnodkar and Nayak 2019; Nasnodkar and Nayak 2017).**

2.3.4.1 Exchangeable fraction (F1)

The metal present in this fraction is most loosely bound to the sediment particles and can get desorb and release into the adjacent environment due to changes in ionic composition of water. The exchangeable fraction was extracted as follows:

1 g of the powdered sediment sub-sample was treated with 8 mL of 1N $MgCl_2$ into 50 mL centrifuge tube for 1 hour with continuous agitation in the orbital shaker at room temperature. Later, the treated sample was centrifuged at 8000 rpm for 10 minutes. The supernatant was filtered through Whatman filter paper into the 25 mL volumetric flask and the final volume was made to 25 mL using MilliQ water. The extracted sample was then stored in pre-cleaned polyethylene bottle at refrigerated temperature until further analysis. The sediment residue (I) in centrifuge tube was washed with MilliQ water and was used for next step.

2.3.4.2 Carbonate fraction (F2)

The second step is the extraction of metals associated with the carbonate fraction. The metal in this fraction of the sediment can be leached out by treatment with sodium acetate at pH 5. The residue (I) was treated with 8 mL of 1 N sodium acetate whose pH was adjusted to 5 with a glacial acetic acid. The mixture was continuously agitated in an orbital shaker for 5 hours. Later, the sample was centrifuged at 8000 rpm for 10 minutes. The supernatant was filtered into the 25 mL volumetric flask using Whatman filter paper and the final volume was made to 25 mL using MilliQ water. The extracted sample was stored in a pre-cleaned polyethylene bottle at refrigerated temperature until further analysis. The sediment residue (II) in centrifuge tube was washed with MilliQ water and was used for next step.

2.3.4.3 Fe-Mn oxides fraction (F3)

In the marine environment, the dissolved Fe and Mn under oxic conditions precipitate as oxides and hydroxides and forms coatings on the surface of sediment particles. The Fe and Mn oxides are referred as effective scavengers of metals in the marine environment as they hold high concentration of metals viz., Cu, Zn, Cr, Ni, Co, etc. The metals associated with the Fe-Mn oxides fraction was extracted as follows:

The residue (II) was treated with 20 mL of 0.04 M hydroxylamine hydrochloride in 25% acetic acid and was kept in a water bath at 95$\pm$ 3°C for 6 hours with frequent gentle shaking in between the extraction time. Later, the treated sample was allowed to cool down and centrifuged at 8000 rpm for 10 minutes. The supernatant was filtered through Whatman filter paper into the 25 mL volumetric flask and the final volume was made to25 mL using MilliQ water. The leachate was stored in a pre-cleaned polyethylene bottle at refrigerated temperature until further analysis. The sediment residue (III) in centrifuge tube was washed with MilliQ water and was used for next step.

2.3.4.4 Organic matter/sulphide fraction (F4)

Organic matter/sulphide fraction includes the metals bound to organic matter and sulphides. The metal in this fraction was extracted as follows:

The residue (III) was treated with 3 mL of 0.02 M HNO_3 and 5 mL of 30 % H_2O_2 at pH 2 and was kept in a water bath at 85°C for 2 hours. Later, additional 3 mL of 30 % H_2O_2 at pH 2 was added to the mixture and was kept back in a water bath for additional 3 hours. Further, the mixture was treated with 5 mL of 3.2 M ammonium acetate in 20 % HNO_3 and was subjected to continuous agitation for 30 minutes in an orbital shaker. After agitation, the sample mixture was centrifuged at 8000 rpm for 10 minutes. The supernatant was filtered through Whatman filter paper into 25 mL volumetric flask and the final volume was made to 25 mL using MilliQ water. The extracted sample was stored in a pre-cleaned polyethylene bottle at refrigerated temperature until further analysis. The sediment residue (IV) in centrifuge tube was washed with MilliQ water and was used for next step.

2.3.4.5 Residual fraction (F5)

The residue IV contains detrital silicate minerals, resistance sulfides and small quantity of refractory organic materials. The treatment with HF, HNO_3, $HClO_4$ acid mixture leads to complete digestion of the residual fraction.

The residue (IV) was treated with 10 mL of acid mixture (HF, HNO_3, $HClO_4$) in the ratio of 7:3:1, respectively in a Teflon beaker and was acid digested following the same protocol as that of total metal extraction. The extracted solution was then filtered through Whatman filter paper in 25 mL volumetric flask. The volume of filtrate (extracted sample) was made to 25 mL using MilliQ water and was transferred into a pre-cleaned polyethylene bottle and was stored at refrigerated temperature until further analysis.

The concentration of Fe, Mn, Zn, Cu, Co and Ni in all sediment fractions was determined using the AAS.

2.4 Biota digestion

The analysis of metals in the fish tissues was carried out as follows:

The frozen fish samples were thawed at room temperature. The total length and weight of each fish per species was recorded. The fish samples were dissected and the muscle, gills, liver and kidney tissues were separated. The dissected tissues were kept for oven drying at 60℃ for 72 hours or until completely dried. The dried biota samples were powdered using an agate mortar and pestle.

1 g of the powdered biota sample was acid digested using 2 mL of HNO_3 and 1 mL of $HClO_4$ at 120℃ on a hot plate for 3 hours **(Yuzereroglu et al. 2010).** After complete digestion, few mL of MilliQ water was used for extraction of the digested sample into solution form. The solution was then filtered through Whatman filter paper into the 25 mL volumetric flask and the final volume was made to 25 mL with MilliQ water. It was then transferred into the pre-cleaned polyethylene bottle and was stored in a refrigerator until further analysis.

The concentration of Fe, Mn, Zn, Cu, Co and Ni in the biota sample was analysed using the AAS.

2.5 Metal pollution indices

The following pollution indices were used to understand the contamination and pollution of metals in the sediments of the Caranzalem beach.

2.5.1 Contamination Factor (CF)

To assess the level of contamination of metals in the sediments, the CF was calculated **(Barbieri 2016)** as follows:

$$CF = Cmetal / Cbackground$$

Where, C_{metal} was the concentration of metal in the studied sediment sample and $C_{background}$ was the background value of the same metal taken as Upper Crustal Average (UCA) value **(Wedepohl 1995)**. The CF is classified into four categories **(Pekey et al. 2004)**: CF value < 1 refers to low contamination; 1 ≤ CF value < 3 refers to moderate contamination; 3 ≤ CF value < 6 refers to high contamination; and CF value > 6 refers to very high contamination.

2.5.2 Geo-accumulation Index (I_{geo})

The I_{geo} proposed by **Muller (1979)** was used to assess the metal pollution in the sediments of the Caranzalem beach. The I_{geo} value was calculated using the following equation:

$$\mathrm{Igeo} = \log_2 \frac{\mathrm{Cn}}{1.5 \times \mathrm{Bn}}$$

Where, Cn represented the concentration of metal in studied sediment sample and Bn was the background value of the same metal from upper crust **(Wedephol 1995)**. To account for variances in background values caused by lithological differences, the factor 1.5 was used**.** The degree of metal pollution was evaluated using the classification given in the Table 2.3 **(Rubio et al. 2000; Praveena et al. 2008)**.

Table 2.3: 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 moderate polluted
< 0	0	Practically unpolluted

2.6 Metal toxicity assessment

The toxicity of metals in the coastal sediments was assessed using the Risk Assessment Code (RAC), Screening Quick Reference Table (SQUIRT) and modified Biota Sediment Accumulation Factor (mBSAF). These indices provide with the indication of ecological state of the environment.

2.6.1 Risk Assessment Code (RAC)

The RAC was used to determine the risk of metals to the sediment associated biota. It is the sum of percentage~~s~~ of exchangeable and carbonate fractions of a metal in the sediment. The assessment of risk of metal to biota was carried out following the criteria proposed by **Perrin et al. (1985)**. The RAC value < 1 % indicates no risk, RAC value 1 – 10 % indicates low risk, RAC value 11 – 30 % indicates medium risk, RAC value 31 –50 % indicates high risk, and RAC value > 50 % indicates very high risk and possibility of metal entering into the food chain.

2.6.2 Screening Quick Reference Table (SQUIRT)

The SQUIRT was developed by National Oceanic and Atmospheric Administration (NOAA). Metal toxicity to sediment associated biota was assessed by comparing its bioavailable concentration (sum of exchangeable, carbonate, Fe-Mn oxides and organic matter/sulphide fractions) in sediments with the Sediment Quality Values (SQV) as described in the Sediment Quality Guidelines (SQG). The terms used and the guidelines were categorized into five classes by **Buchmann (1999)** Table 2.4.

Table 2.4: Screening Quick Reference Table (SQUIRT).

Metals	Threshold Effect Level (TEL)	Effect Range Low (ERL)	Probable Effect Low (PEL)	Effect Range Median (ERM)	Apparent Effect Threshold (AET)
Fe (%)	-	-	-	-	22 (Neanthes)
Mn (ppm)	-	-	-	-	260 (Neanthes)
Zn (ppm)	124	150	271	410	410 (Infaunal Community Impacts)
Cu (ppm)	18.7	34	108	270	390 (Microtox & Oyster Larvae)
Co (ppm)	-	-	-	-	10 (Neanthes)
Ni (ppm)	15.9	20.9	42.8	51.6	110 (Echinoderm Larvae)

2.6.3 modified Biota Sediment Accumulation Factor (mBSAF)

The bioaccumulation of metals by biota from the associated sediments was evaluated through the determination of mBSAF proposed by **Dias and Nayak (2016).**

$$mBSAF = \frac{Metal\ concentration\ in\ organism\ tissue}{Bioavailable\ metal\ concentration\ in\ sediment}$$

The mBSAF of < 1 suggest that the biota is de-concentrator of metal, whereas the value ranging from 1 to 2, and > 2 suggest biota as micro-concentrator and macro-concentrator of metal, respectively.

2.7 Human health risk assessment

2.7.1 Target Hazard Quotient (THQ)

The non-carcinogenic risk related to the consumption of fish and its associated metals was evaluated using the THQ. This method is available in the US EPA Region III risk-based concentration table **(USEPA 2000)**.

$$\text{THQ} = \frac{EF \times ED \times FIR \times C}{Rfd \times BW \times AT} \times 10^{-3}$$

Where, EF is the exposure frequency (350 days/year), ED is the exposure duration (70 years), FIR is the food ingestion rate (37.9 g/day) **(Wu et al. 2018)**, C is the concentration trace elements in the fish samples (µg/g, dry weight), AT is the average exposure duration for non-carcinogens (25,550 day for an adult) **(Núñez et al. 2018)**, BW is the average body weight (55.9 kg) **(Wang et al. 2017)**, Rfd is the oral reference dose (µg/kg/day), the RfD values were referred from **Food and Nutrition Board (2004)**, **Uche et al. (2017)** and **USEPA (2000, 2011a and b)**. The THQ of > 1 shows a high risk of long-term non-carcinogenic effects and THQ of < 1 does not show any obvious risk.

2.8 Statistical analysis

The processing of raw data and plotting of various parameters were carried out using the softwares viz., Microsoft Excel 16, Q-GIS, Grapher 14 and STATISTICA.

CHAPTER 3

RESULTS

AND

DISCUSSION

3.1 Sedimentological analysis

3.1.1 Grain size and TOC

Table 3.1: The concentration of sediment components and TOC in sediments of the Caranzalem beach.

Months	Sand %	Silt %	Clay %	TOC %
August	92.20	5.33	2.48	0.20
October	93.65	6.35	0	0.17
November	91.94	8.06	0	0.21
December	93.88	6.12	0	0.22
January	93.10	2.15	4.76	0.21

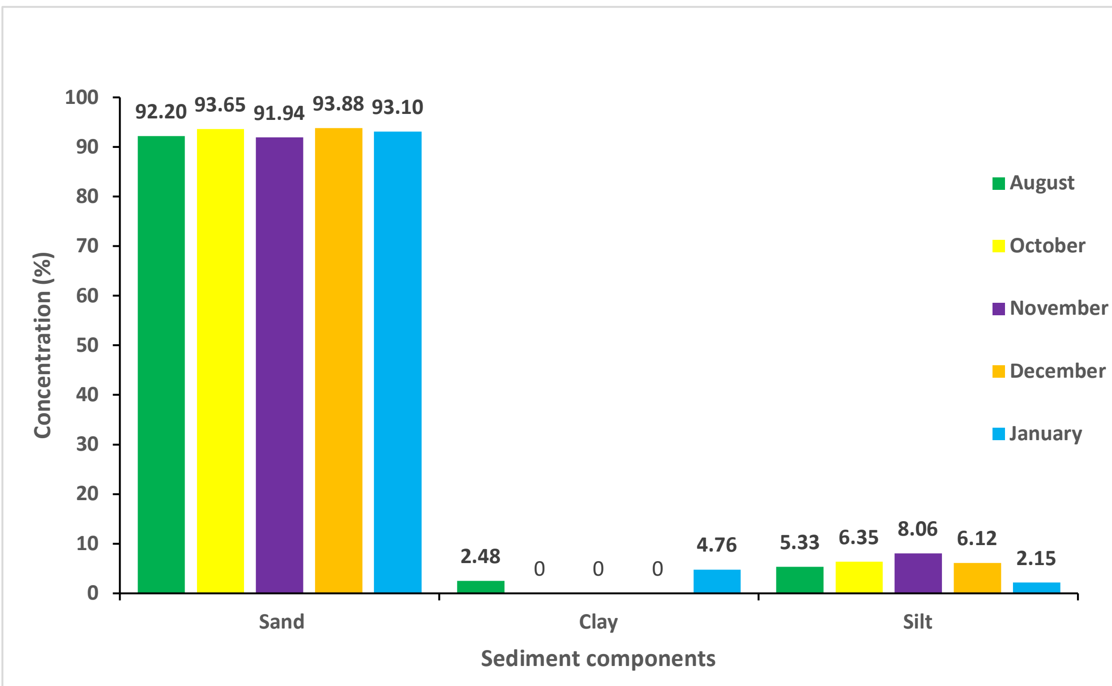


Fig 3.1: The concentration of sand, silt and clay in sediments of the Caranzalem beach.

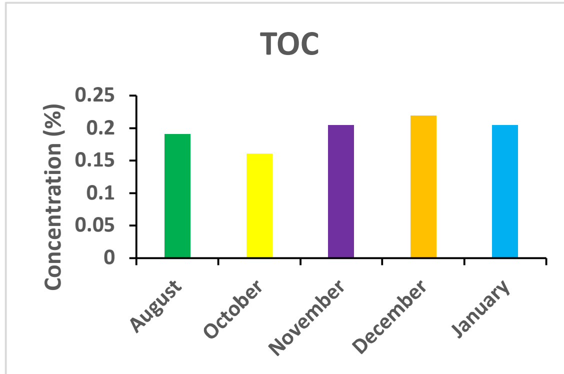


Fig 3.2: The concentration of TOC in sediments of the Caranzalem beach.

The concentration of sediment components and TOC in sediments of the Caranzalem beach for the months of August, October, November, December and January is presented in the Table 3.1 and Fig. 3.1 and 2. The sediments of the Caranzalem beach were enriched with coarser sediments having sand % greater than 90 %. The concentration of sand ranged from 91.94 to 93.88 %. The finer sediments (silt and clay) were highly negligible in the sediments. The TOC ranged from 0.16 to 0.22 %. The dominance of sand sized particles in the sediments was attributed to high hydrodynamics at the beach region **(Nasnodkar and Nayak 2015)**. The beaches around the coastline are exposed to strong action of waves and tides. The high energy associated with waves and tides facilitate retention of coarser sand particles, while the finer sediments are transported towards upstream (middle) region of the estuary in proximity **(Nasnodkar and Nayak 2015)**. The low proportion of TOC in the beach sediments highlighted its dilution due to the presence of sand particles. The coarser sediments viz., sand have smaller surface area/volume ratio and therefore, support low adsorption sites for organic and inorganic constituents than silt and clay particles **(Burone et al. 2003)**.

3.2 Geochemical analysis

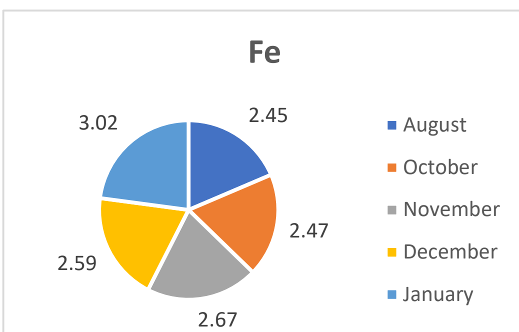
3.2.1 Total metals

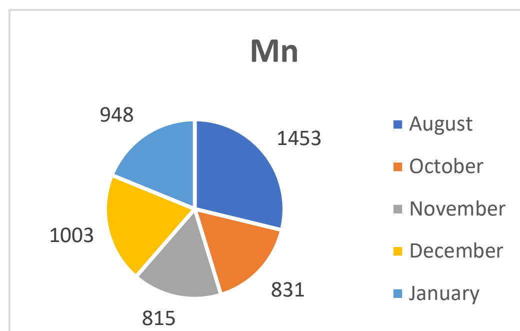
The total concentration of metals in sediments of the Caranzalem beach for the months of August, October, November, December and January is presented in the Table 3.2 and Fig. 3.2. The Fe in the beach sediments ranged from 2.45 to 3.02 %, while Mn varied from 815 to 1453 ppm. The metal viz., Zn, Cu, Co and Ni ranged from 45 to 68 ppm, 22 to 26 ppm, 8 to 14 ppm and 47 to 57 ppm respectively. The sediments of the Caranzalem beach were dominated with Mn during all months than rest of the metals. Moreover, the concentration of Mn, Cu and Ni was more than the upper crustal average value. Also, Zn (October) and Co (August, November and January) exceeded the upper crustal average value. The level of Fe was below the upper crustal average value. The Caranzalem coast is in proximity to the Mandovi Estuary which displayed enrichment of metals in the recent sediments due to anthropogenic activities viz., open – cast ferromanganese ore mining, industrial, agricultural and domestic waste **(Nasnodkar and Nayak 2017)**. The high river runoff; and strong tidal and wave action enables dilution of metals in the Mandovi Estuary transported by river and its tributaries. Further, there is discharge of metals from the Mandovi Estuary to the adjacent coastal region, including Caranzalem. Also, the mined ore was transported in an open system using barges through the estuarine channels of Mandovi **(Nasnodkar and Nayak 2017)**. Thus, mining and other anthropogenic activities might have increased the proportion of Mn in the sediments of the Caranzalem beach. Moreover, Mn precipitates in the coastal environment at higher salinity than Fe which might have also enhanced its level in the beach sediments. Furthermore, Fe and Mn are present in their oxide or hydroxide forms in the surface sediments (oxygen rich) and facilitate the scavenging of other trace metals viz., Zn, Cu, Co and Ni **(Fernandes and Nayak 2016)**. Additionally, the coarser (sand) sediments being denser in size than finer (silt and clay) sediments remain at a given place for a longer duration **(Gaonkar and Matta 2020)**. It enables development of Fe – oxide coatings on the surface of the sand particles that in turn help in the adsorption of trace metals. Thus, human - induced activities and geochemical processes within the coastal regions might have facilitated the adsorption of metals onto coarser sediments.

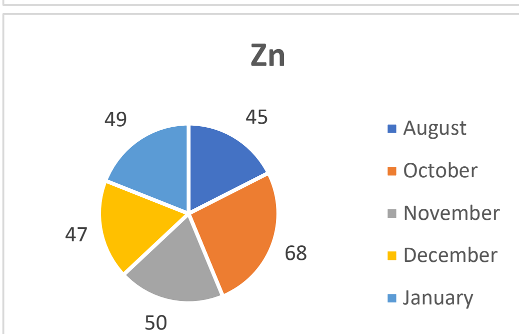
Table 3.2: The concentration of total metals in sediments of the Caranzalem beach.

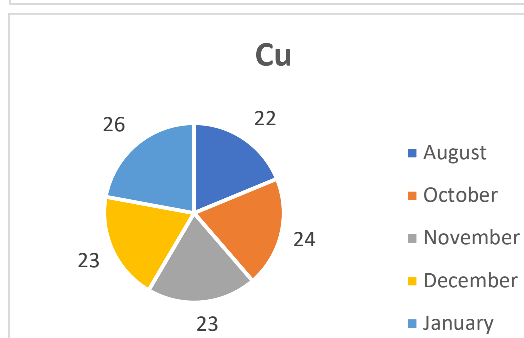
Months	**Fe (%)**	**Mn (ppm)**	**Zn (ppm)**	**Cu (ppm)**	**Co (ppm)**	**Ni (ppm)**
August	2.45	1453	45	22	13	47
October	2.47	831	68	24	10	50
November	2.67	815	50	23	14	57
December	2.59	1003	47	23	8	49
January	3.02	948	49	26	14	49
Upper crustal average (Wedepohl 1995)	3.08	527	52	14.3	11.6	18.6

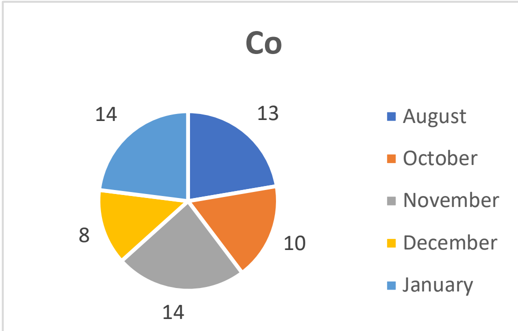
Among the metals, Mn displayed noticeable variability in its concentration from August to January. It might be due to changes in its source with time and geochemical processes governing its precipitation in sediments.











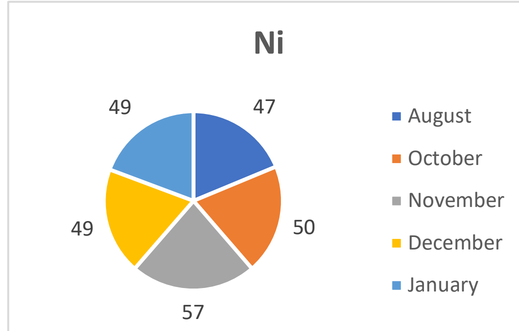


Fig 3.3: The total metal concentration in sediments of Caranzalem beach.

3.2.2 Pollution indices

3.2.2.1 Contamination Factor (CF)

Table 3.3: Contamination Factor (CF) of metals in sediments.

Months	CF					
	Fe	Mn	Zn	Cu	Co	Ni
August	0.79	2.76	0.87	1.56	1.14	2.54
October	0.80	1.58	1.31	1.65	0.89	2.70
November	0.87	1.55	0.96	1.63	1.20	3.08
December	0.84	1.90	0.90	1.61	0.70	2.63
January	0.98	1.80	0.95	1.83	1.17	2.61

The CF revealed low contamination of Fe in sediments from August to January (Table 3.5). The Mn and Cu were moderately contaminated in sediments of the Caranzalem beach. The Zn showed low contamination during August, November, December and January, while was moderately contaminated during October period. The Co displayed low contamination during October and December months, and indicated moderate level of contamination during August, November and January months. The sediments of the Caranzalem beach were moderately contaminated with Ni from August to January. The determination of CF in sediments revealed moderate level of contamination mainly from metals viz., Mn, Cu and Ni. The major sources of these elements at the Caranzalem beach might be from the earlier open – cast ferromanganese ore mining and the transportation of these mined ore in an open system using barges through the Mandovi estuarine channel; and also through various industrial, agricultural, domestic and municipal wastes etc. **(Nasnodkar and Nayak 2017).**

3.2.2.2 Geo – accumulation Index (Igeo)

Table 3.4: Geo – accumulation Index (Igeo) of metals in sediments.

Months	Igeo					
	Fe	Mn	Zn	Cu	Co	Ni
August	-0.92	0.88	-0.78	0.05	-0.40	0.76
October	-0.90	0.07	-0.20	0.13	-0.76	0.85
November	-0.79	0.04	-0.64	0.12	-0.32	1.04
December	-0.84	0.34	-0.74	0.10	-1.11	0.81
January	-0.62	0.26	-0.66	0.29	-0.35	0.80

The Igeo classified sediments of the Caranzalem beach as practical unpolluted with Fe, Zn and Co (Table 3.6). The Mn, Co and Ni fell under unpolluted to moderately polluted class. Although, Igeo revealed low degree of metal pollution in the sediments of the Caranzalem beach but, construed anthropogenic sources of metals viz., Mn, Co and Ni.

3.2.3 Metal speciation

Table 3.5: The concentration of geochemical forms of metals in sediments of the Caranzalem beach. (ND = Not Detected)

Metal	Months	Exchangeable (F1)	Carbonate (F2)	Fe – Mn Oxides (F3)	Organic matter/sulphide (F4)	Residual (F5)
Fe	August	0.02	0.07	17.20	0.98	81.72
	October	0.07	0.46	45.80	1.90	51.77
	November	0.02	0.19	14.87	0.70	84.22
	December	0.02	0.14	15.90	0.78	83.17
	January	0.01	0.07	9.46	0.66	89.79
Mn	August	0.61	60.29	24.89	1.18	13.04
	October	0.51	49.50	13.80	0.72	35.48
	November	0.98	56.55	16.94	1.00	24.53
	December	1.60	50.10	25.60	1.23	21.46
	January	0.80	57.90	22.15	0.78	18.38
Zn	August	6.01	5.56	22.73	17.48	48.22
	October	6.32	5.89	20.48	12.50	54.81
	November	5.94	5.60	22.00	13.83	52.63
	December	5.18	7.25	20.98	15.90	50.70
	January	4.61	5.93	22.23	11.15	56.08
Cu	August	15.57	13.98	16.21	36.94	17.31
	October	22.44	14.90	19.98	21.51	21.17
	November	21.28	15.43	19.44	26.73	17.12
	December	15.37	21.21	17.21	29.97	16.24
	January	10.10	16.25	26.91	26.14	20.59
Co	August	ND	ND	45.97	9.85	44.18
	October	ND	ND	42.68	5.49	51.83
	November	ND	ND	36.65	11.94	51.41
	December	ND	ND	42.76	4.81	52.43
	January	ND	4.11	39.25	6.11	50.54

Ni	August	5.89	6.89	20.54	6.55	60.13
	October	5.66	6.85	20.47	7.19	59.84
	November	5.71	6.46	20.20	6.51	61.11
	December	6.10	7.23	20.42	6.83	59.42
	January	5.85	7.99	20.13	6.29	59.73

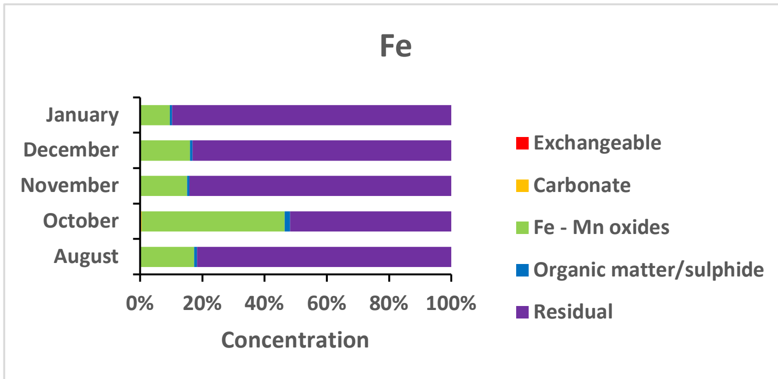
The concentration of metals in the geochemical fractions of the sediments is presented in Table 3.3 and Fig. 3.3. The concentration of Fe was abundant (> 80 %) in the residual fraction for the months of August, November, December and January. It was highest (51.77 %) in the residual fraction for the month of October, but was also significantly (45.80 %) present in the Fe – Mn oxide fraction. Additionally, Fe was > 10 % in the Fe – Mn oxide fraction during August, November and December. The Mn was highest (> 45 %) in the carbonate fraction in sediments from August to January. Also, it was significantly (> 25 %) associated with Fe – Mn oxide (25.60 %) and residual (35.48 %) fractions. It displayed a considerable (> 10 %) concentration in Fe – Mn oxide (August, October, November and January) and residual (August, November, December and January) fractions.

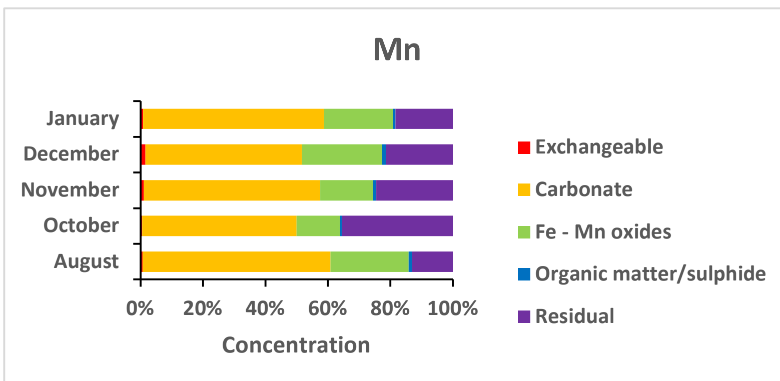
Zn was highest (> 45 %) in the residual fraction and was considerably (> 10 %) bound to Fe – Mn oxide and organic matter / sulphide fractions from August to January. Also, it was more than 10 % in the labile (exchangeable and carbonate) fraction. Cu was highest in the organic matter / sulphide fraction during August (36.94 %), November (26.73 %) and December (29.97 %), while it reported highest concentration in exchangeable and Fe – Mn oxide fractions during October (22.44 %) and January (26.91 %) respectively. It was considerably (> 10 %) present in Fe – Mn oxide (August, October, November and December) and residual fractions (August to December). Cu displayed significant (> 25 %) concentration in the labile fraction in sediments from August to December. Co was highest in Fe – Mn oxide (45.97 %) fraction during August while, it was highest in the residual fraction from October to January (> 50 %). Also, Co was significantly (> 25 %) associated with Fe – Mn oxide (October to January) and residual (August) fractions. Further, it was more than 10 % in the organic matter / sulphide fraction during November. Ni was highest (> 55 %) in the residual fraction from August to January. It was associated with Fe – Mn oxide and labile fractions in considerable (> 10 %) amount from August to January.

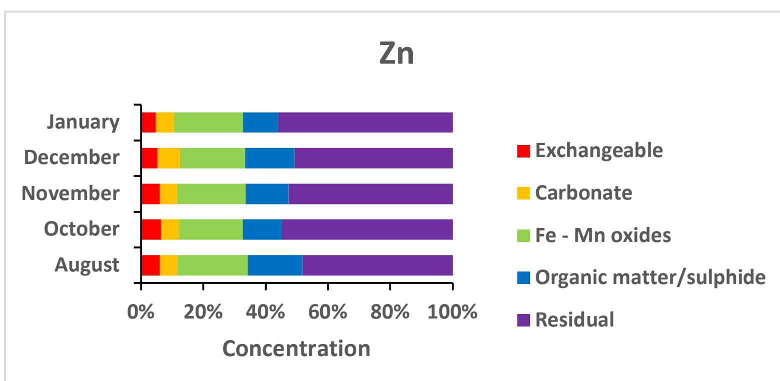
The chemical speciation of metals in the sediments of the Caranzalem beach showed significant (> 25 %) proportion of Fe (August to January), Mn (October), Zn (August to January), Co (August to January) and Ni (August to January) in the residual fraction. It indicated that these metals were derived from the natural weathering of the catchment area rocks. The residual fraction is considered as environmentally unreactive and immobile fraction where metals are strongly held in the lattice structure of minerals in the sediments **(Tessier et al. 1979)**. Therefore, the metals in this fraction revealed natural source of these metals in the Caranzalem beach sediments.

Additionally, metals were also associated with one or more bioavailable fractions. It indicated their anthropogenic sources in the study area. Basically, the metals derived from the anthropogenic sources are adsorbed on the surface of the sediments in their bioavailable forms **(Bhatkhande and Nasnodkar 2022)**. Fe was considerably present in its bioavailable form in the Fe – Mn oxide fraction. Fe is a redox sensitive element and tends to precipitate as oxide / hydroxide under oxic conditions **(Bhutia et al. 2023)**. Thereby, increases its level in the sediments. Similar to Fe, the presence of considerable proportion of Mn in the Fe – Mn oxide fraction was attributed to its precipitation as oxides or hydroxides in sediments. It was also strongly bound to the carbonate fraction. The ionic radii of Mn is similar to that of Ca, which enables Mn to replace Ca in carbonate sediments **(Kanetkar et al. 2022)**. The presence of Zn in considerable amount in Fe – Mn oxide and organic matter / sulphide fractions suggested its scavenging onto oxides and hydroxides of Fe and Mn, and complexation with organic matter forming organo – metallic complexes **(Nasnodkar and Nayak 2019)**. Co and Ni indicated their adsorption onto Fe – Mn oxides and hydroxides in the sediments.

In general, the speciation of metals revealed their bioavailability to biota. For instance, the metals bound to Fe – Mn oxide fraction can get mobilised with depletion in oxygen or development of anoxic conditions **(Zhou et al. 2020)**. The metals bound to organic matter can be mobilised through its degradation by microorganisms **(Fernandes and Nayak 2016)**. This microbial process will involve the utilisation of oxygen and result in anoxic conditions, that will eventually un – stabilize / desorb metals scavenged onto Fe – Mn oxides or hydroxides in sediments **(Giraldo 2018)**. Additionally, the presence of Zn above 10 % in the labile fraction constitute its bioavailability with changes in ionic composition and hydrogen ion concentration of water **(Dias and Nayak 2016)**.







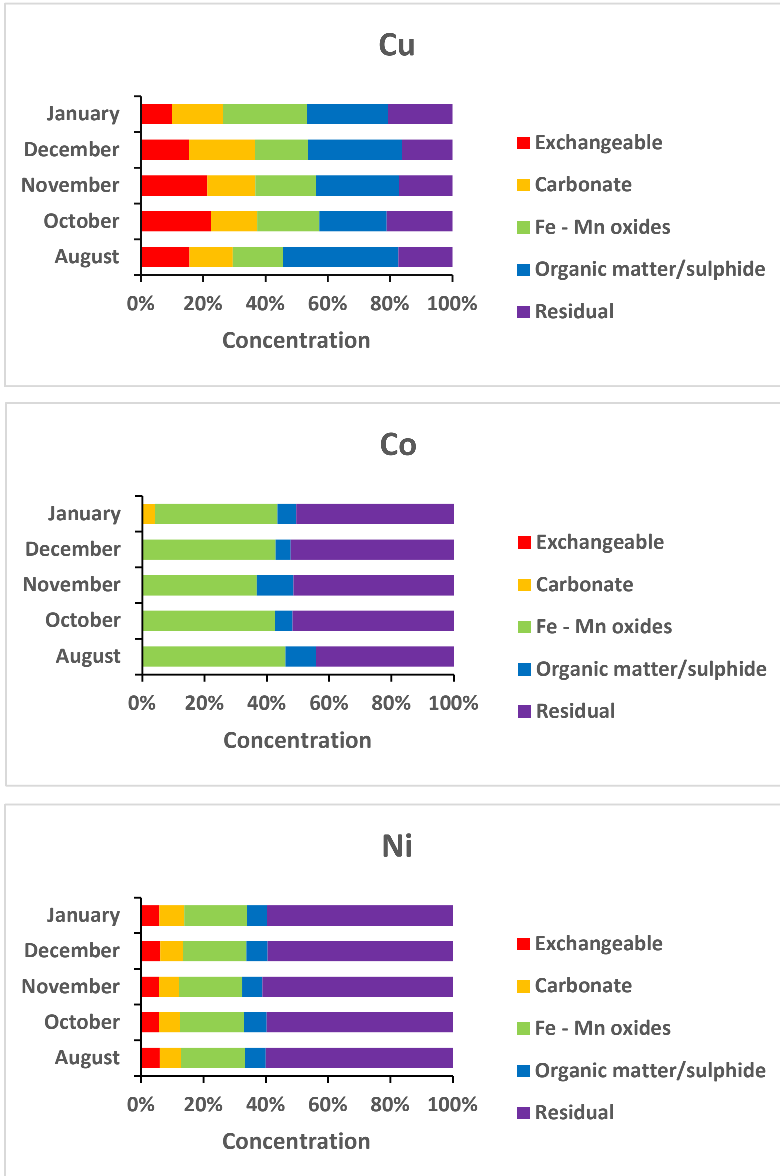


Fig 3.4: The speciation of metals in sediments of the Caranzalem beach.

3.2.4 Metal toxicity assessment

3.2.4.1 Risk Assessment Code (RAC)

Table 3.6: Risk Assessment Code (RAC) for metals in sediments. (ND = Not Detected)

Metals	RAC % (labile fraction: exchangeable and carbonate)				
	August	October	November	December	January
Fe	0.09	0.53	0.21	0.16	0.09
Mn	60.90	50.00	57.54	51.71	58.70
Zn	11.57	12.21	11.53	12.43	10.54
Cu	29.55	37.34	36.71	36.58	26.35
Co	ND	ND	ND	ND	4.11
Ni	12.79	12.50	12.18	13.33	13.84

The RAC analysis indicated very high risk of Mn to marine biota during August, November, December and January (Table 3.6). Also, it displayed high risk during October to biota. Even, Cu revealed its high risk to marine biota during October, November and December months. Zn indicated medium level of risk to biota during August, November and December months, while Cu suggested medium level of risk to biota during August. The medium risk of Ni to biota was observed during August to January period. Thus, RAC indicated very high-high-medium degree of risk of Mn, Zn, Cu and Ni to the marine biota.

3.2.4.2 Screening Quick Reference Table (SQUIRT)

Table 3.7: Screening Quick Reference Table (SQUIRT) and bioavailable concentration of metals in the sediments.

Metal	Threshold Effect Level (TEL)	Effect Range Low (ERL)	Probable Effect Low (PEL)	Effect Range Median (ERM)	Apparent Effect Threshold (AET)	Bioavailable concentration				
						Aug	**Oct**	**Nov**	**Dec**	**Jan**
Fe (%)	-	-	-	-	22 (Neanthes)	0.41	0.41	0.41	0.38	0.25
Mn (ppm)	-	-	-	-	260 (Neanthes)	1011	963	711	678	1039
Zn (ppm)	124	150	271	410	410 (Infaunal Community Impacts)	20	18	19	19	19
Cu (ppm)	18.7	34	108	270	390 (Microtox & Oyster Larvae)	49	41	53	52	45
Co (ppm)	-	-	-	-	10 (Neanthes)	6	5	5	5	6
Ni (ppm)	15.9	20.9	42.8	51.6	110 (Echinoderm Larvae)	13	14	13	12	13

Also, SQUIRT displayed higher concentration of bioavailable Mn in sediments than the Apparent Effect Threshold (AET) value (Table 3.7). Thus, it suggested toxicity of Mn to biota through its mobilization from sediments by action of physico-chemical properties of seawater. Mn is considered as the least toxic essential trace element, however high concentrations of Mn could cause changes in brain function and feeding behaviour; and could lead to a decrease and increase in Fe and Zn concentrations respectively in the body. High concentrations of Zn may become toxic to fish and compete for similar binding sites such as Cu and Fe in the digestive tract during absorption and can reduce hemoglobin levels. Increased levels of Cu concentrations could lead to decrease in metabolic rate and cause oxidative stress due to gill damage **(Lall and Kaushik 2021)**. High Ni concentration can also result in oxidative stress and cause DNA damage **(Palermo et al. 2015).**

3.3 Bioaccumulation of metals in fish.

Table 3.8: The concentration of metals in soft tissues of fish from coastal waters of Caranzalem beach. (ND = Not Detected)

Months	Species	Tissues	Fe (ppm)	Mn (ppm)	Zn (ppm)	Cu (ppm)	Co (ppm)	Ni (ppm)
August	*S. longiceps*	Muscles	116	6	111	17	0.57	2
		Gills	1650	190	268	18	2	4
		Liver	1980	76	197	467	7	23
		Kidney	10874	237	1185	4438	103	314
	S. fimbriata	Muscles	89	4	28	27	2	2
		Gills	2567	107	319	84	3	8
		Liver	3192	47	162	423	10	33
		Kidney	6713	106	349	1152	33	117
	T. jarbua	Muscles	97	4	57	27	0.79	2
		Gills	898	66	203	99	2	8
		Liver	1010	31	111	172	4	13
		Kidney	2847	55	246	597	ND	61
	J. belangerii	Muscles	57	2	16	14	ND	2
		Gills	477	36	138	68	2	6
		Liver	1188	15	86	131	4	13
		Kidney	3845	70	351	1149	ND	102
October	*N. nasus*	Muscles	103	4	29	38	ND	2
		Gills	1267	90	116	48	1	5
		Liver	1412	52	198	79	ND	8
		Kidney	1510	41	1574	560	ND	43
	M. cephalus	Muscles	88	3	30	31	0.58	3
		Gills	1794	97	89	96	2	8
		Liver	2085	22	131	356	ND	21
		Kidney	5354	102	467	1455	47	159
	L. lactarius	Muscles	65	3	26	22	ND	4
		Gills	714	48	165	73	3	6
		Liver	1450	34	164	575	ND	45

		Kidney	6260	175	810	3707	104	291
	O. ruber	Muscles	74	3	21	30	0.82	3
		Gills	50	5	15	20	ND	2
		Liver	139	6	36	110	ND	5
		Kidney	1416	28	142	427	18	51
	P. indicus	Muscles	43	2	21	16	ND	2
		Gills	545	49	191	61	2	6
		Liver	509	9	137	134	ND	12
		Kidney	1183	26	224	330	17	35
	G. filamentous	Muscles	62	6	127	27	ND	3
		Gills	546	68	436	74	1	5
		Liver	1656	44	565	711	13	51
		Kidney	5552	151	1292	2430	102	274
November	*R. kanagurta*	Muscles	20	1	9	10	0.71	1
		Gills	3024	213	269	19	3	6
		Liver	348	22	411	73	2	5
		Kidney	1055	80	393	175	8	30
	N. nasus	Muscles	26	1	14	8	0.54	1
		Gills	1245	22	26	11	0.95	2
		Liver	648	38	614	200	5	15
		Kidney	1176	23	801	105	4	16
	G. filamentous	Muscles	51	4	35	18	0.55	2
		Gills	714	140	149	17	2	3
		Liver	1338	23	347	56	3	6
		Kidney	1692	60	1486	311	8	30
	A. djedeba	Muscles	60	3	117	24	0.66	2
		Gills	2428	66	323	32	1	4
		Liver	94	2	22	14	0.93	2
		Kidney	1233	20	497	276	ND	37
December	*M. cephalus*	Muscles	221	5	101	37	ND	2
		Gills	3750	342	126	41	3	7
		Liver	91	6	33	34	3	3

		Kidney	1150	24	325	208	8	21
	R. kanagurta	Muscles	222	7	35	26	0.58	2
		Gills	17199	2073	871	25	3	7
		Liver	558	20	234	55	2	4
		Kidney	1138	60	291	253	7	18
	N. nasus	Muscles	216	8	35	32	0.63	2
		Gills	3173	1419	178	35	2	7
		Liver	1481	30	155	229	8	18
		Kidney	2502	110	1705	492	12	35
	G. filamentous	Muscles	244	16	77	33	0.55	3
		Gills	2556	145	176	72	3	8
		Liver	1485	68	209	304	11	16
		Kidney	4384	158	1155	1991	69	155
January	*R. kanagurta*	Muscles	146	4	129	38	1	2
		Gills	2398	227	279	27	2	5
		Liver	523	19	98	72	3	4
		Kidney	1717	70	548	591	16	40
	S. longiceps	Muscles	459	8	196	42	0.73	2
		Gills	3071	671	566	20	2	4
		Liver	8853	102	318	344	16	30
		Kidney	17705	66	576	876	30	51
	S. barracuda	Muscles	68	3	22	30	ND	2
		Gills	1387	107	322	45	2	4
		Liver	316	13	221	100	ND	4
		Kidney	1316	37	480	395	8	23
	M. cephalus	Muscles	99	5	91	22	0.87	2
		Gills	3250	684	307	57	4	9
		Liver	1791	21	307	157	6	9
		Kidney	2500	91	869	1329	24	54

The concentration of metals in soft tissues of fish from the coastal waters of Caranzalem beach is presented in the Table 3.8 and Fig 3.5, 3.6, 3.7, 3.8, 3.9, 3.10. The fish species collected in the month of August (*S. longiceps, S. fimbriata, T. jarbua, J. belangerii*), October (*N. nasus, M. cephalus, L. lactarius, O. ruber, P. indicus, G. filamentous – except muscles*), November (*R. kanagurta – except liver, N. nasus, G. filamentous, A. djedeba*), December (*M. cephalus, R. kanagurta, N. nasus, G. filamentous*) and January (*R. kanagurta, S. longiceps, S. barracuda, M. cephalus*) accumulated highest concentration of Fe in their soft tissues. It was followed by either Zn or Cu.

The fish species showed high preference towards Fe, Zn and Cu which was attributed to their importance in growth and metabolic activities **(WHO 1989)**. Fe is essential for transport of oxygen and cell growth regulation **(Lall and Kaushik 2021).** Zn is an important micronutrient for all living organisms and is a catalyst for 300 different enzymes in aquatic life **(Job et al. 2023)**. Cu is a vital component for different enzymes and is necessary for the formation of hemoglobin **(Sivaperumal et al. 2007)**. These essential elements are present in the bodies of living organisms and have an important role in different physiological processes.

In August, *S. longiceps, S. fimbriata* (similar concentration of Mn in gills and kidney)*, T. jarbua* (except Mn and Co), *J. belangerii* (except Co) exhibited highest accumulation of all metals in the kidney than other tissues. Among the remaining soft tissues, it was liver and gills which held considerable proportion of metals. The muscles tissues retained lowest concentration of most of the metals.

In October, *N. nasus* (except Mn), *M. cephalus*, *L. lactarius*, *O. ruber*, *P. indicus* (except Mn) and *G. filamentous* showed high accumulation of metals in kidney, followed by liver or gills. The lowest concentration of most metals was reported in the muscles.

In November, *R. Kanagurta* the metals viz., Fe and Mn were more in the gills, while Zn was high in the liver. The Cu, Co and Ni were accumulated more in the kidney. *N. nasus* had more of Fe in the gills, while accumulated high concentration of Mn, Cu and Cu in the liver. The metals viz., Zn and Ni were more in the Kidney. *G.*

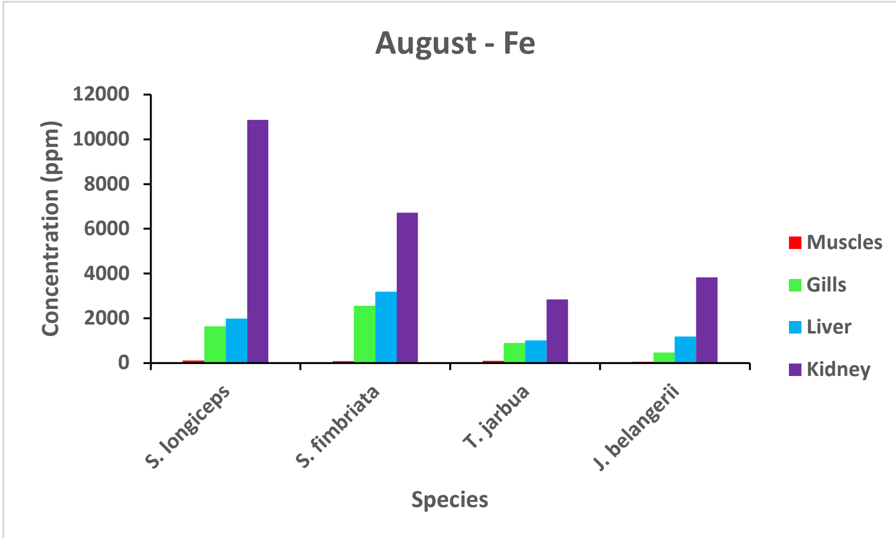
Filamentous showed high accumulation of Fe, Zn, Cu, Co and Ni in the kidney, whereas Mn was more in the gills. Fe and Mn were highly accumulated in the gills, while rest of the metals were more in the kidney of *A. djedeba*. The muscle tissue had lowest concentration of metals in fish species.

In December, *M. cephalus* and *N. nasus* showed high concentration of Fe and Mn in the gills and more of Zn, Cu, Co and Ni in the kidney. *R. kanagurta* accumulated more of Fe, Mn and Zn in the gills and showed high concentration of Cu, Co and Ni in the kidney. *G. filamentous* showed high accumulation of all metals in the kidney. The muscle tissue had lowest concentration of metals in fish species.

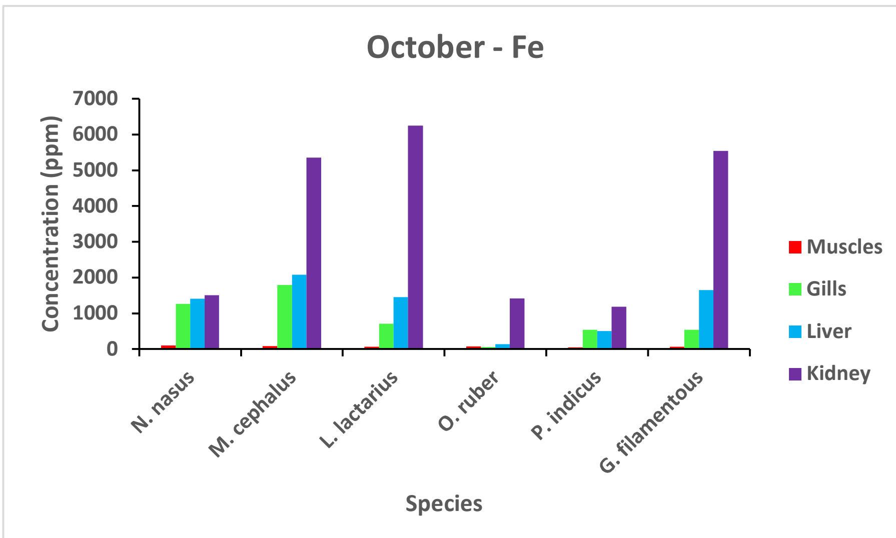
In January, *R. kanagurta*, *S. barracuda* and *M. cephalus* exhibited high concentration of Fe and Mn in gills and more of Zn, Cu, Co and Ni in kidney. *S. longiceps* showed high accumulation of Fe, Zn, Cu, Co and Ni in the kidney, whereas Mn was more in the gills. The muscle tissue had lowest concentration of metals in fish species.

In general, the most of the fish species collected from the coastal water of the Caranzalem beach revealed high retention of most metals in the kidney tissue, followed by gills or liver. The muscle tissue had lowest concentration of metals. Different metals choose different tissues based on their metabolic activity. Kidney is a major site for metal accumulation in fishes due to its role in physiological functions such as filtration, excretion and ion regulation **(Javed and Usmani 2017)**. Since gills are in direct contact with the surrounding water and suspended material they might show a higher concentration of metals. Due to the process of osmoregulation and exchange of gas the gills act as a barrier between the metal ion exchange from the water **(Ahmed et al. 2016)**. Among all the other tissues liver acts as a primary organ for metal storage **(Roesijadi 1996; Amiard et al. 2006)** and plays an important role in metabolic processes of metals in fish and is related to natural binding of metallothionein (MT) proteins **(Görür et al. 2012)**. It is well known that muscles are not an active site for metal biotransformation and accumulation **(Elnabris et al. 2013)**. Therefore, less metal concentration was observed in the muscle tissues.

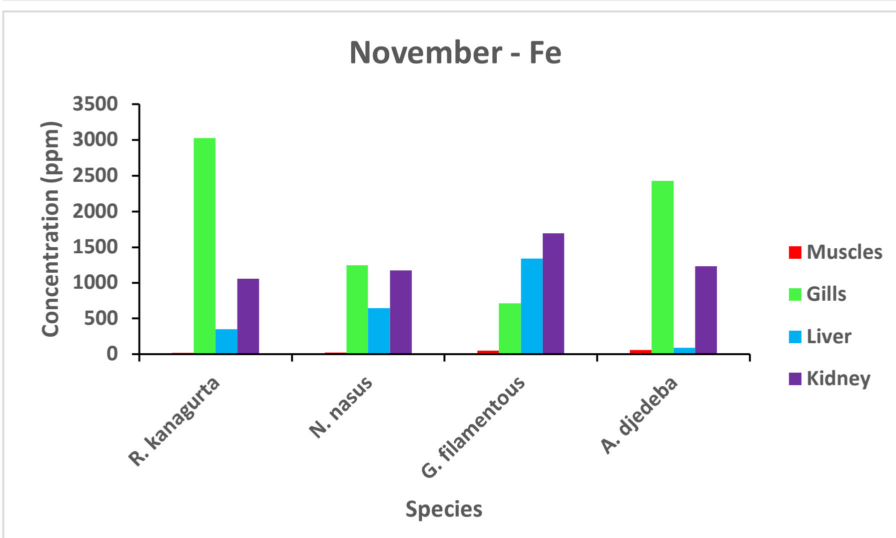
The concentration of a given metal varied among different fish species, and also displayed variability in concentration in similar species collected during different months of sampling. The discrepancies in the level of metals in fish species were attributed to intrinsic (genotype, phenotype, sex, age, size, etc.,) and extrinsic factors (sources of metals, pH, salinity, Eh, dissolved oxygen, temperature, ionic composition, etc.,) governing the bioavailability and bioaccumulation processes **(Sankar et al. 2006; Anandkumar et al. 2018)**. Therefore, it is important to study the bioaccumulation of metal contaminants in edible and economically important marine fishes. Since, it has a direct impact on human health through consumption it is mandatory to determine the products of these contaminants and its impact on human health **(Patchaiyappan et al. 2023)**.



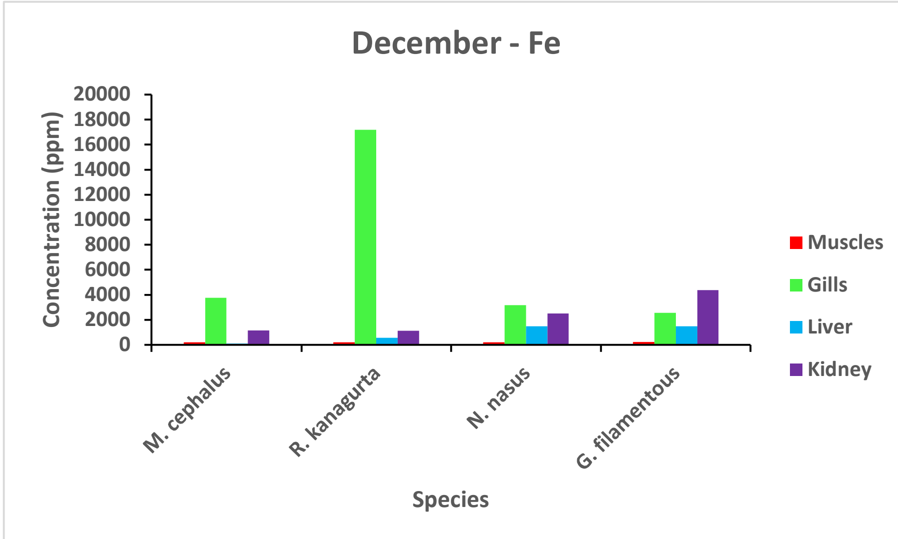
August - Fe
Concentration (ppm)
12000
10000
8000
6000
4000
2000
0
S. longiceps
S. fimbriata
T. jarbua
J. belangerii
Species
Muscles
Gills
Liver
Kidney



October - Fe
Concentration (ppm)
7000
6000
5000
4000
3000
2000
1000
0
N. nasus
M. cephalus
L. lactarius
O. ruber
P. indicus
G. filamentous
Species
Muscles
Gills
Liver
Kidney



November - Fe
Concentration (ppm)
3500
3000
2500
2000
1500
1000
500
0
R. kanagurta
N. nasus
G. filamentous
A. djedeba
Species
Muscles
Gills
Liver
Kidney



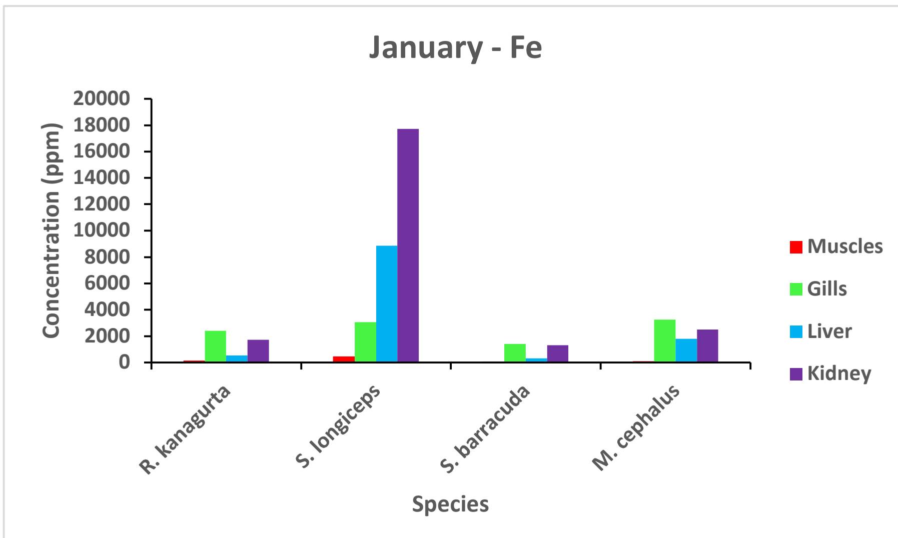
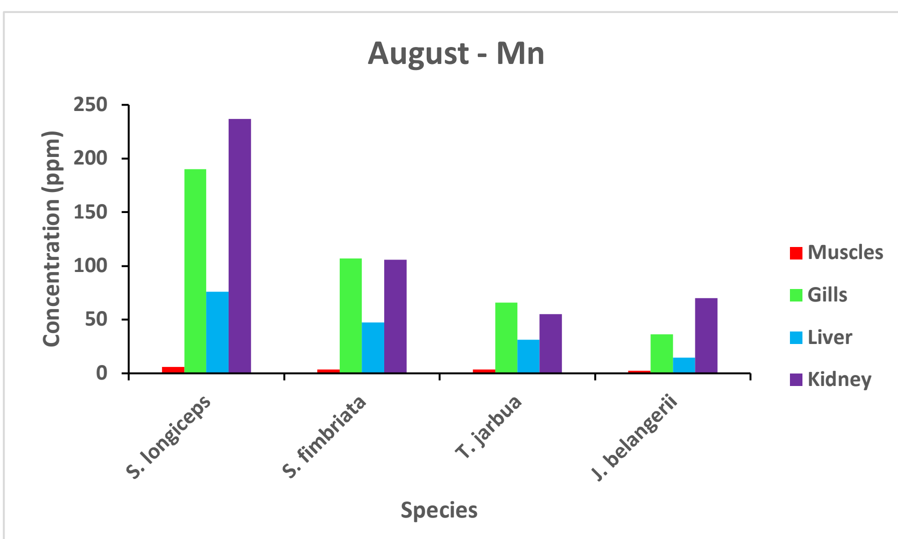
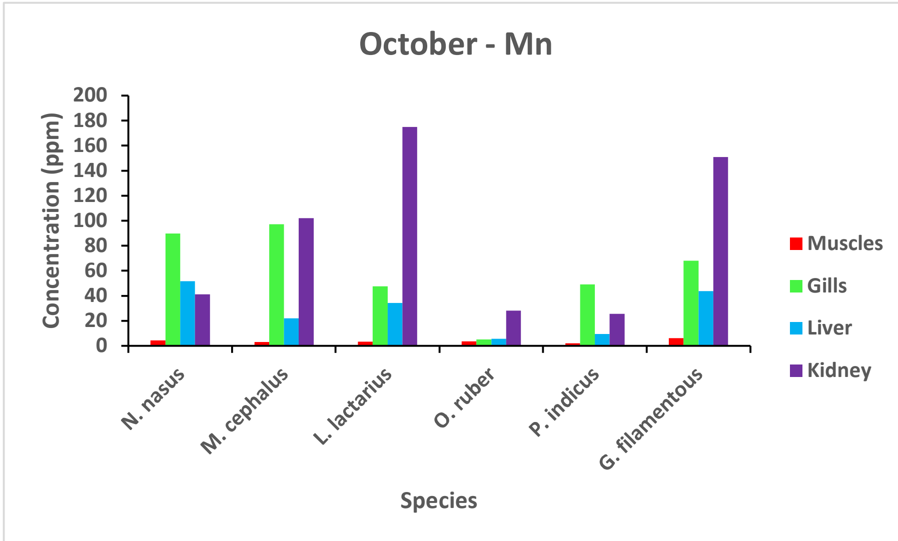
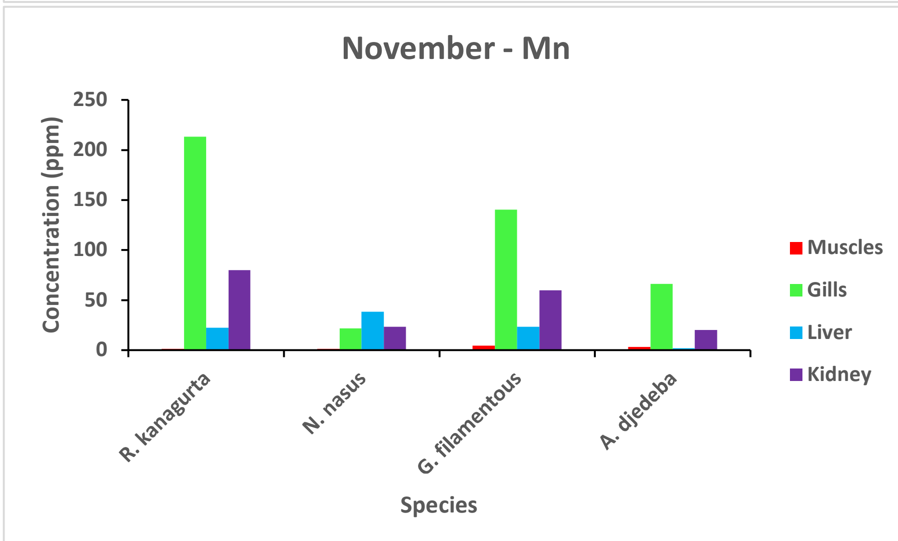
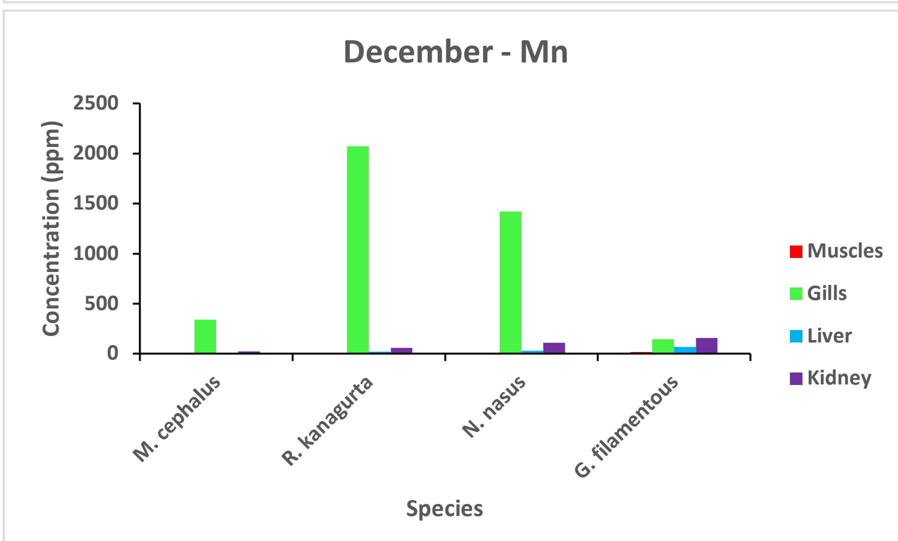


Fig 3.5: The concentration of Fe in tissues of fish from the Caranzalem beach.




October - Mn
Concentration (ppm)
200
180
160
140
120
100
80
60
40
20
0
N. nasus
M. cephalus
L. lactarius
O. ruber
P. indicus
G. filamentous
Species
Muscles
Gills
Liver
Kidney


November - Mn
Concentration (ppm)
250
200
150
100
50
0
R. kanagurta
N. nasus
G. filamentous
A. djedeba
Species
Muscles
Gills
Liver
Kidney


December - Mn
Concentration (ppm)
2500
2000
1500
1000
500
0
M. cephalus
R. kanagurta
N. nasus
G. filamentous
Species
Muscles
Gills
Liver
Kidney

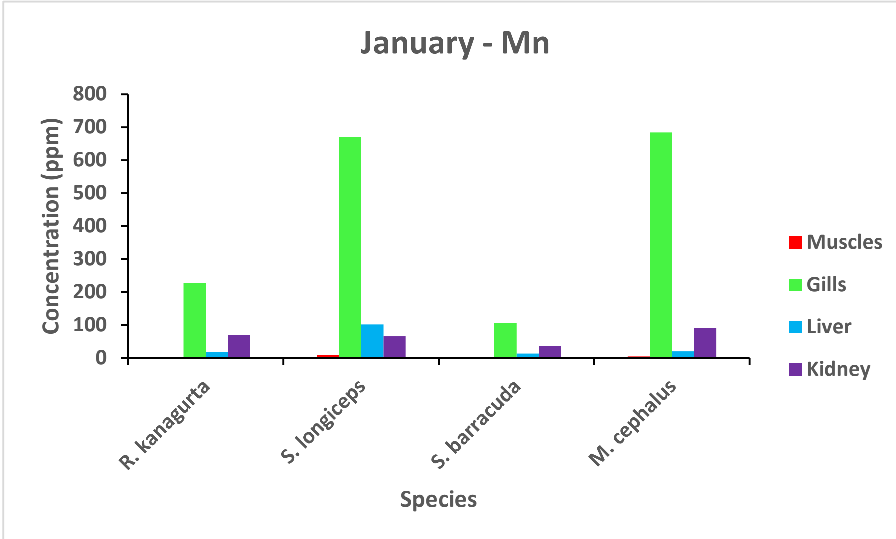
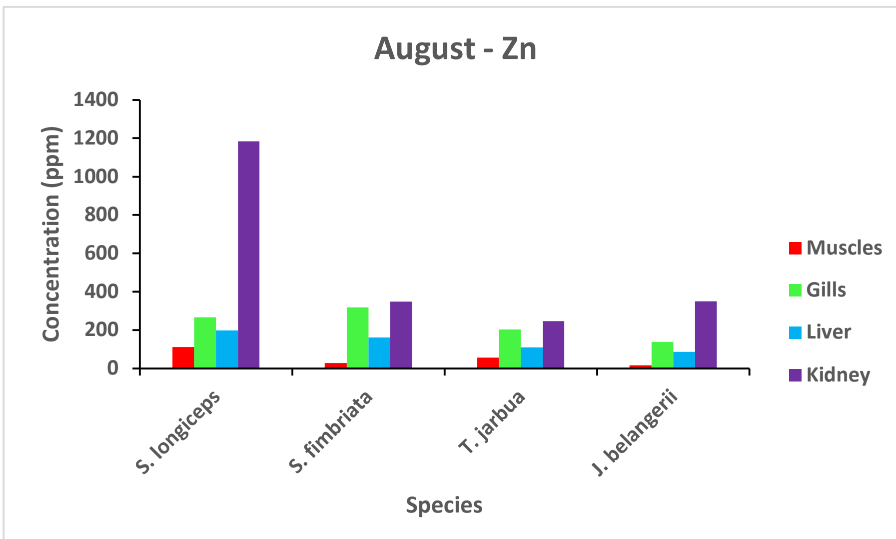
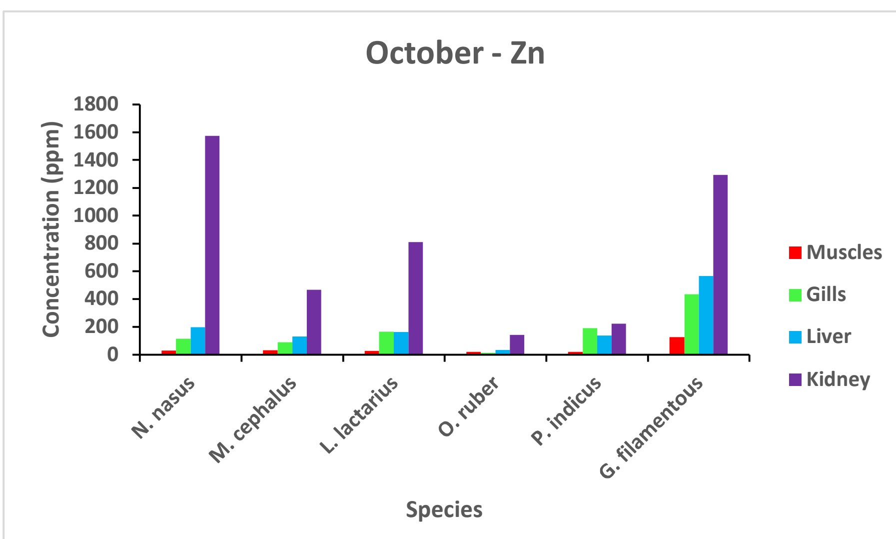


Fig 3.6: The concentration of Mn in tissues of fish from the Caranzalem beach.





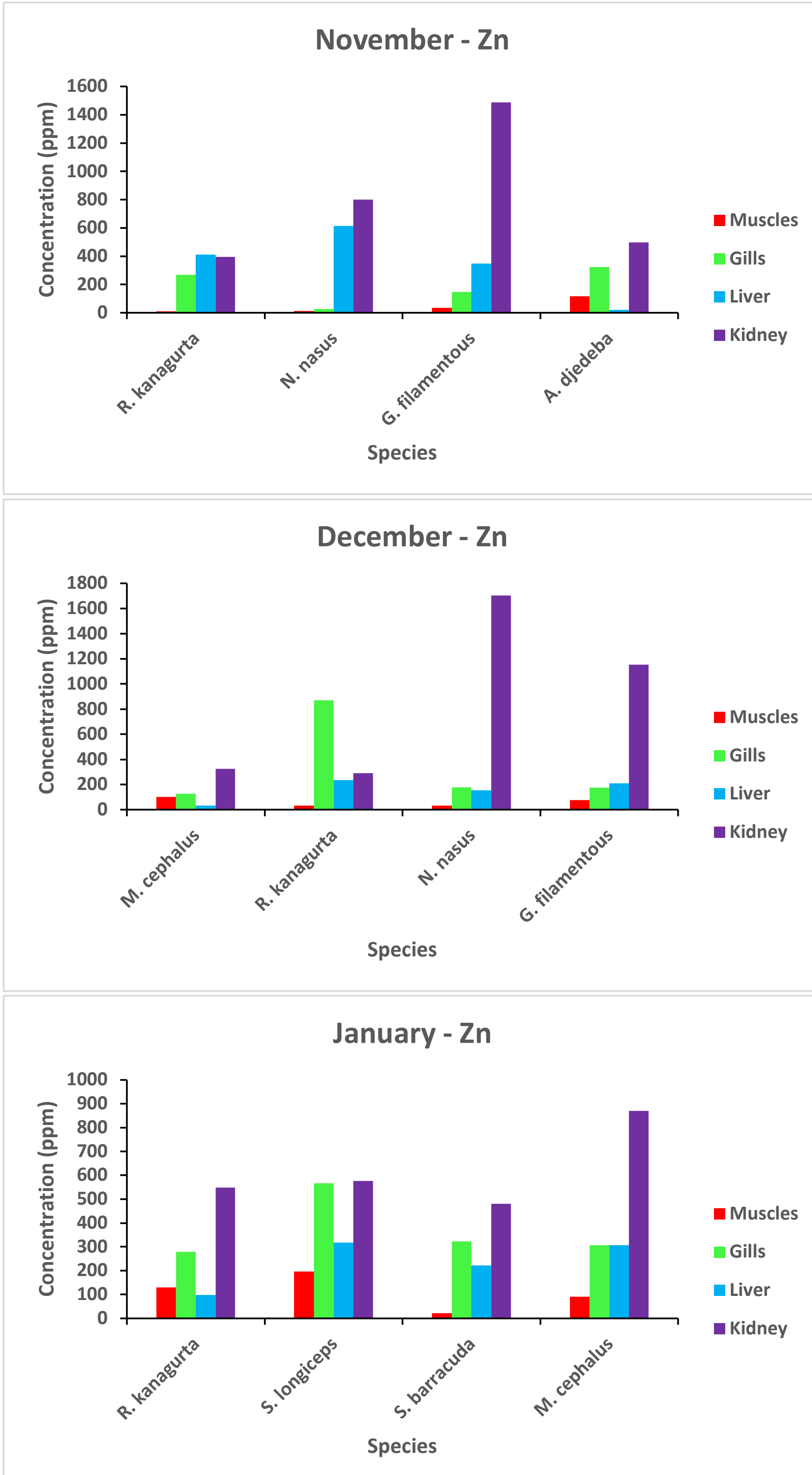
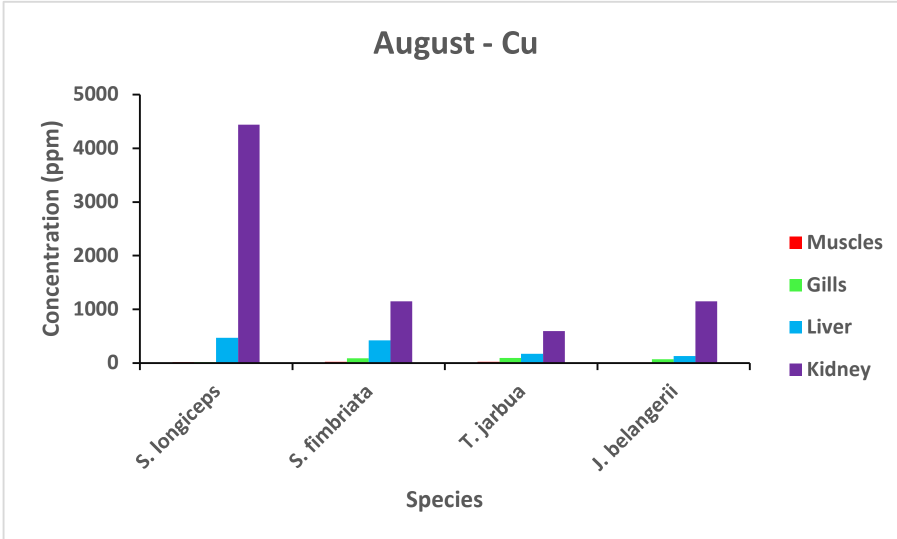
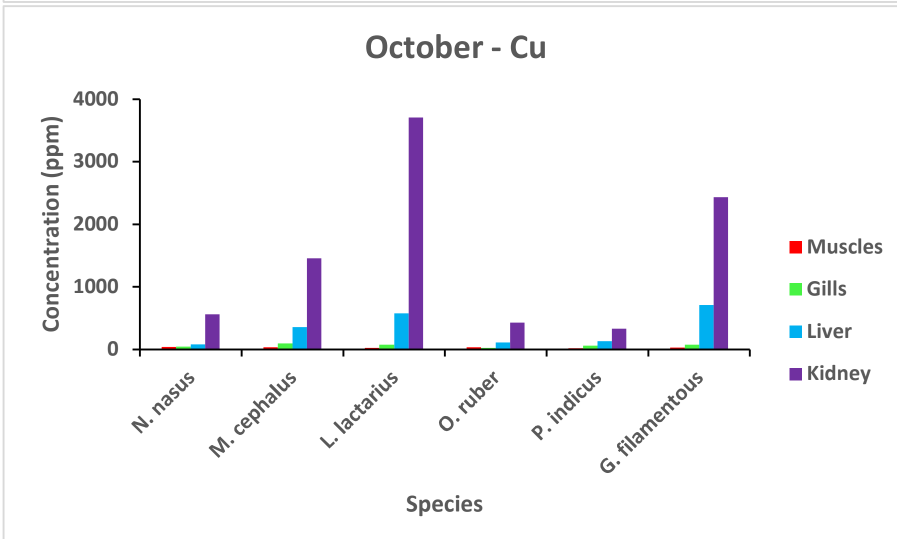
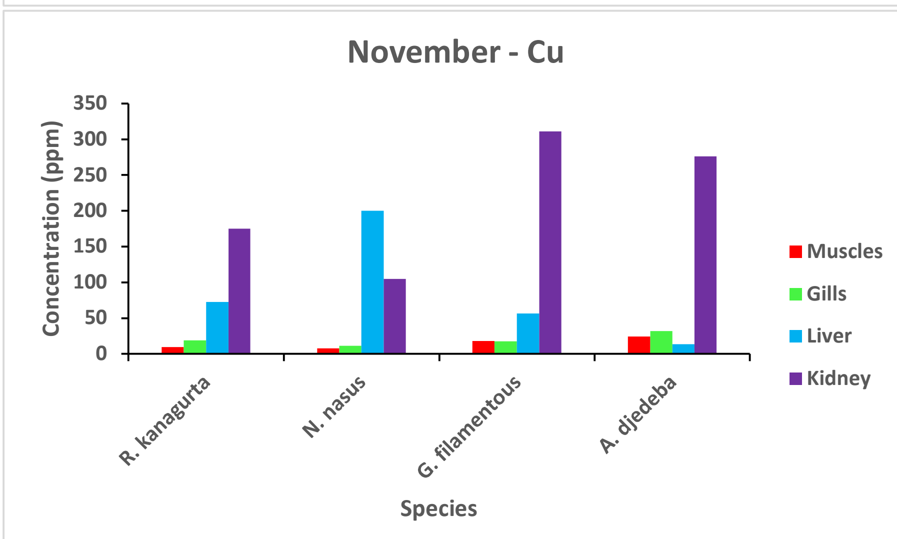


Fig 3.7: The concentration of Zn in tissues of fish from the Caranzalem beach.


August - Cu
Concentration (ppm)
5000
4000
3000
2000
1000
0
S. longiceps
S. fimbriata
T. jarbua
J. belangerii
Species
Muscles
Gills
Liver
Kidney


October - Cu
Concentration (ppm)
4000
3000
2000
1000
0
N. nasus
M. cephalus
L. lactarius
O. ruber
P. indicus
G. filamentous
Species
Muscles
Gills
Liver
Kidney


November - Cu
Concentration (ppm)
350
300
250
200
150
100
50
0
R. kanagurta
N. nasus
G. filamentous
A. djedeba
Species
Muscles
Gills
Liver
Kidney

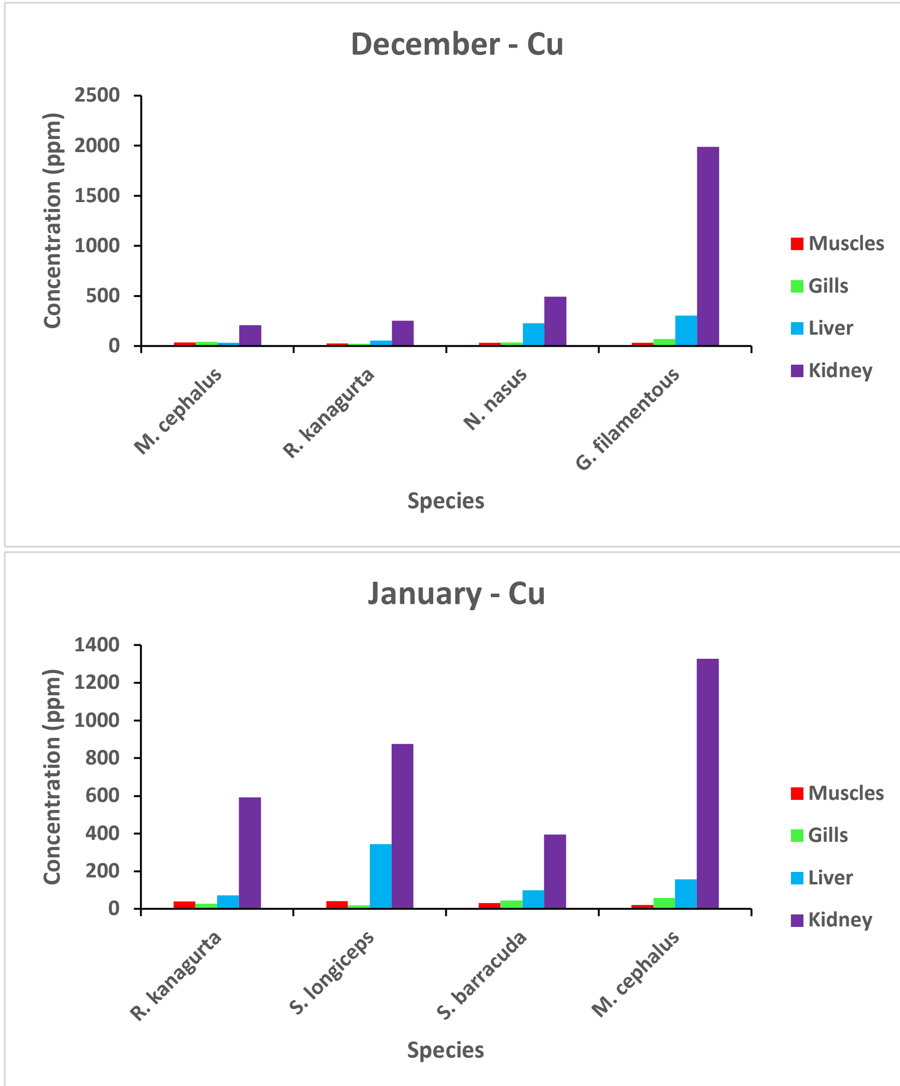
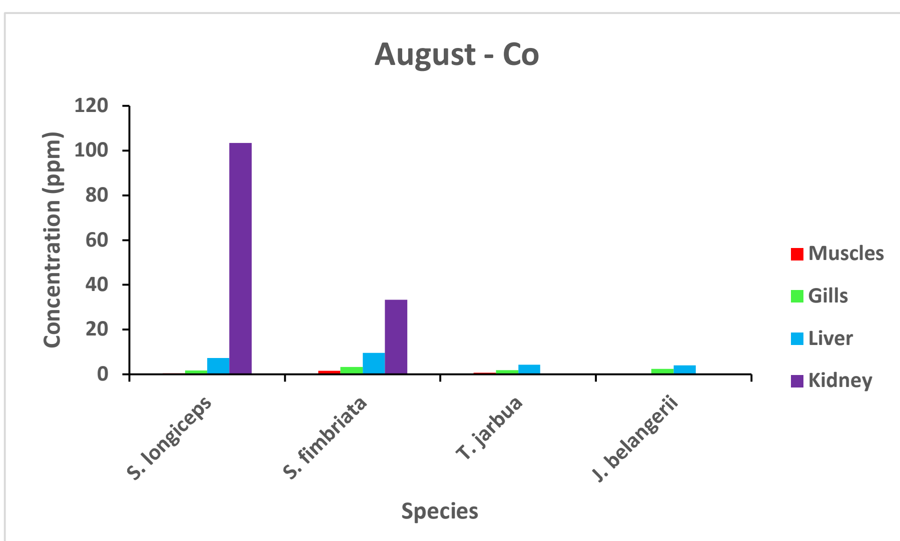
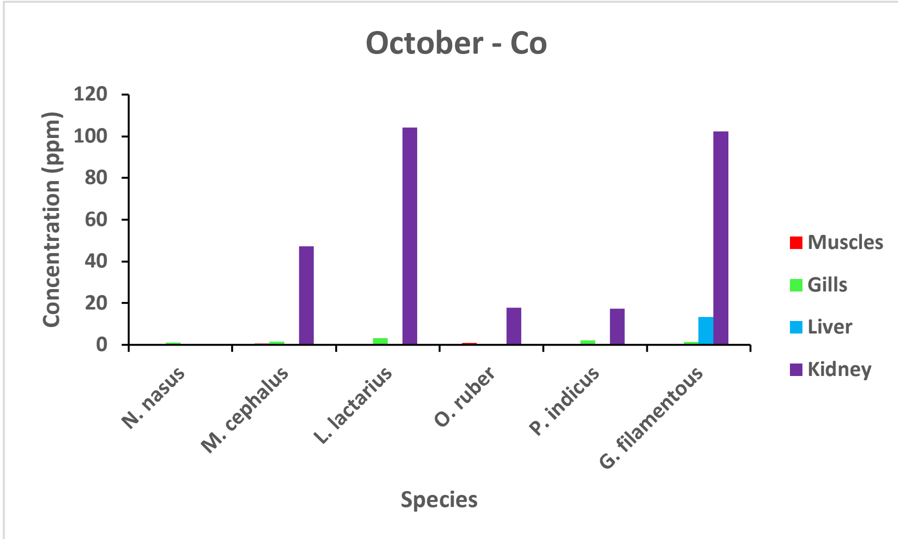
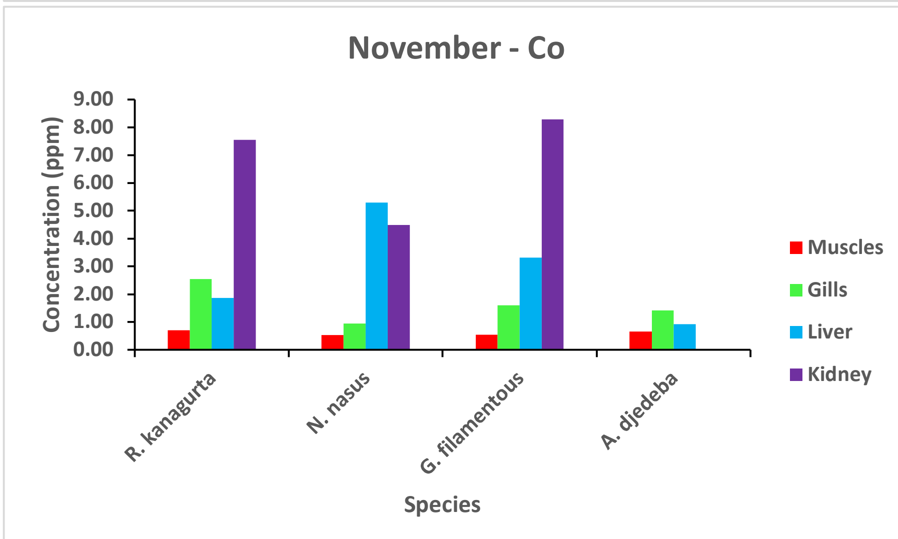
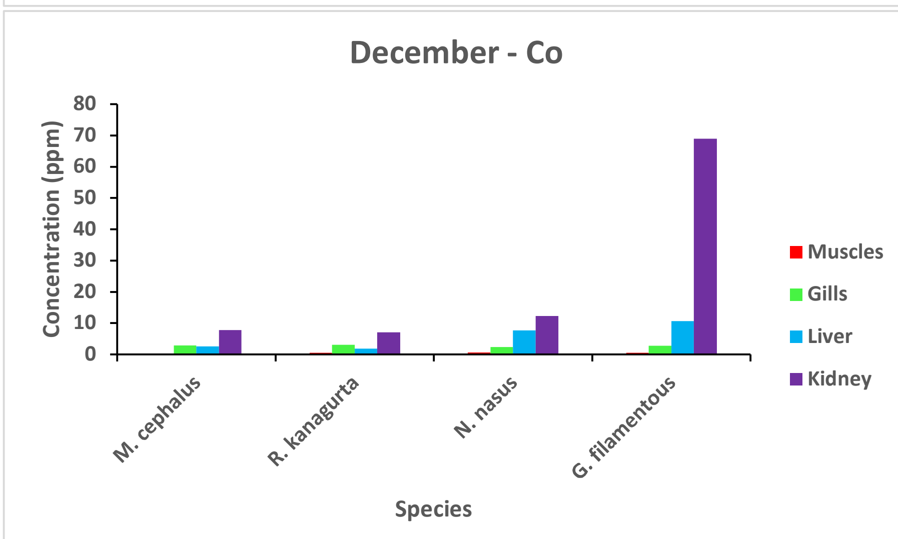


Fig 3.8: The concentration of Cu in tissues of fish from the Caranzalem beach.




October - Co
Concentration (ppm)
120
100
80
60
40
20
0
N. nasus
M. cephalus
L. lactarius
O. ruber
P. indicus
G. filamentous
Species
Muscles
Gills
Liver
Kidney


November - Co
Concentration (ppm)
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
R. kanagurta
N. nasus
G. filamentous
A. djedeba
Species
Muscles
Gills
Liver
Kidney


December - Co
Concentration (ppm)
80
70
60
50
40
30
20
10
0
M. cephalus
R. kanagurta
N. nasus
G. filamentous
Species
Muscles
Gills
Liver
Kidney

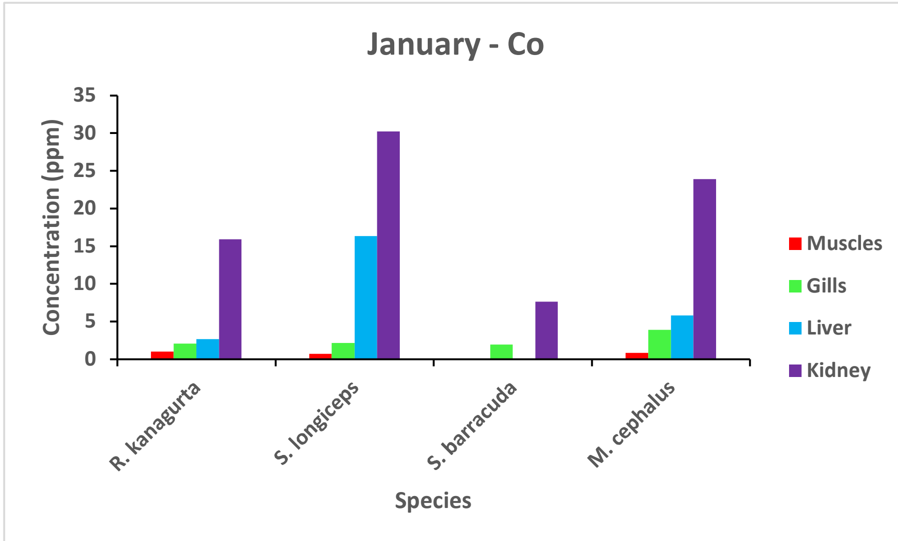
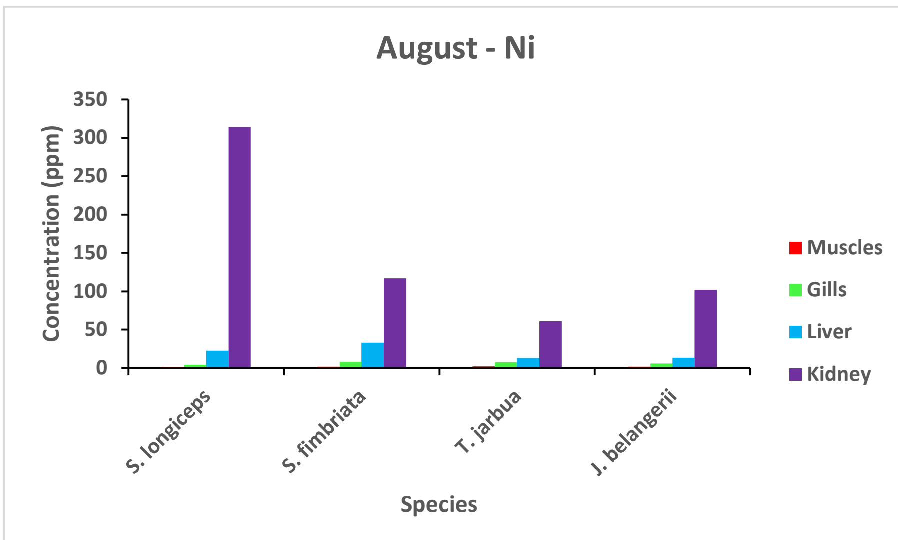
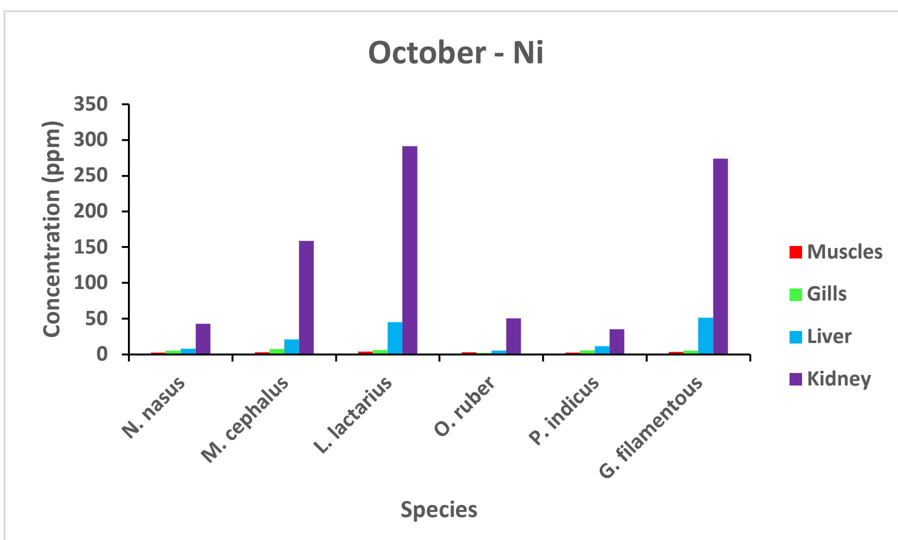


Fig 3.9: The concentration of Co in tissues of fish from the Caranzalem beach.





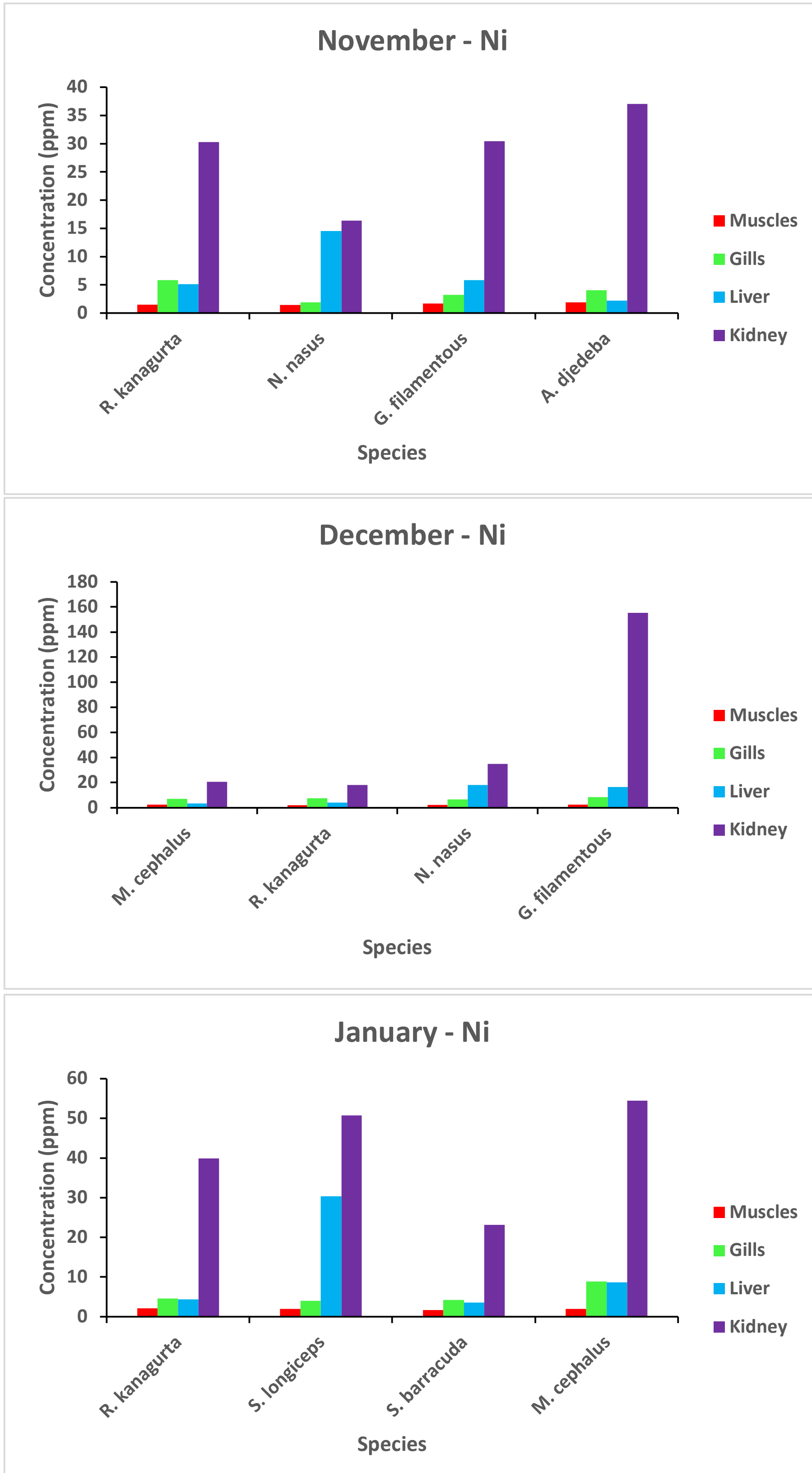


Fig 3.10: The concentration of Ni in tissues of fish from the Caranzalem beach.

3.3.1 modified Biota Sediment Accumulation Factor (mBSAF)

Table 3.9: modified Biota Sediment Accumulation Factor (mBSAF)

Months	Species	mBSAF					
		Fe	Mn	Zn	Cu	Co	Ni
August	*S. longiceps*	3.58	0.50	88.06	100.37	18.84	26.32
	S. fimbriata	3.08	0.26	42.88	34.26	7.99	12.32
	T. jarbua	1.19	0.15	30.85	18.18	1.15	6.46
	J. belangerii	1.36	0.12	29.56	27.66	1.08	9.41
October	*N. nasus*	1.04	0.19	106.48	17.72	0.22	4.17
	M. cephalus	2.26	0.23	39.84	47.34	9.87	13.62
	L. lactarius	2.06	0.27	64.69	106.94	21.44	24.77
	O. ruber	0.41	0.04	11.88	14.32	3.74	4.33
	P. indicus	0.55	0.09	31.86	13.21	3.90	3.92
	G. filamentous	1.90	0.28	134.41	79.20	23.47	23.83
November	*R. kanagurta*	1.09	0.45	56.98	5.21	2.53	3.29
	N. nasus	0.76	0.12	76.58	6.11	2.26	2.63
	G. filamentous	0.93	0.32	106.16	7.60	2.75	3.16
	A. djedeba	0.94	0.13	50.49	6.53	0.60	3.48
December	*M. cephalus*	1.36	0.56	30.81	6.16	2.64	2.80
	R. kanagurta	4.98	3.18	75.25	6.89	2.48	2.64
	N. nasus	1.92	2.31	109.04	15.15	4.59	5.16
	G. filamentous	2.26	0.57	85.14	46.13	16.57	15.20
January	*R. kanagurta*	1.92	0.31	55.48	16.18	3.61	3.91
	S. longiceps	12.06	0.82	87.17	28.49	8.25	6.69
	S. barracuda	1.24	0.15	55.01	12.67	1.59	2.50
	M. cephalus	3.06	0.77	82.82	34.76	5.74	5.68

During August, all species (*S. longiceps*, *S. fimbriata*, *T. jarbua* and *J. belangerii*) were macro-accumulator of Zn, Cu and Ni; and de-accumulator of Mn (Table 3.9). Also, *S. longiceps* and *S. fimbriata* were macro-accumulator of Fe and Co. *T. jarbua* and *J. belangerii* were micro-accumulator of Fe and Co. During October, all species (*N. nasus, M. cephalus, L. lactarius, O. ruber, P. indicus* and *G. filamentous)* were macro-accumulator of Zn, Cu and Ni; and de-accumulator of Mn. Also, *M. cephalus* and *L. lactarius* were macro-accumulator of Fe and Co. Similarly, *O. ruber, P. indicus* and *G. filamentous* were macro-accumulator of Co. The *N. nasus* and *G. filamentous* were micro-accumulator of Fe. Also, *O. ruber* and *P. indicus* were de-accumulator of Fe. During November, all species (*R. kanagurta, N. nasus, G. filamentous* and *A. djedeba*) were macro-accumulator of Zn, Cu and Ni; and de-accumulator of Mn. Also, *R. kanagurta, N. nasus* and *G. filamentous* were macro-accumulator of Co. The *R. kanagurta* was a micro-accumulator of Fe, whereas, *N. nasus* and *G. filamentous* were de-accumulator of Fe; and *A. djedeba* was de-accumulator of Fe and Co. During December, all species (*M. cephalus, R. kanagurta, N. nasus* and *G. filamentous*) were macro-accumulator of Zn, Cu, Co and Ni. Similarly, *R. kanagurta* was a macro-accumulator of Fe and Mn, *N. nasus* was a macro-accumulator of Mn, and *G. filamentous* was a macro-accumulator of Fe. The *M. cephalus* and *N. nasus* were micro-accumulator of Fe. The *M. cephalus* and *G. filamentous* were de-accumulator of Mn. During January, all species (*R. kanagurta, S. longiceps, S. barracuda* and *M. cephalus*) were macro-accumulator of Zn, Cu and Ni; and de-accumulator of Mn. Also, *S. longiceps* and *M. cephalus* were macro-accumulator of Fe and Co; and *R. kanagurta* was a macro-accumulator of Co. The *R. kanagurta* was a micro-accumulator of Fe, whereas, *S. barracuda* was a micro-accumulator Fe and Co. The mBSAF revealed high affinity of edible fishes towards Zn, Cu and Ni. It was attributed to their importance in growth and metabolic activities. Considering the results of mBSAF the edible fishes had an affinity towards the metals in the increasing order Mn<Fe<Co<Ni<Cu<Zn.

3.3.2 Target Hazard Quotient (THQ)

Table 3.10: Target Hazard Quotient (THQ). (ND = Not Detected)

Months	Species	THQ					
		Fe	Mn	Zn	Cu	Co	Ni
August	*S. longiceps*	10.80	0.03	0.24	11.24	0.01	0.05
	S. fimbriata	8.29	0.02	0.06	17.72	0.02	0.06
	T. jarbua	8.98	0.02	0.12	17.41	0.01	0.07
	J. belangerii	5.27	0.01	0.03	8.85	ND	0.05
October	*N. nasus*	9.56	0.02	0.06	24.64	ND	0.07
	M. cephalus	8.13	0.01	0.07	20.20	0.01	0.09
	L. lactarius	6.05	0.02	0.06	13.99	ND	0.13
	O. ruber	6.83	0.02	0.05	19.24	0.01	0.09
	P. indicus	3.98	0.01	0.05	10.52	ND	0.08
	G. filamentous	5.73	0.03	0.27	17.61	ND	0.11
November	*R. kanagurta*	1.88	0.01	0.02	6.20	0.01	0.05
	N. nasus	2.38	0.01	0.03	5.12	0.01	0.05
	G. filamentous	4.78	0.02	0.08	11.55	0.01	0.06
	A. djedeba	5.55	0.01	0.25	15.80	0.01	0.06
December	*M. cephalus*	20.54	0.03	0.22	24.12	ND	0.08
	R. kanagurta	20.57	0.03	0.07	16.97	ND	0.07
	N. nasus	20.07	0.04	0.07	20.64	ND	0.08
	G. filamentous	22.69	0.08	0.17	21.18	ND	0.08
January	*R. kanagurta*	13.52	0.02	0.28	24.81	0.02	0.07
	S. longiceps	42.63	0.04	0.43	27.55	0.01	0.06
	S. barracuda	6.35	0.01	0.05	19.47	ND	0.05
	M. cephalus	9.18	0.02	0.20	14.15	0.01	0.06

The THQ was determined to evaluate the non-carcinogenic risk due to metals. A THQ value exceeding 1 indicates that there might be potential health risk, whereas, THQ value less than 1 indicates that there is no non-carcinogenic risk to human health. The metals viz., Mn, Zn, Co and Ni revealed THQ less than 1 in edible fish species collected during the months of August, October, November, December and January. Thus, these metals did not pose non-carcinogenic risk to consumers of edible biota. On the other hand, the THQ value for Fe and Cu was greater than 1 and therefore, revealed possibility of non-carcinogenic risk to the consumers of these edible biota. Hence, it is necessary to spread awareness and take effective measures to reduce the levels of metal concentration at the Caranzalem beach.

CHAPTER 4

SUMMARY

AND

CONCLUSIONS

The present study was conducted to determine total metals and their speciation in sediments of the Caranzalem beach and to understand bioaccumulation of metals in soft tissues of edible fish. The sediment and fish samples were retrieved during the months of August, October, November, December and January. The beach sediments were enriched with sand (> 90 %) which was attributed to high hydrodynamics at the beach region. The coarser sediments cause dilution of TOC. The total metals viz., Mn, Cu, Ni as well as Zn (October) and Co (August, November and January) exceeded the upper crustal average value in sediments. Therefore, it indicated enrichment of metals in the sediments of the Caranzalem beach due to anthropogenic activities viz., open-cast ferromanganese ore mining, industrial, agricultural and domestic waste discharge. The CF revealed moderate degree of contamination of Mn, Cu and Ni. The anthropogenic sources of metals viz., ., Mn, Co and Ni were also construed through Igeo. The study of speciation of metals revealed their bioavailability in sediments. Among the bioavailable fractions, metals mainly associated with Fe-Mn oxide and organic matter/sulphide fractions. It suggested bioavailability of metals with changes in Eh and microbial degradation of organic matter. The metals viz., Mn, Zn, Cu and Ni were present in > 10 % in the labile fraction in sediments and thus, revealed high risk of mobilization from sediments to water column to associated biota with changes in ionic composition and hydrogen ion concentration. RAC indicated very high-high-medium degree of risk of Mn, Zn, Cu and Ni to marine biota. Also, SQUIRT suggested toxicity of Mn to biota. Majority of the fish species collected from the coastal waters of Caranzalem revealed high retention of most metals in the kidney tissues, followed by gills or liver. The mBSAF revealed high affinity of edible fishes towards Zn, Cu and Ni. It was attributed to their importance in growth and metabolic activities. The fish species were macro concentrator of Zn, Cu and Ni. The THQ values for Fe and Cu were greater than 1 thus revealed non-carcinogenic risk to humans through their consumption.

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