JOURNAL INDIAN ASSOCIATION OF SEDIMENTOLOGISTS ISSN NO 2582 – 2020
Vol. 38, Issue 2, 2021, pp. 63-78
DOI: https://doi.org/10.51710/jias.v38i2.141

Changing Tropical Estuarine Sedimentary Environments with Time and Metals Contamination, West Coast of India

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Abstract

Estuaries are one of the major sub-environments of the coastal zone wherein freshwaters interact and mix with saline waters, and facilitate deposition of finer sediments, organic matter, and metals. Intertidal mudflat and mangrove sediment cores collected from estuaries along the central west coast of India were investigated for various sedimentological and geochemical parameters to understand the changes in the sedimentary depositional environments and various factors influencing the processes. Additionally, estuarine biota was examined to understand the bioaccumulation of metals with respect to bioavailability. The results indicated considerable changes in the depositional environments with time owing to sea-level changes; geomorphology of the estuaries; rainfall and river runoff; anthropogenic activities including construction of dams and bridges. The sediments in the estuaries are considerably polluted by metals and pose toxicity risks to the estuarine biota due to high metal bioavailability. Marine gastropods and mangrove plants act as prospective bio-indicators, and the bioremediation potential of mangroves for contaminated sediments was identified. Metal bioaccumulation in edible benthic biota can be harmful to the human health.

Introduction

The Indian subcontinent has a large coastline of 7,517 km and spans along the Arabian Sea from the coastline of the Gulf of Kutch to Cape Comorin that comprises the West Coast of India and extends further on until the eastern shoreline near the Sundarbans comprising the East Coast of India. The west coast is around 1400 km in length and is intersected by many short swift rivers that form estuaries on encountering the waters of the Arabian Sea. A large number of ports are located along the west coast due to its broken and indented features. Further, many economically important activities are carried out in the catchment areas of these estuaries. These estuaries are important for their ability to filter sediment and contaminants from the water before it flows into the oceans. They are also vital habitats for thousands of marine species because the protected environments and abundant food which provide an ideal location for marine organisms to reproduce.

Estuaries are important zones of mixing of freshwater with saline water (Fig. 1) and sediment transfer between fluvial and marine systems, often forming sinks for material moving downstream, alongshore or landwards, and consequently for dissolved and particulate contaminants (Ridgway and Shimmield, 2002). Despite high hydrodynamics, estuaries are sites of accumulation of fine-grained sediments, organic matter and metals originated from various marine and terrestrial sources including those of human-induced. Estuaries constitute many different habitats such as river deltas, shallow open waters, salt marshes, mud- and sand flats, sandy beaches, rocky shores, sea-grass beds, mangrove forests, and tidal pools. Out of these mudflats and mangroves are an important habitat for wildlife, food, and recreation and very effective in coastal protection. They also respond to sea-level changes and therefore have received considerable attention in the recent years.

Mangroves are forested wetlands living along coasts within low latitudes. Mangroves occur in a variety of coastal settings dominated by rivers, tides, and waves and develop and persist over timescales in which morphological evolution of coastlines occurs; they are pioneers colonizing newly formed mudflats, but they can also shift their intertidal position in the face of environmental change (Alongi, 2016). Mangroves are of great importance economically to coastal inhabitants and ecologically as an integral part of the coastal zone and are a prime source of wood for fuel and construction; chemicals for traditional medicine; food; breeding grounds and nursery sites for many terrestrial and marine organisms; sites of accumulation of sediments, carbon, nutrients, and contaminants; as well as offering some protection from erosion and catastrophic events, such as tsunami and cyclones (Alongi, 2008). The mangrove trees are known to supply large amounts of organic matter, which is being consumed by many small aquatic animals. These organisms in turn provide food for fish and other higher organisms.

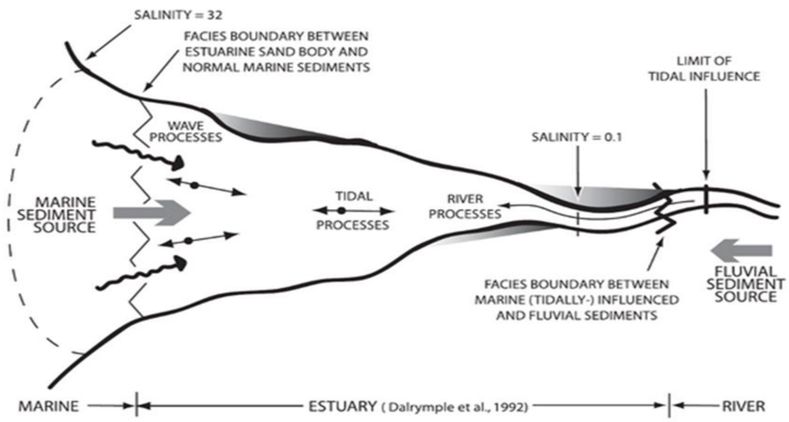


Fig. 1: Schematic diagram of an estuary showing various processes, and marine and fluvial sediment sources.

Likewise, Mudflats are sedimentary intertidal habitats formed by deposition in low energy coastal environments. Their sediment consists mostly of silts and clays with high organic matter content. They commonly are present between subtidal channels and vegetated salt marshes and hence, tend to dissipate wave energy, thus reducing the risk of eroding salt marshes, damaging coastal defenses, and flooding the low-lying lands. The mud surface also plays an important role in nutrient chemistry. In areas receiving pollutants, the sediments sequester contaminants and thus, may contain high concentrations of heavy metals. The surface of the mudflat sediment is often apparently devoid of vegetation, although mats of benthic micro-algae are common that produce mucilage (mucopolysaccharides) that binds the sediment (Maddock, 2008).

The estuaries are known for sediment deposition and act as a sink for metals in the environment. The estuary receives metals from both the natural processes as well as anthropogenic activities (Fig. 2) and are transferred from solution to sediment by adsorption onto suspended particulate matter, and are further deposited and trapped in the sediments (Spencer et al., 2003). The metals get assimilated along with organic matter, Fe/Mn oxides, sulfide, and clay in the sediment, and undergo geochemical modifications resulting in their species. The sediment characteristics such as pH, cation exchange capacity, organic matter content, redox conditions, chloride content, and salinity determine metal sorption and precipitation processes, which are associated with metal mobility, bioavailability, and potential toxicity (Du Laing et al., 2002). After deposition and burial, metals are affected by a variety of physical, chemical, and biological processes that are responsible for mixing and remobilizing metals into the water column (Lee and Cundy, 2001). Some metals or parts of the metal may be immobilized in the sediments and undergo compaction and diagenesis eventually. The sediment-associated metals have the potential to become ecotoxic due to their mobility and bioavailability, and this in turn affects both ecosystems and life through a process of bioaccumulation and biomagnification (Buccolieri et al., 2006; Ip et al., 2007).

The study of estuarine sediments helps us to understand contamination on the one hand and changing depositional environments on the other. The surface sediment interacts and exchanges with suspended materials, thereby involving in the release of metals to the overlying water (Zvinowanda et al., 2009). The top few centimeters of the sediments, therefore, reflect the continuously changing degree of contamination of present times. The bottom sediments, however, record its history (Seshan et al., 2010). The metal concentration in sediment core profiles provides information on the palaeo-weathering processes and post-depositional mobility of metals (Subramanian and Mohanchandran, 1994).

Several researchers have investigated the metal geochemistry to understand the metal source, contamination, mobility and bioavailability of metals in estuarine mangrove and mudflat sediments along the west coast of India (Nayak et al., 2016; Fernandes and Nayak, 2016, 2015; Fernandes et al., 2014; Noronha D'Mello and Nayak, 2015; Nasnodkar and Nayak, 2015; Pande and Nayak, 2013a, 2013b; Siraswar and Nayak, 2013, 2012, 2011; Singh and Nayak, 2009, 2006; Fernandes and Nayak, 2016, 2014, 2013,2012, 2010, 2009; Fernandes et al., 2011; Volvloikar and Nayak, 2015, 2014a, 2014b, 2013a, 2013b; Singh et al., 2014, 2013, 2008). Besides, studies on bioaccumulation and bioremediation potential in estuaries have also been assessed (Noronha-D'Mello and Nayak, 2016; Dias and Nayak, 2016; Cruz et al., 2020). Further, studies have been carried out employing various proxies such a sediment grain size, clay minerals, diatoms, isotopes to understand the past-climate variations (Pande et al., 2015; Volvloikar et al., 2014).

Fig. 2: Various anthropogenic metal sources input to the estuary.

The objective of this review is to understand the changes in the depositional environments in the mangroves and mud flats within estuaries along the west coast of India (Fig.3). Also, the bioavailability of metals in the sediments and the bioaccumulation and bioremediation potential of estuarine biota have been examined.

Methodology

Sediment cores collected (Fig. 4B) from the estuarine mudflats (Fig. 4A) and mangroves from the Maharashtra, Goa, and Karnataka coast, along the west coast of India, were sub-sampled at 2 cm interval using a plastic knife and transferred to plastic bags to avoid metal contamination. The sub-samples were then transferred to the laboratory and refrigerated at 4°C until further analysis. The samples were oven-dried and divided into two portions. One part of the sub-samples was used grain size analysis following the method by Folk (1974). Further, clay was separated and was used for the analysis of clay minerals using X-ray diffraction. Magnetic susceptibility measurements of the sediments were carried out using a Bartington MS2 system for various magnetic parameters. A second dried portion of the sub-sample was ground using an agate pestle and mortar and was used for the analysis of total organic carbon (Walkley and Black, 1934), total Nitrogen (Grasshoff, 1999), and total phosphorous (Murphy and Riley, 1962). Digestion of the ground sediments for total metal analysis was carried out using the protocol proposed by Jarvis and Jarvis (1985). Further, the chemical speciation of metals was also carried out using the sequential extraction procedure by Tessier et al. (1979). The metals were analyzed on a flame atomic absorption spectrophotometer, Varian AA240FS model using an air –acetylene mixture for trace metals and nitrous oxide acetylene mixture for selected major elements. ^{210}Pb dating was carried out on the sediments following the standard radiochemical procedure given by Flynn (1968). Also, stable carbon isotope ratios of total organic carbon ($\delta^{13}C_{org}$) and total organic carbon to total nitrogen (TOC/TN) were analyzed on an elemental analyzer coupled with a continuous flow stable isotope ratio mass spectrometer (IRMS). Further, diatom analysis was done following the method detailed by Battarbee (1986) in estuaries along the Maharashtra coast. Gastropod samples from the estuarine environments were collected and analyzed for metals following the procedure of Yüzereroğlu et al. (2010) in Zuari estuary, Goa. Mangrove pneumatophore samples were also analyzed for metal content following the procedure given by MacFarlane and Burchett

(2002) in Zuari estuary, Goa. Microbiological studies were carried out on the mudflat sediments using heterotrophic bacterial counts In Mandovi estuary, Goa.

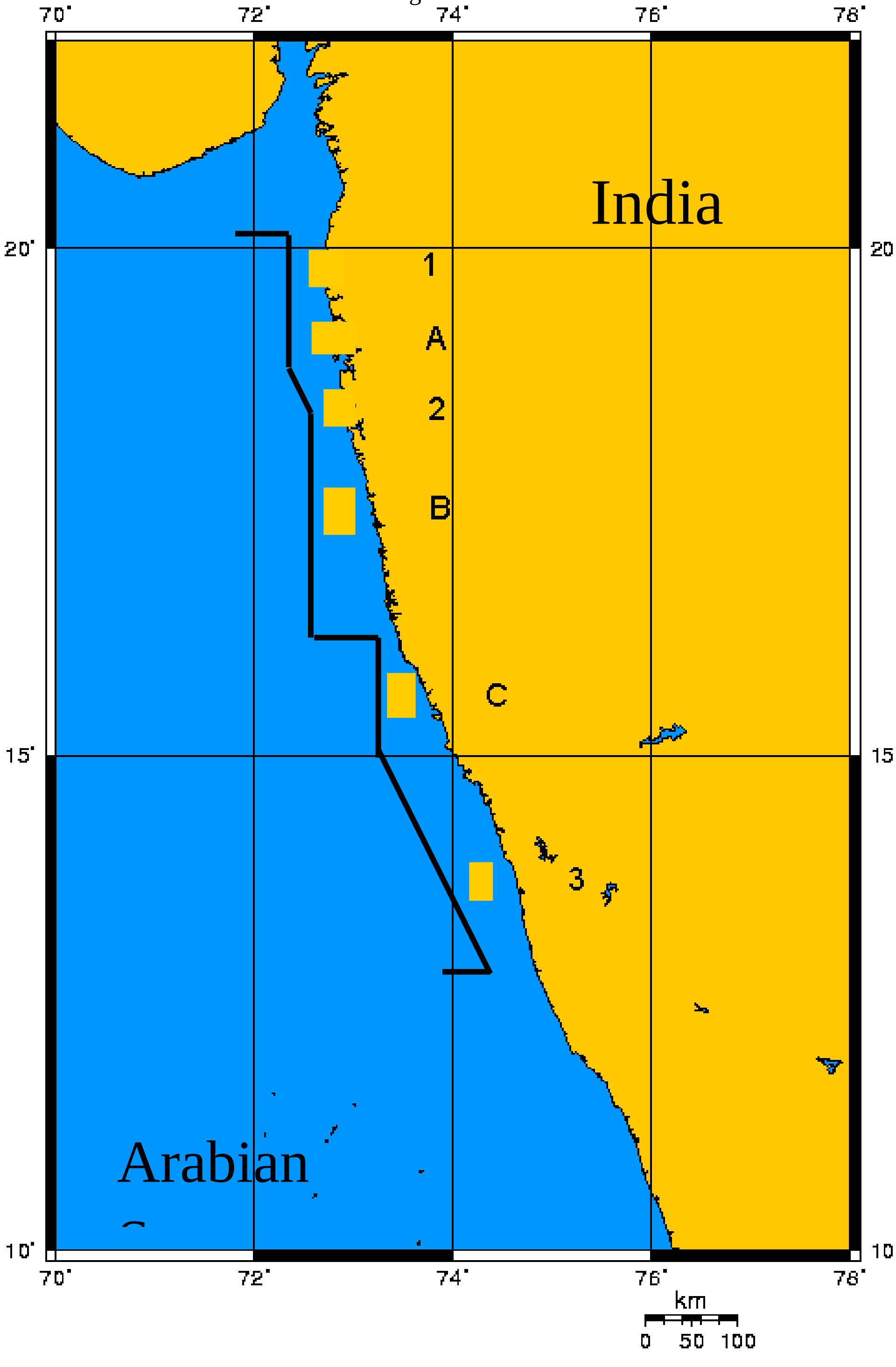


Fig. 3: Sediment core samples were collected from mangroves and mudflats within estuaries of Maharashtra, Goa and Karnataka coasts - marked area.


A


B

Fig.4: Mudflat exposed during low tide (A), Sediment core collected from a mudflat sedimentary environment (B).

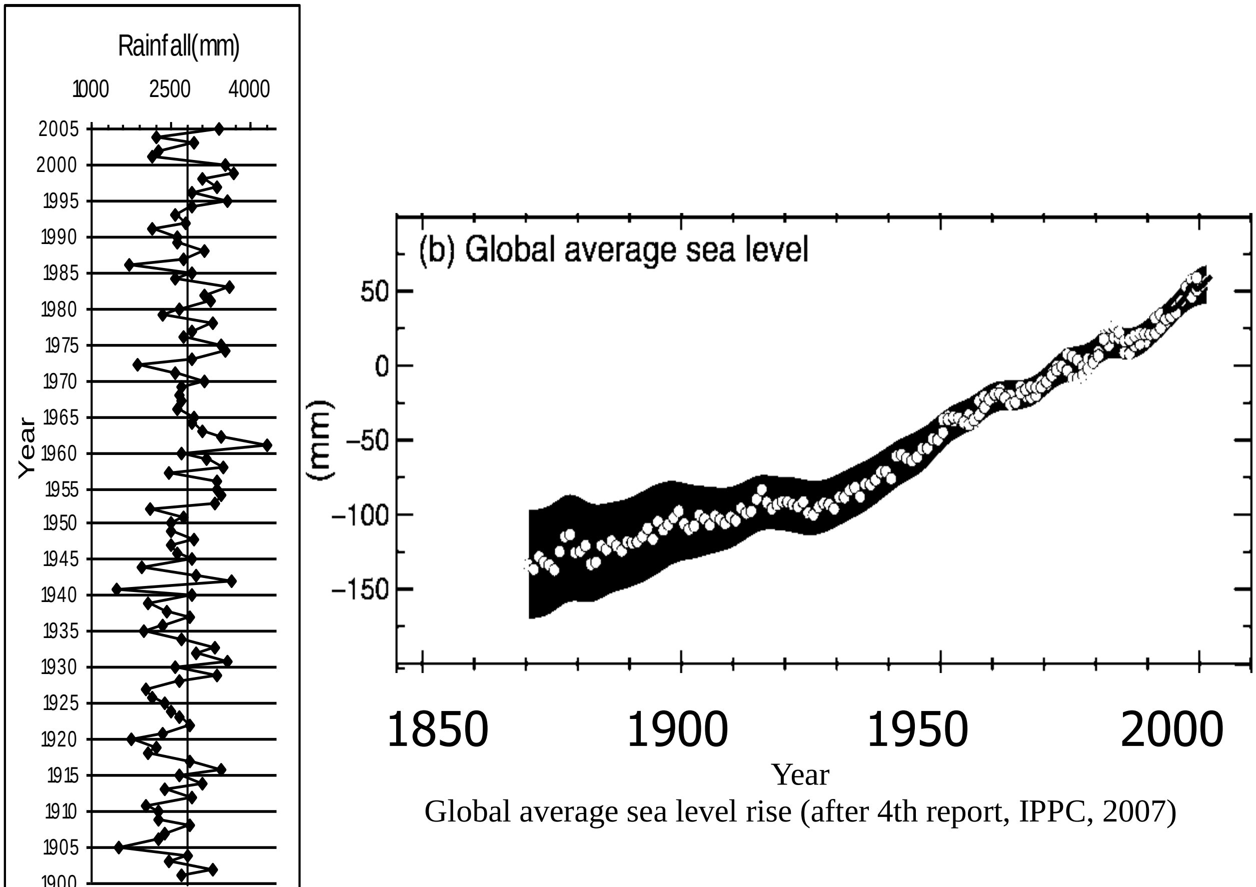
Results and Discussion

Estuarine sedimentation as a record of sea-level changes and monsoon variations

In estuarine intertidal regions, sedimentation and erosion processes are controlled by a combination of sediment availability, sediment property, local morphology, hydrodynamics parameters including tidal cycles, river flow, and wind-generated waves, and biological activity (Deloffre et al., 2007). Studies carried out by various researchers indicated the potential use of mudflats and mangroves as a record of past climate due to their high sedimentation rates, their ability to preserve various sediment components, and their response to changing environmental conditions.

Singh et al. (2013) studied sediment cores collected from the estuarine mudflats of the central west coast of India namely Kolamb creek (Malvan), Mandovi estuary (Panaji), and Tadri creek (Gokarn), and highlighted on variations in sediment characteristics with time. They recorded a higher sedimentation rate for the upper portions of the cores corresponding to increased deposition of finer sediment components, magnetic minerals, organic matter, and metals which were related to geology and/or human activities in the catchment area and variation in rainfall (Fig.5). Another factor accountable for variations in sedimentation is the local sea-level rise, which is directly related to the morphology and sedimentation pattern in the estuary and creeks. According to the fourth assessment report of the Inter-Governmental Panel on Climate Change (IPCC, 2007), the global average sea-level (Fig. 5) rose at an average rate of 1.8 (1.3 to 2.3) mm per year from 1961 to 2003. The rate was faster from 1993 to 2003, i.e. about 3.1 (2.4 to 3.8) mm per year. The average sea-level rise for India has been reported as 2.5 mm/year since the 1950s (Das and Radhakrishna, 1993). Agarwal (1990) considered the west coast of India to be an emergent type and identified a rise in sea level to the order of 0.3 m during the past 57 years. Therefore, many of the large estuaries along the west coast would be most affected by the sea level rise. The rise in sea level may have facilitated the deposition of the increased amount of sediments released through anthropogenic activities such as mining in the hinterland (Singh et al., 2014).

Further, research carried out on the sediments of the Vaitarna estuary, Northern Maharashtra coast of India (Volvloikar and Nayak, 2014a; Volvloikar et al., 2014) using sediment components, grain size (Fig. 6), metals, and $\delta^{13}C_{org}$, revealed significant changes in the sedimentary depositional environment over time. The study on the sediment cores revealed that the sediments of the core at deeper parts had a considerable amount of terrestrial material whereas the recent sediments had more marine characteristics. Also, it was reported that organic matter of terrestrial origin was received during heavy rainfall regimes in the past and the sedimentological and geochemical data corresponded well to the high rainfall between the years 1954 and 1961. Notably, the Vaitarna estuary is dammed in the upstream region that may have resulted in a reduced freshwater influx into the estuary and hence increased seawater influx. Also, the higher deposition of clay fraction bound metals in recent years has been suggested as the result of increased marine inundation which resulted in greater flocculation and facilitated deposition of metals and finer clay particles. The gradual increase in Cu, Zn, Mn, and Al concentration towards the surface of the cores strongly suggested an increase in marine inundation. Volvloikar and Nayak (2013a) also analyzed sediment cores collected from mangroves within macro-tidal Dudh creeks, Northern Maharashtra coast, India. It was found that in the Dudh creek core, a higher percentage of coarser sediments were recorded in the middle section of the core and was attributed to the washing of finer particles and deposition of coarser sedimentary particles from surrounding catchments under the influence of heavy rainfall recorded in the past (1953–1960) in this region. The decrease in precipitation in successive years favored the deposition of finer particles in recent years.



a b

Fig. 5: Variation of annual rainfall in Goa during last 100 years (a), and global average sea level after IPPC (b)

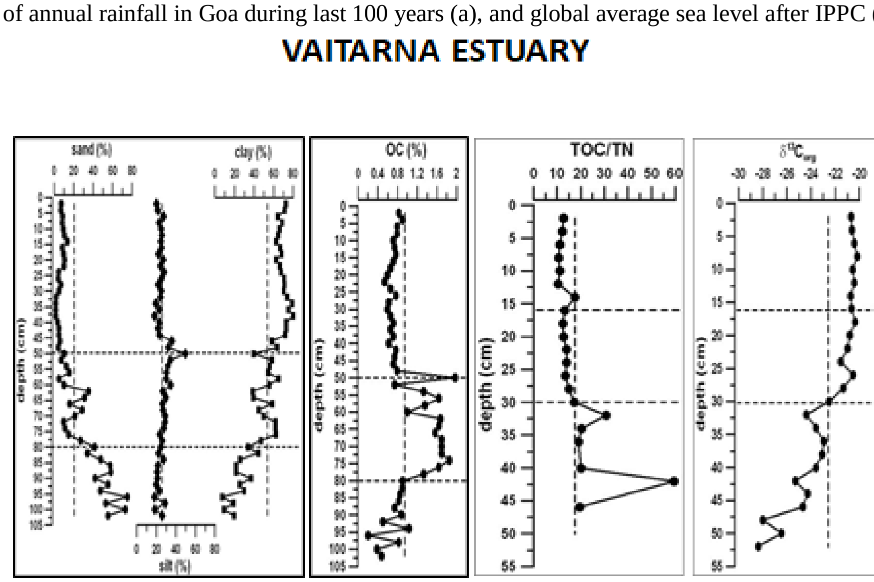


Fig. 6: Down core variation in sediment components of Vaitarna Estuary, Maharashtra (Volvoikar and Nayak, 2014a; Volvoikar et al., 2014).

Sediment cores collected from a tidally influenced Manori creek (Fernandes et al., 2011) were analyzed to understand the metal distribution, thereby understanding the depositional environments of the region. The results showed that coarse sediments were higher in the lower portion of both the cores which decreased up to the mid-core section and the increased input of sand might have resulted from increased precipitation during that period of deposition. Additionally, the C:N ratio helped in identifying marine and terrestrial influence in the two sediment cores. The TOC/TN ratio in the deeper sediments of the core indicated greater input of eroded material from the surrounding land that was concluded from the high sand percentage observed in the lower portion of the cores. The core collected from the upstream region indicated an irregular profile of ^{210}Pb activity that may be explained by complex hydrodynamics, changing sedimentary environments, or rapid changes in sediment supply, source, or energy conditions. Fernandes and Nayak (2014) collected sediment cores from the intertidal regions of Thane creek and Ulhas estuary, located along the southeastern part of Mumbai, and analyzed for sediment components and metal content. In the Ulhas estuary core, a distinct part of the core was characterized by higher sand content and was attributed to high monsoonal runoff and may have led to the lower concentration of some of the elements wherein the sandy type sediments being organically poor have little ability to retain the metal ions. Further, a higher sedimentation rate was also reported in the Ulhas estuary (Fernandes and Nayak, 2012a; Ram et al., 2003) in the recent years.

Further, Pande et al. (2015) examined sediment cores of Mandad River and the Rajapuri creek, central west coast of India, to reconstruct the recent environmental changes using geochemical and diatom records. A change over from river-dominated to the marine dominated depositional environments over the years was reported. The relatively higher sand percentage, elevated TOC/TN ratio, and predominance of freshwater diatoms revealed greater river runoff in the past, while, decrease in TOC/TN ratio and increased dominance of marine diatoms supported marine influence in recent years. Sediment cores collected from the Dharmatmar creek and Amba river mudflats (Pande and Nayak, 2013b) exhibited higher sand in the lower portion of the cores that indicated, both varying rainfall and runoff may have been responsible for the formation of sediment beds with coarser sediments between finer sediments. Investigation on the distribution of sediment components, organic carbon, and metals both spatial and depth-wise in tidal flats of Kundalika Estuary, central west coast of India (Pande and Nayak, 2013b) revealed that strong flood and ebb currents during spring tides, high river discharge or during extreme events such as storm surges may have affected the depositional environments in the past.

Further, Nayak et al. (2016) analyzed the sediment cores collected from the Vaghotan estuary and related the sedimentological data to the rainfall. It was noted that the peak of sand percentage corresponded with high rainfall. It was concluded that during the period of high rainfall, the movement of coarser material transported from the upstream region towards the mouth of the estuary was obstructed on encountering the large marine influx from the Vijaydurg bay which resulted in the deposition of the coarser material in the estuary.

Noronha D'Mello and Nayak (2015) also examined sediment cores collected from the Zuari estuary and found the sediments were deposited under varying depositional environments with time. Rao et al. (2015), used clay mineralogy to understand the provenance and estuarine process. Nasnodkar and Nayak (2015), studied sediment cores collected from the Mandovi, Sharavathi, and Gurupur, west coast of India. Form their sedimentological data it was found that there was a considerable change in the depositional environments of the sediments over time. A major dam was constructed in the mid-1960s on the Sharavathi River and smaller dams on tributaries of Mandovi, for diversion and use of river water for drinking and irrigational purposes in the recent years. This had caused a decrease in freshwater runoff and this in turn enhanced tidal surge regulating changed mixing processes leading to the deposition of fine-grained sediments in recent years. Additionally, considerable finer sediments were added in recent years due to the anthropogenic activities like mining, industrial discharge, agricultural practices, and domestic wastes along with natural processes within their catchment area. It was also reported that an increase in coarser sediments was observed in recent years in the Gurupur estuary due to changes in estuarine geomorphology over time. Fernandes et al. (2014) investigated the depositional environments of mudflats and Mangroves of the Shastri estuary, west coast of India, and found considerable changes in depositional environments from the past to the present.

Overall, from the above case studies, it can be concluded that there were considerable variations in the depositional environments with time. The geomorphology of the estuaries, rainfall, river runoff, construction of dams, bridges, and other anthropogenic activities have considerably influenced the depositional environments. It is prominently noted from the above studies, that there is a strong transition in the estuarine environments from freshwater dominated in the past to marine inundated in recent times. These changes were mainly attributed to the rise in sea level, decrease in rainfall and the construction of dams in recent times that was evident from the higher percentage of coarser sediments in the deeper part of the cores and finer sediments in recent times. In heavy rainfall regimes, the rate of erosion of rocks in the catchment area was considerably high and this material was carried by the runoff by streams into the rivers. The movement of coarser material transported from the upstream region towards the mouth of the estuary was obstructed by encountering the large marine influx from the sea into the estuary. During a deposition in the calm estuarine intertidal environments, the coarser material tends to settle down faster while the finer sediments are washed off and transported in suspension. Thus, the presence of coarser material in the sediment cores could be indicative of periods of high rainfall. This is also supported by the geochemical data wherein less metal concentrations were found along with the high sand content and high metal content in the upper part associated with high clay and organic matter (Singh et al., 2014) (Fig. 7).Further, anthropogenic activities in the catchment areas of the estuaries have considerably affected sedimentation. Activities like mining and transportation of ores added a considerable amount of material into the estuaries. Further, many of the estuaries such as Vaitarna, Rajapuri, Zuari, Sharavathi are dammed in the upstream regions for diversion and use of river water for drinking and irrigational purposes in the recent years that resulted in a reduced freshwater runoff. This in turn enhanced the tidal surge into the estuary and hence more saline water intrusion towards the upper reaches of the estuaries in the recent times. Thus, the mixing processes were affected leading to increased flocculation and deposition of fine-grained sediments in recent years. Additionally, increased anthropogenic activities in the catchment area that discharge a considerable amount of contaminants has caused increased flocculation of material.

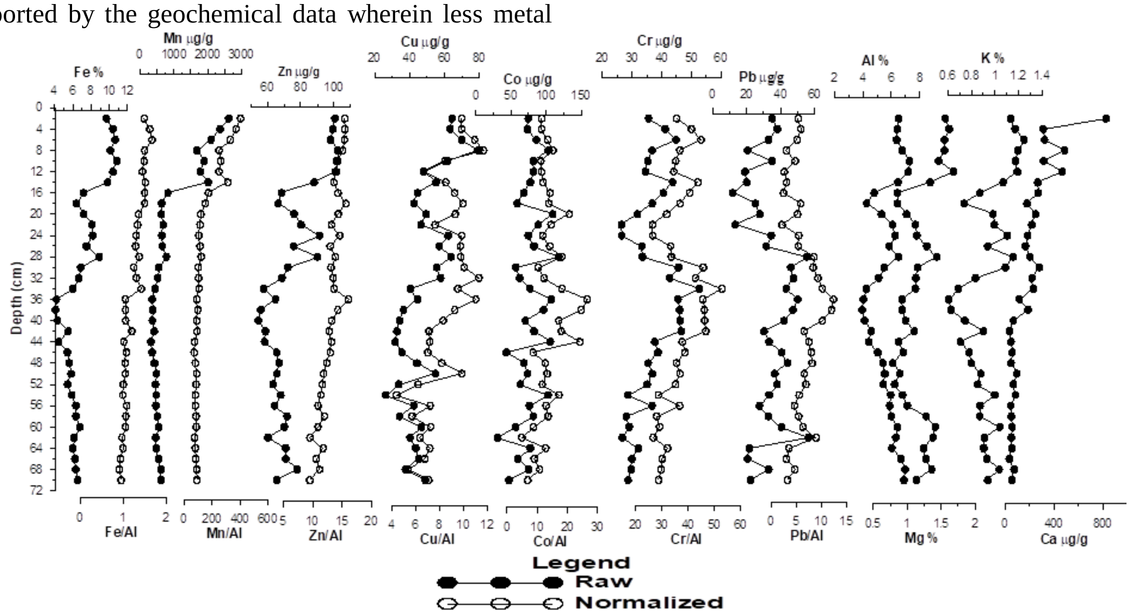


Fig. 7: Down core variation of metals in Mandovi Estuary, Goa (Singh et al., 2014)

Records of contamination history, bioindicator and bioremediation potential

Estuarine sediments are one of the largest repositories of metal pollutants. When discharged into aquatic ecosystems, metals can be absorbed on to suspended solids, and then accumulate into sediments. The sediments act as sinks, and may in turn act as sources of metals (Tang et al., 2014). The contamination of the aquatic system by metals, especially in the sediment, has become one of the most challenging pollution issues owing to the abundance, persistence, toxicity, and subsequent bio-accumulation of these metals. Contaminated sediments pose a potential risk to aquatic environments and human health because they release recalcitrant chemicals that can harm organisms and enter aquatic food chains that lead to humans (Paller and Knox, 2013). Estuarine mangroves and mudflats are thus important in contaminant monitoring studies as they are habitats for several macro-faunal species.

Total metal concentrations do not necessarily correspond with metal availability for biota. To differentiate between natural and anthropogenic loads of metal it is necessary to understand the sedimentology and geochemistry of the region (Herut and Sandler, 2006). Speciation of metals in the sediments allows identifying the percentage of metals supplied from a natural and anthropogenic source. Bioavailability is defined as the degree to which chemicals present in the sediment/soil are absorbed or metabolized by ecological receptors or is available for interactions with biological systems (ISO, 2005). It depends on the specific target organism, contaminant, and sedimentary environments and includes exposure time, transfer of contaminants from sediment to organisms, their accumulation in the organisms, and the subsequent effects of the contaminants (Paller and Knox, 2013). Only the contaminant fraction is available for biological uptake and has the potential to cause harm to human health or ecological risks. To understand bioavailability and bioaccumulation, selective chemical leaches of sediment and plant materials and organism tissues were be analyzed and the results compared.

Several studies were carried out on the estuarine mudflats and mangroves along the west coast of India, to assess the contamination and fate of metals and their bioavailability. Volvoikar and Nayak (2013a, b) studied the sediments of the mudflats and mangroves of the Khonda and Dudh creek and found that the Dudh creek sediments are highly deteriorated by human activities. An increase in metal concentration towards the surface of the core was regarded as the outcome of enhanced anthropogenic activities in recent years. High metal concentrations in the Dudh creek were mainly impacted by industrial effluents while in the Khonda creek it was attributed to the addition of metals from domestic and agricultural wastes. Further, speciation of metals carried out indicated a high concentration of metals in the bioavailable fractions supporting anthropogenic input and therefore suggested a risk of toxicity to sediment-associated biota of Dudh creek (Volvoikar and Nayak, 2015). Geochemical studies carried out on the sediments of the Vaitarna estuary (Volvoikar and Nayak, 2014a) revealed considerable inputs of metals in recent times, and most metals were enriched in bulk sediments, indicating an association with coarser particles and Fe-Mn oxyhydroxides.

Further, studies carried out on the sediments of the Ulhas estuary and Thane creek, Mumbai (Fernandes and Nayak, 2012a; 2014) indicated that metals in the sediments of both sites were greatly influenced by anthropogenic sources that included the use of fertilizers and herbicides, municipal sewage and industrial effluents. An enhanced rate of human activities coupled with the direct discharge of untreated sewage and effluents from the multifarious industries situated in the upper stretch of the creek and estuary had resulted in an increase of metal in the coastal region. Besides, there was a risk of the second cycle of pollution in Ulhas estuary due to routine dredging which released metals by sediment disturbance and/or changes in sediment chemistry. Further, a study carried out on sediment cores from the mangrove ecosystem of the Mumbai region, indicated that the sediments are moderately polluted with Pb and Cu in Manori creek and with Mn in Thane creek (Fernandes and Nayak, 2012b). In the Manori creek, mechanized boats for fishing have led to the emission of Pb and its deposition at a local scale whereas the increasing use of Cu as an anti-fouling agent on fishing trawlers and other commercial boats may have been one of the reasons for the increase in Cu concentration in the recent years. However, in the Thane creek, the increasing amount of organic pollutants has considerably affected metal geochemistry in the sediments. Further, a speciation study carried out on the sediments of the two regions showed a low risk to the aquatic environments, except for Mn in the creek sediments (Fernandes and Nayak, 2014).

The sediments of the Kundalika estuary (Pande and Nayak, 2013a) exhibited recent input of anthropogenic contaminants owing to extensive use of fertilizers, population growth, and urban waste. Also, the sediment of the Dharmatmar creek and Amba River were found to be moderately polluted with metals (Pande and Nayak, 2013b). Sediments of the Vaghotan estuary were also found to be contaminated by metals due to enhanced human-induced activities in the catchment area in recent times and concentration of Co posed a higher risk to biota (Nayak et al., 2016) in the mudflat sediments. The mudflat sediments of the Kolamb creek, Mandovi estuary, and Tadri creek exhibited an increase in finer sediments and metals in recent times which were attributed to an increase in human activities like agriculture, alteration of land use patterns, mining, construction, and development in the catchment area, in the recent years (Singh et al., 2014). The Zuari estuary mudflats and the adjoining Cumbharjua canal were studied by Singh et al. (2013) and reported enrichment of metals revealing a high degree of contamination and reflected mining and industrial sources. Further, studies on the Zuari estuarine mangrove (Noronha-D’Mello and Nayak, 2015) and mudflat (Gadkar et al., 2019) sediments revealed enrichment of Fe, Mn, and Cr in mangroves and, Mn, Cu and Co in mudflat sediments and fractionation of metals indicated that Mn posed a considerable risk to biota.

Along the Karnataka coast, bioavailability studies carried out on the sediment of the Sharavathi River (Fernandes M. et al., 2014) revealed a higher concentration of Mn in bioavailable phases related to increased addition of material from anthropogenic sources. Mn and Co concentrations in the sediments when compared with sediment quality guidelines exceeded the apparent threshold level indicating their toxicity to the environments of Sharavathi estuary.

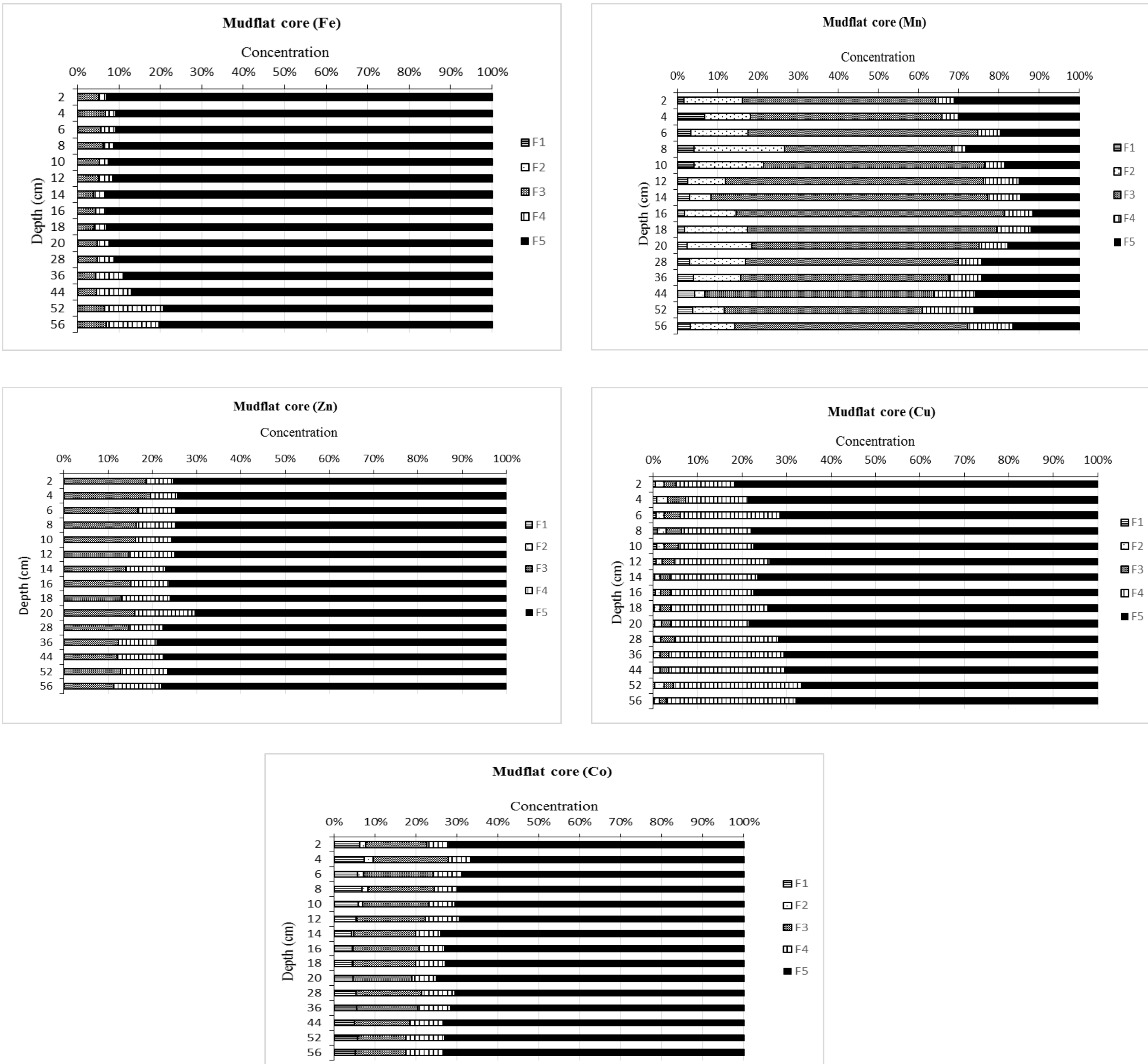


Fig. 8: Different chemical phases of Fe, Mn, Zn, Cu and Co separated using sequential extraction procedure (Gadkar et al., 2019)

The mudflat sediments of the Swarna and Gurpur estuaries were investigated (Fernandes M. and Nayak, 2015) to understand the bioavailability of metals and their toxicity. They reported that Mn, Ni, Cu, and Co show bioavailability in Gurpur estuary and are of anthropogenic addition in the recent years whereas in Swarna estuary, metals showed diagenetic remobilization and diffusion to the water column from surface sediments. Also, Co and Cr in bulk sediments of both estuaries exceeded the apparent threshold level value, and Co in the bioavailable fractions in Swarna exceeded the AET, indicating its toxicity to the environments of Swarna estuary. Fernandes and Nayak (2016) investigated cores from the mudflats and mangroves of the Sharavathi estuary for metal content in the different grain size fractions and reported that the pollution load index computed for both the cores indicated higher metal enrichment in the clay fraction.

Thus, estuaries have been the focal point for a wide variety of human activities and have become sites of a major port, industrial, urban, and recreational development. From the above studies, the sediments of intertidal mudflats and mangroves along the west coast of India considerably hold a high concentration of metal contaminants received through inputs from agricultural fertilizers, industrial and domestic waste discharges, mining transportation, and recreational activities in the catchment areas of the estuaries. These metals in the sediment posed considerable toxicity risk to the biota due to their high concentrations in the bioavailable fractions which the organisms can readily take up. Also, a physical disturbance resulting in sediment re-suspension may increase desorption of contaminants from sediment particles to water and thus increase the bioavailability of contaminants to water column organisms. Thus, there is an increasing concern about pollutants entering the aquatic environments which can have detrimental effects by finding its way into estuarine waters and affecting biotic communities. The metals assimilated by the organisms can further undergo bioaccumulation in the organism tissues and biomagnification. However, some organisms have the ability to concentrate a high amount of metals in their tissues and can be used as bioindicators whereas other organisms can affect the geochemistry of metals in the sediments and be useful for bioremediation purposes. Further, the behavior of trace metals in an environment is critically dependent on their chemical form, which influences mobility, bioavailability, and toxicity to the organisms (de Andrade Passoset al., 2010). Therefore the sediment geochemistry and biology of the particular organism must be understood in order to explain the mechanisms that control metal bioaccumulation (Griscom and Fisher, 2004).

Marine bivalves and gastropods are sedentary, filter-feeders, feeding on suspended particles coupled with their ability to accumulate metals have made them as important candidates to study metal pollution (Phillips, 1980). Most importantly, the concentration of many pollutants in the tissue of bivalves appears to be proportional to the concentration of pollutants in the surrounding water (Amiard et al., 1987). Several authors have reported trace metal concentration in estuaries and studied bioaccumulation in tissues of bio-indicator organisms. Studies by Gawade et al. (2013) on edible clam *Polymesodaerosa* from Mandovi estuary, west coast of India showed that bivalves accumulate higher metal concentration compared to fish indicating that feeding habits, habitat, size, and regulatory ability play important roles in bioaccumulation. Dias and Nayak (2016) made an attempt to understand the relation between bioavailability in sediments and bioaccumulation of metals in tissues of mollusks along the Zuari estuary. They reported that the order of mobility from most to least bioavailable forms was Mn>Zn >Cu > Ni > Co > Fe and Zn showed higher toxicity level and bioavailability. Bioaccumulation of Cu and Zn was higher than bioavailability in both gastropods and bivalves (Table 2) which indicated their preference in metal accumulation over their life span period. Further, metal concentrations were comparatively higher in gastropods. The uptake of metals by mollusks, however, did not exceed the recommended levels. Metals were bound to different fractions with different bonding strengths influencing mobility and bioavailability. Thus, the interactions between metal geochemistry and animal physiology determine the differences in bioavailability among heavy metals (Wang et al., 2002).

Table 1: Concentration of metals in the soft tissues of organisms (ppm). Class Gastropoda (stations — M1, S2, M3 and M5) and Class Bivalvia (stations — S4 and S6)(Dias and Nayak, 2016)

Station Species name	Fe (ppm)	Mn (ppm)	Cu (ppm)	Zn (ppm)	Ni (ppm)	Co (ppm)
(M1) Neritina (Dostia) violaceae	3248.15	958.45	43.70	221.35	14.45	14.65
(S2) Telescopiumtelescopium	5981.55	679.65	106.15	197.10	41.65	3.70
(M3) Cerathideacingulata	1738.80	238.30	40.65	136.15	16.90	18.90
(S4) Katelysiaopima	1363.10	105.50	11.80	150.10	6.00	2.50
(M5) Cerathideacingulata	725.45	609.00	76.25	133.25	11.55	9.05
(S6) Polymesodaerosa	2405.05	153.45	9.40	147.50	11.50	7.10

Mangroves have the ability to sequester or partition metals in their substratum, which protects coastal environments from contamination. However, high metal concentrations in sediment may be deleterious to plants in these ecosystems due to bio-accumulation in tissues (Jin-Eong, 1995; Harty, 1997; Birch et al., 2015). The metals deposited in sediment may be re-mobilized through plant uptake and eventually transported by plant detritus thus increasing the possibility of heavy metals entering the coastal food chain (Subramanian et al., 2001). Earlier research found that the sediment of the mangrove environments could sink a substantial quantity of toxic contaminants, particularly heavy metals, without much damage to the vegetation (Badarudeen et al., 2014). The special ability of mangrove plants' to survive in high-salt and anoxic conditions and high tolerance to contaminant stress contribute to their potential use in preventing dispersion of anthropogenic pollutants into aquatic ecosystems (Alongi et al., 2004; Yang et al., 2008). The factors affecting metal accumulation by plants can be biological like species, growth stage, generation, and non-biological like temperature, season, salinity, pH, metal concentration (Bonanno and Giudice, 2010). The assessment of metals in mangrove sediment is therefore of prime importance as sediment is a useful indicator of metal flux in developing areas and their study helps in initiating management strategies. The contamination and bioavailability of metals in sediments and the metal bioaccumulation in mangrove plants (pneumatophores) were assessed in the sediments of the Zuari estuary, west coast of India (Noronha –D'Mello and Nayak, 2016). They reported that the high content of Mn in the bioavailable fraction of sediment was potentially toxic to biota. Further, mangrove plants accumulated bioavailable Fe, Cu, and Zn in the pneumatophores (Table 2) as compared to other analyzed parts of plants that suggested their potential phytoremediation ability. In general, the phytoextraction of contaminants from sediments involves translocation from root to other plant parts and hyper-accumulation of contaminants requires species tolerance to high bioavailable metals concentrations (MacFarlane et al., 2007). Such conditions were found to be presented by the mangrove plants and thus have a high potential for bioremediation of contaminated sediments. Also, the mangrove plants were able to accumulate metals following the metal content available in the underlying sediment therefore reflect as bioindicator potential. Nath et al. (2014) reported a strong positive correlation between metals in sediment and pneumatophores and suggested the potential use of pneumatophore tissues as a bio-indicator of estuarine contamination.

Table 2: Bioaccumulation in mangrove Pneumatophores (Noronha –D'Mello and Nayak, 2016)

Avicennia Officinalis	*Snnertiaalba*	
Unit	μg/g	
Fe	4015.0	840.0
Mn	1045.0	75.0
Cr	10.0	3.9
Co	3.6	2.7
Ni	4.7	2.4
Cu	17.0	7.8
Zn	52.0	14.4

Bioaccumulation in mangrove is very significant. Bacteria also play a key role in nutrient recycling and the transfer of energy and material to higher trophic levels and thus are at the base of the food chain. Further, benthic invertebrates are known for the link in the transfer of metals to higher trophic levels due to their close association with sediments and also for their ability to accumulate metals (Morillo et al., 2002). Further, they are a major component in the diet of many fish (Summers, 1980). The high content of bioavailable metals may cause deleterious effects on aquatic life because of their high toxicity. This sensitivity of bacteria to metals is an important attribute in environmental indicators as impacts may be assessed earlier in the system before the loss of biodiversity and healthy functioning of the food chain. Besides, bacteria have a rapid generation time which is advantageous in facilitating early-detection of ecosystem stress (Ford et al., 1998). Also, bacterial communities in the sediments provide greater potential for detecting the effects of anthropogenic contaminants across different estuarine areas. Siraswar (2014) investigated the impact of bioavailable metals on bacterial structure from the sediments of the Mandovi estuary, west coast of India. It was found that bioavailable Mn and Pb concentrations posed a high toxicity risk to sediment-dwelling biota. The bacterial population structure was affected by changes in sediment grain size and organic carbon. Further, a metal tolerance study (Mn and Pb) on heterotrophic bacteria suggested that the microbial populations were highly sensitive to metal concentration and could be used as bio-indicators of stress conditions. Also, the bacteria showed high metal tolerance to Pb and Mn at 1000 ppm in the laboratory experiments, which indicated they have developed metal resistance mechanisms over the years. In terms of sensitivity, efficiency and ecological relevance, bacterial communities, therefore, present an attractive alternative to macro-faunal communities for use as indicators of sediment health. Hence, it was concluded that mudflats could serve as avenues for the transformation of native bacterial flora to strains with increased heavy metal tolerance, acting as sinks for bacteria potential bioremediations of heavy metals.

Conclusions

Various studies carried out on the tropical estuaries along the central west coast of India on intertidal mangrove and mudflat sedimentary environments revealed considerable variations in sedimentation pattern and metal deposition with time. The sedimentation in the estuaries along the coast was considerably impacted by the geomorphology of the estuaries, rainfall, river runoff, construction of dams, bridges, and other anthropogenic activities. The role of sea-level changes, rainfall variations, and human activities was well recorded in the sediment cores of the estuaries. Increased marine inundation in recent times was noted in most of the estuaries. Besides, an increase in anthropogenic influence in recent times was evident from the metal abundance in the upper parts of the cores. Furthermore, speciation analysis of metals in the sediment helped in estimating the metal bioavailability and their toxicity to biota. Additionally, marine bivalves, mangrove plant pneumatophores, and heterotrophic bacteria in the sediments were identified as prospective bio-indicators, and mangrove plants have the potential for bioremediation of contaminated sediments. Further bioaccumulation of metals in edible benthic biota can be harmful to the human health.

Acknowledgment

The author thanks the Council of Scientific and Industrial Research (CSIR) for awarding the Emeritus Scientist position and thanks Ministry of Earth Sciences for financial support to carry out studies on mudflats and mangroves within estuaries along west coast of India.

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Received: 17th September, 2020
Revised accepted: 27th December, 2021