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Estuary as a Sedimentary Depositional Environment - A Review

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Abstract

Estuaries are one of the important sub environments of the coastal zone wherein fresh waters mix with saline waters, and facilitate deposition of finer sediments, organic matter and metals. Sediments are distributed after sorting with respect to their size which is controlled and regulated by tides within the estuaries. In this process, highly dynamic environment near the mouth retains coarser sediments and finer sediments along with organic matter get deposited within mid estuary. Mudflats and mangroves in the mid estuary are sites of deposition. Anthropogenic activities like mining, industry, enhanced agricultural practices, dam construction and diverting fresh water in the recent years change the quantity of input from land altering the estuarine processes. Rate of deposition and composition of sediments have changed. Dominance of marine processes in the recent years is recorded.

Keyword : Estuary, Sediments, depositional environment, metal enrichment

Introduction

The coastal zone is characterized by variety of landforms like the beaches, lagoons, islands, estuaries and so on. Estuaries are coastal bodies of water, occupying an existing river valley and their characters are typified by the discharge of rivers and therefore they are regarded as complementary extensions of rivers. In simple terms, an estuary is the region where a river meets an inlet of the sea. Estuarine regimes are governed by several factors such as river inflow, tides, waves, winds and meteorological forces making the system more complicated and dynamic thus temperature, salinity and turbidity fluctuate on daily, fortnightly and seasonal basis and reach more extremes in estuarine waters than they do at sea or in rivers. Thus, estuaries present a diverse and perhaps the most complex environment; hence they pose a constraint on any attempts at giving a specific definition and organizing a systematic classification.

The term "estuary" is derived from Latin word, aestuarium meaning marsh or channel, which itself is derived from aestus, meaning tide or billowing movement, related to word aestas meaning summer. The definition of an estuary differs from one researcher to the other based on their scientific approach. One of the widely used definitions of an estuary has been given by Pritchard (1967) and is as follows. "An estuary is a semi-enclosed coastal body of water, which has a free connection with the open sea, and within which sea water is measurably diluted with fresh water derived from land drainage." According to Fairbridge (1980) "An estuary is an inlet of the sea reaching into a river valley as far as the upper limit of tidal rise, usually being divisible into three sectors (Fig.1) : a) a marine or lower estuary, which has free connections with the open sea; b) a middle estuary subject to strong salt and freshwater mixing; and c) fluvial or an upper estuary, characterized by freshwater but subject to strong tidal action. The limits between these sectors are variable and subject to constant changes in the river discharge and tide.

Estuaries are rich in nutrients and are potential sources for microbes, flora and fauna and thus provide shelter to thousands of animal and plant species. Further, they are the important sites of ports and harbors, vital for shipping, transportation and industry. Dredging, transportation, dumping, shoreline reconstruction to accommodate human housing, agricultural practices and industries affect the health of the estuaries by giving rise to pollution in many ways. As the population grows, demands for the natural sources increases. Increase in population affects the natural balance of estuarine ecosystems threatening their integrity. Therefore, it is necessary to protect the estuaries to conserve the natural resources.

Classification

Classification of estuaries is a difficult task. However, attempts have been made to classify them on the basis of

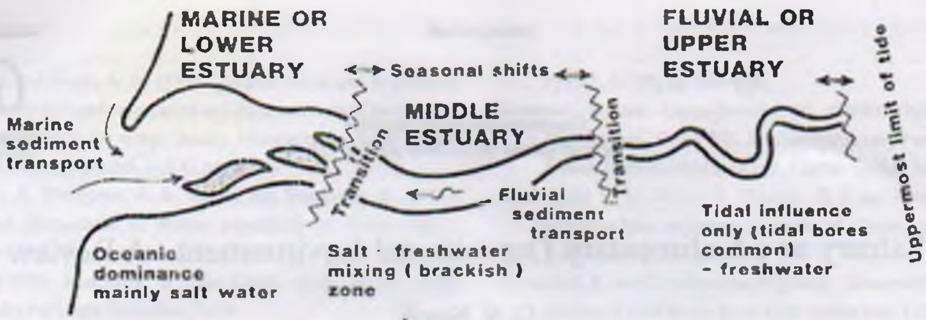

Fig. 1: Estuary showing three divisions – Lower, middle and upper estuary: The boundaries are the transition zones that shift according to season, weather and tides (After, Fairbridge, 1980).

geomorphological set up of the estuary (Pritchard, 1967); on the basis of tidal range (Davies, 1964), which was further elaborated by Hayes (1975) and on circulation pattern or advection-diffusion criteria (Pritchard, 1967).

Based on geology / geomorphology, Pritchard (1967) gave the following classification a) Drowned river valleys estuaries or coastal plain estuaries - These are formed as a result of sub aerial weathering and / or sea level rise. They usually are relatively shallow, V-shaped and show meandering characteristics. Their depth and width increases uniformly towards the mouth of the estuary. b) Rias - These are special type of drowned river valley estuaries which have dissected mouth. c) Fjords - Fjords are estuaries that have been formed by glacial erosion, generally occur at higher latitudes, are relatively long and deep, and possess a shallow sill at the fjord mouth and fjord intersections. d) Bar-built estuaries - These estuaries are formed by the same processes as in the drowned river valleys. The difference is that sedimentation has kept pace with inundation, with a characteristic bar forming at the mouth. e) Estuaries formed due to tectonic processes - These are formed due to faulting, folding, earthquake, volcanoes or other diastrophic movements.

Based on tides, estuaries are classified as follows. a) Micro-tidal estuaries - These are formed wherever the tidal range is less than 2 m and are dominated by freshwater discharge, which leads to "salt wedge" type estuary. These are highly stratified. b) Meso-tidal estuaries - These are formed wherever the tidal range is between 2 to 4 m. These estuaries have meandering characteristics. In this type of estuaries, formation of two deltas takes place called as ebb tide delta and flood tide delta (Boothroyd, 1978) due to time velocity asymmetry. c) Macro-tidal estuaries - These are formed wherever there are strong tidal currents (tidal range is more than 4 m). These are trumpet in shape. Long linear sand bars are formed parallel to tidal flow near the mouth of the estuary.

Based on flow pattern / circulation, Pritchard (1955) gave the following classification. a) Type A: Salt wedge estuary - These are highly stratified and are river dominated. These exist wherever there is small tidal range and they show sharp salinity changes. They hold large quantity of suspended load. b) Type B: Partially mixed estuary - This type of estuaries occur when the volume rate of flow of the estuary during a flood tide is about ten times the volume rate of inflow of freshwater from the river. Both advection and turbulent mixing occurs across the freshwater-saltwater interface in this type of estuary. They show variation in salinity and there is large accumulation of suspended matter. c) Well mixed or fully mixed estuaries - These estuaries are shallow and wide with stronger tidal currents relative to the river flow in them. In well-mixed estuaries, salinity hardly varies with depth, although it may vary considerably across the width of the estuary. These estuaries have marine dominance and are influenced by the earth rotation.

The estuary is an ephemeral feature in long term geologic history and must be regarded as a dynamically evolving landform that will go through a life cycle from valley creation, followed by the drowning phase and ending with the progressive infillings. Every estuary is unique and is subjected to differing physical constraints and therefore, evolving at different rates. Almost all the estuaries have originated as a result of the recent rise in sea level which has initiated around 18,000 years ago when sea level was approximately 100 to 125 m below the present level. With warming up of the atmosphere, glaciers began to retreat, consequently raising the sea level. As a result, the sea advanced across the shelf and progressively drowned the river channels giving rise to present estuaries. Around 5000 to 3000 years ago estuaries reached their peak in development, in number, size and complexity.

Sediments

Estuaries are the favorable environments of deposition of sediments derived from both the catchment area (terrestrial) and the marine sources. So, the sedimentation in estuaries is within three distinguishable regimes viz. estuarine fluvial, estuarine brackish and estuarine marine. These sequences inter-finger with fluvial and marine sediments at the inner and outer limits of the estuary respectively (Dalrymple *et al.*, 1992). Sediments are transported into the estuary from the sea as well as are washed in from the land surrounding the estuary either in the form of suspended matter or as bed load with considerable variations in size. Fine sedimentary deposits or mud are a characteristic feature of estuaries. Sediment distribution in estuaries is mainly controlled by the influence of tidal and river currents and also on the particle size of the sediments. Erosion, transportation and deposition of sediments in different depositional environments may possess distinctive sediment size distributions (Priju and Narayana, 2007). However, other factors such as geo-morphology, bedrock geology and sediment input from the catchment area basically through runoff can modify the general pattern (Turekian and Wedepohl, 1961). The relations between these factors are complex and often inter-dependent. The dependence of the mobility of the sediment on the hydraulic conditions leads to a progressive sorting of the sediments with respect to composition and size. The most significant sorting is the coarse (gravel and sand), which are found in the more energetic areas and fine (silt and clay) sediments, which accumulate in low energy conditions or quiet waters. The rate of deposition or the settling velocity of sediments is related to particle diameter. Fine particles in estuaries are either single particles dispersed in suspension or they may coalesce and form composite particles which are referred as flocs, aggregates, or agglomerates (Nichols and Biggs, 1985). In many estuaries, the suspended matter develops "turbidity maxima". The position of the turbidity maxima is generally determined by the contribution of suspended sediment from the seaward end of the estuary. These suspended particles, which are derived from several sources act as scavenger for trace metals because of their adsorption characteristics and thus play a vital role in transportation of metals into the estuary. The adsorption of metals on to the suspended matter is mainly controlled by the grain size of the sediment. Seasonal differences in metal concentration in suspended matter due to the effect of grain size have been reported by Qiao *et al.* (2007). Further, suspended matter acts as food for many organisms present in the estuaries. Trace metals available and bound to suspended particles remain biologically available in the fluid medium, and then may be incorporated into the food web by filter or suspension feeders or even by direct ingestion of the nutrient. It is well known fact that trace metals are micronutrients, that are essential for biological life or others that are adsorbed on to the suspended matter or in suspension. But at higher doses even these nutritionally essential metals can cause adverse effects. Therefore, estuaries are rightly described as chemical reaction vessels in which solutions with different chemistries are mixed in the presence of reactive particles (Goldberg, 1978).

Further, like suspended matter, bed load sediments also play a key role in the geochemical and biological processes of an estuarine ecosystem. Since estuaries are major repositories of metal and, in addition to providing the environmental status; they are also used to estimate the level of pollution in a region (Caccaia *et al.*, 2003; Simeonov *et al.*, 2007). Once released into the environment, trace metals may interact with suspended matter and will be subsequently removed from the water column facilitating deposition. Metals are not necessarily fixed permanently by the sediment, but may be recycled via biological and chemical agents, both within the sedimentary compartment and also back into the water column (Salomons and Forstner, 1984). Once deposited in the sediment, these metals can be accumulated by benthic-dwelling organisms which live and feed on the sediment (Tessier *et al.*, 1994; Zoumis *et al.*, 2001). Benthic organisms are food for several higher trophic levels and these transformations of contaminants can lead to several adverse effects (Thompson and Lowe, 2004; Anderson *et al.*, 2007). Metals are natural constituents in nature, but anthropogenic activities can cause elevated levels of these metals in various parts of the system (El. Hassan and Jiries, 2001; Homady *et al.*, 2002). Once the metal concentration exceeds certain level, they may lead to severe environmental problems.

It is also necessary to note here that the sediments are composed of different geochemical phases such as clay, silt, sand, organic material, oxides of iron and manganese, carbonate and sulphide complexes that act as potential binding sites for metals entering an estuarine system (Jonathan *et al.*, 2004). In the sediments, metals can be present in various forms and generally exhibit different physical and chemical behaviour in terms of chemical interactions, mobility, biological availability and potential toxicity (Almas *et al.*, 2006). Studies of metal distribution among various geochemical phases of sediment is particularly important in estuaries since speciation is likely to be influenced by the constantly changing environmental conditions including salinity, pH and sediment redox potential (Calmano *et al.*, 1993; Paludan and Morris, 1999, Valdes *et al.*, 2005).

Dispersal of sediments in the estuary is controlled by the estuarine circulation pattern and also by the changes in the dynamic properties of river water in the estuarine environment, which results in the accumulation of fine-grained sediment with a high organic matter content. Sometimes finer sediments and organic matter through adsorption play an important role in the transport of trace metals to the sediments (Burton and Liss, 1976; Ip *et al.*, 2007). Natural processes and human activities have resulted in elevated concentration of organic carbon in sediments. Sources of organic carbon include organic matter from land runoff, shoreline erosion and primary productivity all of which eventually settle to the bottom and are incorporated into the sediments. It has been also established that organic carbon gets selectively enriched in fine particles of estuarine sediments (Hunt, 1981). It is also well documented that metal concentrations increase in the regions that are dominated by fine particulate matter (Zhou *et al.*, 2003; Hakanson *et al.*, 2004). Sediment characteristics allow accumulation and integration of metal over time (Thompson *et al.*, 1984; Tsai *et al.*, 2003). So, it was obligatory to measure the abundance of different sediment parameters viz. sand, silt, clay and organic carbon and to understand their role in distribution of trace metals in bed load sediments.

Clay minerals are powerful source indicative tools in the interpretation of marine depositional processes. The clay mineral studies reflect weathering conditions imprinted on the rock particles that were found in the source terrains (Maldonado and Stanley, 1981; Stanley and Liyanage, 1986). Mineralogy of fine grained material has also been used to understand the nature of the sedimentary environment (Brown *et al.*, 1977) and to understand the effects of diagenetic processes on mineralogy (Hower *et al.*, 1976). Velde (1995) had related the clay mineral distribution to the climatic control as follows i) the presence of kaolinite suggests well drained source areas with intense hydrolyses under warm and humid climate. ii) chlorite is mainly available at higher latitudes as a result of physical erosion of magmatic and metamorphic rocks and the chemical alteration is limited. iii) illite also increases towards the higher latitudes and it reflects the decrease in intensity of hydrolysis and thus an enhancement of mechanical alteration. iv) smectite distribution is not straight forward due to their double source i.e. alteration and / or authigenesis. Several researchers carried out studies on the clay mineralogy *viz.* Edzwald and O'Melia (1975), Rao and Rao (1993), Bukhari and Nayak (1996), Bican-Brisan and Hosu (2006).

Many researchers have explored the relationship between mineral magnetic measurements and chemical / physical properties of the sediments and soils (Oldfield *et al.*, 1986; Xie *et al.*, 2000; Booth *et al.*, 2005; Zhang *et al.*, 2007). With the development of environmental magnetism, magnetic measurements have been identified as a suitable tool for evaluating pollution studies. Many researchers have worked on monitoring environmental quality and discriminating pollution sources, either independently or in combination with geochemical analysis (Oldfield *et al.*, 1978; Urbat *et al.*, 2004; Shilton *et al.*, 2005). Chan *et al.* (2001) had studied the magnetic properties and heavy metal contents of contaminated seabed sediments of Peny's Bay, Hong Kong. Their results revealed a difference in the magnetic properties between contaminated and uncontaminated sediments and also, they found relatively higher magnetic susceptibility and greater heavy metal content in < 63 μm fraction of sediment. Mineral magnetic measurements serve as a proxy for geochemical radioactivity, organic matter content and particle size data (Xie *et al.*, 1999, 2000; Zhang *et al.*, 2001).

Diatoms are the major component of phytoplankton and are the dominant organisms in the estuarine and coastal environments due to their nutrient replete conditions. Diatoms also form an important component of the microphytobenthos population. These photosynthetic algae contribute more than 50% of primary production in estuarine and shallow coastal environments (Underwood and Kromkamp, 1999). Diatoms are characterized by siliceous cell wall which gets preserved in sediments after their death. The diatom population is controlled by multiple factors which include sediment grain size, light, temperature, nutrients, pH, etc (Whitton and Rott, 1996; Facca and Sfrico, 2007; Pan and Stevenson, 1996). Diatoms are ubiquitous organisms with high species diversity and short life cycle. Therefore, they react quickly to environmental conditions (Duong *et al.*, 2007). Diatoms thrive in water of particular salinity and get preserved in sediments due to their siliceous cell wall. Diatom assemblages have been used to interpret changes in the degree of marine (Zong, 1997) and fresh water influence (Almeida and Gil, 2001). Diatoms are also good indicators of pollution levels (Duong *et al.*, 2007). Diatoms, single celled microscopic organisms belonging to class Bacillariophyceae, have been used as a proxy to reconstruct the depositional environment since these organisms are sensitive to changes in salinity, nutrient, pH, etc.

Further, it is well documented that metals are bound to different components of the sediment (Salomons and Forstner, 1984; Fan *et al.*, 2002), and different phases have been defined (Tessier et al., 1979; Yu *et al.*, 2001), for example; exchangeable ions, adsorbed ions / carbonates, Fe and Mn oxides, sulphides / organics and metals bound to lithogenic minerals and residual. Measurement of total concentration of metals may not reflect the potential availability for biota (Loring, 1981). Numerous extraction schemes for soils and sediments have been described. Among these the procedure of Tessier *et al.* (1979) is one of the most thoroughly researched and widely used procedures to evaluate the possible chemical associations of metals in the sediments and soils.

Vast literature is available on different aspects of the estuaries, all over the world. With rapid increase in population and industrialization during the last few decades, the estuaries have come under increasing stress due to anthropogenic activities that disturbs the pristine system. This made the researchers to work on estuaries on different aspects in order to understand environmental status and suggest remedies. Geochemical investigation in various Indian estuaries both along east coast and west coast have been undertaken to study the environmental conditions, by Venugopal *et al.* (1982), Nair *et al.* (1987), Biksham and Subramanian (1988), Desai (2008), Ramanathan *et al.* (1988), Subramanian and Jha (1988), Subramanian *et al.* (1985, 1988), Zingde *et al.* (1988), Devavarma *et al.* (1991, 1993), Rao and Swamy (1991), Modak *et al.* (1992), Nayak and Bukhari (1992), Nair *et al.* (1993), Nayak (1993), Bukhari (1994), Mohan, (1995), Bukhari and Nayak (1996), Nair and Ramachandran, (2002), Singh (2000), Singh *et al.* (2005), Balachandran *et al.* (2005, 2006), Alagarsamy (1988, 2006), Ganesan and Kannan (1995), Sriniwas (1998) and Nayak *et al.* (2008).

Biksham *et al.* (1991) had studied the heavy metal distribution in suspended and bed load sediments from the Godavari River basin. They reported higher concentrations of metals in the suspended sediments than in the bed load sediments. In this study, all the metals showed high correlation among themselves and the correlation was more pronounced in the suspended sediments than in the bed load sediments. Bukhari (1994) had studied the systematic distribution of total suspended sediments (TSM) in Mandovi Estuary, Goa. He observed general decreasing trend of TSM from mouth towards upstream of the estuary during pre-monsoon and post-monsoon seasons whereas, higher concentrations were reported towards the head region during monsoon season. He also reported high concentration of metals in the suspended sediments compared to bed load sediments. Distribution of trace metals in the Hindon River system, India, was studied by Jain and Sharma (2001). Their study has revealed that the fine sediment fraction, organic matter and Fe / Mn played an important role in transport of metal ions. Sadhuram *et al.* (2005) reported high values of total suspended matter in both surface and bottom water of Hooghly Estuary, India, showing the impact of fresh water on sediment transportation.

Several studies were carried out on the geochemical behaviour and distribution of total concentration of metal contaminants in estuarine bed load sediments. Geochemisry of surface sediments provide important clues regarding the source and the processes through which metals get accumulated. In the estuarine environment, the two processes that can potentially contribute to the surface sediment geochemistry include riverine input and sediment diagenesis. Diagenetic reactions are important near the sediment-water interface in responding to redox changes and affecting metal concentration. Iron and manganese oxides (oxyhydroxides) are also considered as strong scavengers of metals, affecting trace metal mobilization because they precipitate under oxic conditions and dissolve in anoxic environment. According to Lin and Chen (1998), dissolved and particulate organic matter in the water column acts as scavenger for metals and once these elements are trapped they are precipitated and incorporated into the sediment. Metal concentration in sediments within the estuaries can be influenced by factors such as salinity (Coakley *et al.*, 1993), water discharge (Forstner and Whittmann, 1981), flow rates (Schoellhamer, 1995) and geomorphological setup. Most of the studies carried out on total metal concentration in sediments recognized the important role of organic carbon and grain size on the geochemical behaviour of these elements. The metal concentrations reported by numerous researchers in the various Indian estuaries are presented in the Table 1. Biksham and Subramanian (1988) assessed the elemental composition of Godavari River sediments. They had stated that when compared to Indian mean value, Godavari sediments are enriched in heavy metals and are depleted in Al and K. Nair and Ramachandran (2002) had studied the textural and trace elemental distribution in the surface sediments of the Beypore Estuary. Their studies revealed that textural characteristics and organic carbon had substantial influence on the elemental distribution.

Major and minor elements were studied in the recent sediments off Gulf of Mannar along the southeast coast of India by Jonathan *et al.* (2004). Their studies revealed that the enrichment of Cr, Pb, Cd, Cu, Co, Ni, and Zn along the Gulf of Mannar and indicated that the area has been contaminated by riverine sources and industries nearby. Factor analysis obtained by them showed higher loading in acid leachable and its association with $CaCO_3$. Alagarsamy (2006) had studied the systematic seasonal distribution of trace metals such as Fe, Mn, Co, Cu, Zn and Pb in the Mandovi Estuary, west coast of India. He has evaluated sediment enrichment of metals by using "Geoaccumulation Index". His results revealed that the surface sediments of Mandovi Estuary are moderately or strongly contaminated to some extent by Fe and Mn. Cu and Zn showed the influence of organic wastes from municipal sewage entering into the estuary, in the river mouth region. Balachandran *et al.* (2006) had studied the coastal and estuarine sediments of Cochin with reference to heavy metal concentrations to identify the different processes of deposition. They studied the element interactions using principal component analysis (PCA) which separated two clusters comprising of heavy metal possessing significant relation with texture, which belong to sediments in the shelf region and second set of heavy metals showing poor correlation with sediment texture, which are of estuarine region.

Nasr *et al.* (2006) assessed the heavy metal pollution (Mn, Zn, Cu, Pb, Co, Cr and Ni) in bottom sediments of Aden Port, Yemen. They have used background values depending on the international standards and contamination factor to evaluate the level of sediment contaminations. Priju and Narayana (2006) had studied the spatial and temporal variability of trace metal concentration in a tropical lagoon, south west coast of India, in order to study the environmental implications. Based on the statistical analysis they have made an attempt to understand the natural processes and anthropogenic activities in the region. Ray *et al.* (2006) assessed trace metal content in sediments as well as in suspended matter in the Godavari mangrove ecosystem. They have observed significant correlations between organic carbon and Co, Cr, Pb, Cu and Mn in sediments indicating organic matter as a metal carrier. They have also calculated pollution load index (PLI) to evaluate the level of pollution.

Nair *et al.* (1993) had studied the trace metal speciation of Mn, Fe, Cr, Ni, Zn and Co in surface sediments from the tropical estuary of Cochin. Their studies revealed selective accumulation of Mn and Ni in the carbonate and organic / sulfide fraction. Large portion of Fe and Zn was observed in the residual fraction. The level of Cr and Zn indicated anthropogenic input into the estuary, while Co and Ni showed regional contamination exceeding natural levels. Their investigations also showed diagenetic processes in the estuarine sediment. Singh *et al.* (2005) had studied the chemical fractionation in the Gomati River. sediments and found that most of the metals are associated in the carbonate and exchangeable fractions indicating their bioavailability.

Table 1: Range and average concentrations of different metals in surface sediments from various Indian estuaries.

Location	Fe (%)	Mn (%)	Cr (μg/g)	Cu (μg/g)	Zn (μg/g)	Co (μg/g)	Reference
Zuari Estuary	2.97-16.81 8.23	462.50-5937.50 3035.06	22.75-502.00 186.6	10.50-169.50 58.67	26.25-172.25 87.51	25.50-110.75 48.4	Dessai, 2009
Zuari Estuary	2.23-16.7 7.09	0.04-0.62 0.329	60.33-388.0 162.86	7.0-74.0 35.00	23.67-165.33 88.264	12.0-36.33 22.583	Singh, 2000
Mandovi Estuary	2.2-49.7	<DL-1.61		11.5-77.5	19.9-83.5	2.5-45.3	Alagarsamy, 2006
Mandovi Estuary	2.03-12.8 7.909	0.062-6.079 0.37	68.0-403 264.47	3.67-80.67 36.987	25.00 - 149.67 87.83	3.33-32.0 15.506	Singh, 2000
Mandovi Estuary	2.2-49.7	0.01-1.18		12.9-77.5	21.0-83.5	2.5-45.3	Alagarsamy, 1988
Mandovi Estuary	3.15-11.05	0.085-1.01	224-580	31-88	38.0-102	15-35	Bukhari, 1994
Godavari Estuary	2.67-8.03 5.77	0.04-0.17 0.1	88.0-243.0 137	61.0-157.0 107	66.0-323.0 207	22.0-89.0 50	Srinivas, 1998
Godavari Estuary	0.57-23.90 6.1439	0.01-0.362 0.1056	12-408 142.565	3-262 75.304	4-75 53.434		Biksham *et al.*, 1991
Ganges Estuary	-3.1	0.0553		26	71	36	Subramanian et al., 1988
Gomati River	0.16-0.31 0.266	0.008-0.026 0.0148	2.22-19.13 8.146	BDL-35 5	3.06-101.73 41.66		Singh *et al.*, 2005
Beypore Estuary	1.99-7.09 7.09	0.0205-0.0912 0.038	88-203 133	2-17 5	25-75 44	11-35 21	Nair and Ramachandran, 2002
Cochin Estuary	4.47			32.42	592		Balachandran et al., 2005
Vasamdhara Estuary	3.20-7.10 5.28	0.04-0.09 0.05	8.0-128.0 106	25.0-55.0 37	50.0- 250.0 152	20.0-45.0 32	Devavarma *et al.*, 1991 and 1993
Krishna Estuary	6.6	0.2	114	124	97	29	Rao and Swamy, 1991
Cauvery Estuary	1.35-7.6	0.02-0.14	20-220	10-50		10-200	Ramanathan *et al.*, 1988
Vellar Estuary	3.93	0.4854	222	45	196	48	Mohan, 1995
Tuticorin coast	0.224-0.432 0.316	0.029-0.125 0.078					Ganesan and Kannan, 1995
Narmada	3.14	0.0514	55	46	50	36	Subramanian *et al.*, 1985
Tapti	10.9	0.13	108	126	118	64	Subramanian *et al.*, 1985
Indian River avg.	2.9	0.06	87	28	16	31	Subramanian *et al.*, 1985
World River avg.	4.8	0.105	100	100	350	20	Martin and Maybeck, 1979
Surficial rock	3.59	0.07	97	32	129	13	Martin and Maybeck, 1979
Average shale value	4.67	0.06	83	45	95	19	Turekian and Wedepohl, 1961

*Bold values indicate average concentration.

We, in the Department of Marine Sciences of Goa University have carried out detailed study of suspended and bed load of Mandovi and Zuari estuaries of Goa and working on mudflats and mangrove sediments within estuaries along central west coast of India. Some of results are presented here.

Nayak and Bukhari (1992) reported decrease in suspended matter from mouth of the Zuari Estuary towards upstream during pre-monsoon and post-monsoon. Their study indicated that with the onset of monsoon suspended matter increases remarkably in the estuary. Further, they have also observed that the Zuari Estuary maintains the zone of high suspended matter around the mouth of the Cumbharjua canal during pre-monsoon and post-monsoon, which disappears during monsoon. Based on foraminiferal studies, Panchang *et al.* (2005) concluded that there is reduction in pollution on the Zuari Estuary, which they have stated as due to reduced mining activity in the catchment area. Nayak *et al.* (2008) have studied the abundance and distribution of total suspended matter from Mandovi and Zuari estuaries in three different seasons over the last seventeen years. They have reported that in general, in Zuari Estuary, suspended matter concentration increased in both surface and bottom waters from year 1991 to 2004. Further, they have reported lower values of suspended matter in the year 2007 in post-monsoon season when compared to 2004 data. Similar observations are also made for adjacent Mandovi Estuary which is connected to Zuari Estuary through Cumbharjua canal.

Mudflats and Mangroves

Mudflats cover large "unvegetated" areas in intertidal zones that are exposed during low tide and submerged during high tide (Reineek, 1972). They are often referred as "secret garden" of estuary because a diverse assemblage of cyanobacteria and eukaryotic algae thrive in such sediments (Sylvestre *et al.*, 2004; Miller *et al.*, 1996; MacIntyre *et al.*, 1996). Mudflats generally form in meso and macro tidal environment under large tidal range (Feng, 1985 and Cao *et* *al.*, 1989). Mudflats are characterized by extensive width and breadth and gentle-sloping surfaces. Mudflats can be divided into three sedimentological zones namely high, middle and low mudflats (*Wang et al.*, 1963). The high mudflats are less frequently inundated and predominantly composed of mud. The low mudflats, on the contrary, are submerged by tides in most cases. The middle mudflats are submerged during flood tides, but appear during ebb tides. Recent studies have highlighted the importance of these areas to study past changes in depositional environment, pollution level and sea level rise (Singh and Nayak, 2009; Fernandes and Nayak, 2009, 2012a, b; Siraswar and Nayak, 2011; Fernandes, 2011; Pande and Nayak, 2013a, b; Volvoikar and Nayak, 2013a, b, c and Singh *et al.*, 2012, 2013).

Mangroves are salt tolerant shrubs and trees that act as buffer zone between land and sea (Ramanathan *et al.*, 1999). They harbour the most diverse and abundant fauna and flora. The mangrove vegetation is associated with a unique horizontal root network that enhances the deposition of fine grained suspended sediments and prevents re-suspension and erosion of fine sediments (Soto-Jimenez and Paez-Osuna, 2001; Kumaran *et al.*, 2004). Mangrove environments are highly productive and are sources of organic matter which may be transferred to adjacent coastal waters through the export of detritus and living organisms. Recent geochemical studies indicate that the mangrove sediments are capable of trapping large quantities of pollutants, particularly trace metals, without significant effect on the vegetation.

Mudflats cover large unvegetated areas in intertidal region that are exposed during low tide and submerged during high tide. Mangroves, on the other hand, are salt tolerant shrubs and trees that act as buffer zone between land and sea. They are widespread along coastal estuarine intertidal zone of central west coast of India. The high concentration of fine particles and organic matter in such sediments favors the accumulation of metals. These sediments are not removed readily being cohesive. Each sediment layer deposited may therefore represent a record of the past environmental conditions, reflecting the water quality and possible effects of anthropogenic contamination over a certain period. Several proxies including grain size, nutrients (carbon, nitrogen and phosphorous), pH, C/N ratio, clay minerals and diatoms have been used to infer the changes in depositional environment. We have studied over the year about hundred sediment cores collected from mudflats and mangrove environments varying in length up to 150 cm. The cores are sub-sampled with 2 cm interval and studied for pH, sand, silt, clay, clay minerals, TOC, TN, TP, C/N ratio, bulk sediment chemistry for selected metals (Al, Fe, Mn, Cr, Co, Cu, Ni, Zn and Pb), clay fraction chemistry, diatoms and different species of metals along central west coast of India covering the coast of Maharashtra, Goa and Karnataka.

Tropical estuarine mudflat and mangrove sedimentary sequences preserve an undisturbed record of various environmental changes (Singh and Nayak, 2009). Formation of estuarine mudflats and mangroves at the fluvio-marine interface allows deposition of material originating from diverse sources (Volvoikar and Nayak, 2013 a-c). They are highly productive ecosystems and have high impact on the carbon budget of the tropical and global coastal zone. Because of their sheltered nature, mudflats and mangroves accumulate large quantities of organic matter (Sanders *et al.*, 2010). Inorganic particulates are derived from the weathering of rocks and organic matter from marine planktons, fresh water planktons and terrestrial plant material including mangrove litter. In addition, material from anthropogenic discharges such as sewage and industrial effluents are also deposited in the sediment.

In general in the sediment cores from these environments, sand decreases and finer particles (mud %) increase towards surface, which indicates a gradual change in the depositional environment. The grain size distribution of tidal wetlands is affected by many factors such as changes in sediment source and biological factors in addition to hydrodynamics (Yang *et al.*, 2008). Heavy rainfall leads to increased addition of terrestrial organic matter along with greater freshwater discharge to estuarine environment (Zong *et al.*, 2006). While, construction of dams leads to changes in natural flow of fresh water as well as morphology of estuaries resulting in changes in the sedimentation patterns and increase in salinity (Rodriguez *et al.*, 2001). Such modifications have been found to change the chemical and biological characteristics of estuaries and adjacent coastal regions (Surge *et al.*, 2003). Thus major changes affecting biogeochemical processes operating within estuarine environments worldwide are reduction in freshwater due to diversion or dam building (Rodriguez *et al.*, 2001), local sea level fluctuations (Sanders *et al.*, 2009) in addition to that of metal pollution. However, when the average sand content in mudflats of lower estuaries are compared, it is observed that in general average sand content increases from south to north and is attributed to differences in tidal range.

Higher metal/Al values towards the surface in some of the cores indicate anthropogenic addition of metals in the form of sewage, wastes, to sediment in recent years. Fe oxide coatings on surfaces of coarser particles are known to play an important role in adsorption of metals (Achyuthan *et al.*, 2002). While elevated concentration of metals towards the surface of cores indicates their diagenetic enrichment in addition to anthropogenic input. Organic matter decay and/or reductive dissolution of Fe and Mn oxyhydroxides in sub-surface sediment result in release of reduced metal species to pore water. These metal species tend to migrate towards the oxic surface sediment, where they are re-adsorbed by the Fe and Mn oxyhydroxides (Ruiz-Fernandez *et al.*, 2011).

The variation in C/N ratio along the length of the core is used to reconstruct mixing scenarios of terrigenous v/s marine plant material (Rosenbauer *et al.*, 2009) in estuarine sediments. Decrease in TOC/TN ratios from bottom to surface suggests decrease in deposition of organic matter of terrestrial origin in recent years. The observed high temporal variability in organic matter distribution may therefore have a major impact on the overall carbon dynamics in intertidal ecosystems (Bouillon *et al.*, 2003). Decrease in rainfall upon construction of dams, diversion of freshwater, as well as local relative sea level rise, together, seem to have resulted in reduction in terrestrial organic matter input in recent years, and is probably reflected as lower TOC/TN ratio towards the surface. According to Lamb *et al.* (2006) the direction of change C/N ratio is the most important factor in interpreting environmental changes (relative sea level) rather than the absolute values. Decrease in marine contribution with increasing distance from the mouth to the upstream of the estuary obtained indicates dilution of fluvial derived terrestrial organic matter towards the mouth of the estuary.

Diatoms showed a mixed assemblage of fresh and marine diatoms with predominance of freshwater planktonic diatom *Cyclotella meneghiniana* throughout the cores which could be attributed to the extensive freshwater runoff and is in well agreement with the rainfall data. The waves and tidal processes regulated the variations in marine diatoms namely *Thalassiosira* and *Triceratium*. The relatively higher sand percentage together with elevated C/N ratio and predominance of freshwater diatoms suggested greater river runoff in the past while marine influence is supported by sudden increase in sand percentage, decrease in C/N ratio and increased dominance of marine diatoms in the recent years. Zn, Pb and Mn showed significant correlation with *Cyclotella meneghiniana*, *Nitzschia* and *Rhaphoneis* species indicating their association with diatom distribution.

In mangrove ecosystems, mangrove plant litter fall is the main supplier of terrestrial organic matter fraction to the sedimentary organic matter pool (Prasad and Ramanathan, 2009) and contains more organic matter compared to adjacent mudflat. It is known that humic substances have high metal binding capacity (Sondi *et al.*, 2008) and if they are of marine origin then these humic substances form more stable complexes (Übner *et al.*, 2004) than freshwater/terrestrial source. The higher deposition of metals and finer particles towards surface of the cores may therefore be attributedto reduction in freshwater input and resulting increase in salinity.

Conclusion

A review of the studies carried out on estuaries along central west coast of India, including our own investigations with special reference to sediment components, has helped in understanding depositional environment and processes prevailed with time in addition to tracing the sources and level of metal enrichment along this coast. Effect of human induced activities has changed input of material which in turn is responsible for altering the estuarine processes. Our investigations have revealed increasing marine processes in recent years.

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