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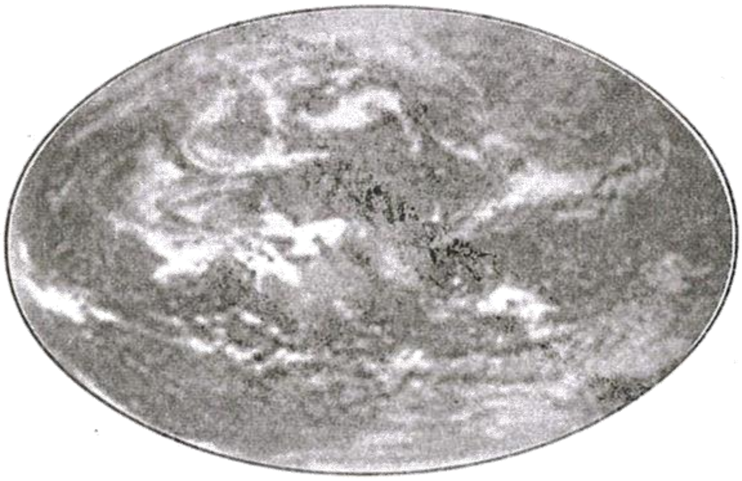

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BIOAVAILABILITY OF METALS IN ESTUARINE SEDIMENTS AND BIOACCUMULATION IN SEDIMENT ASSOCIATED BIOTA AND MANGROVES, WEST COAST OF INDIA

G.N. Nayak

Department of Marine Sciences, Goa University, Goa – 403 206, India.
gnnayak@unigoa.ac.in /gnnayak57@gmail.com / 9545693911

Along the west coast of India, the small rivers are the major pathways for sediment and nutrients from the land through the estuaries to the adjacent sea. The estuaries are dynamic aquatic environments wherein fresh and saline waters interact resulting high sediment deposition.In addition to natural material, anthropogenic activities such as mining, industrial, agricultural, transportation and others also add material to the estuary. The studies carried out, for over two decades, on the mudflat - mangrove sedimentary environments in the tropical estuaries along central west coast of India, revealed that estuarine processes are affected by sea level variation as well as varying fresh water influx and other processes. The hydrodynamic conditions and rate of sedimentation in the estuaries along this coast showed considerable variations with time. The metal concentration showed an increase towards surface of most of the cores indicating their deposition in calmer environment with finer sediments and organic matter.

Within an estuary, systematic sorting of sediment size takes place from the mouth to the head due to the prevailing hydrodynamic conditions. Intertidal flats represent sand flats in lower, marine dominated estuarine regions and mudflats in the middle mixing zones. Distribution of sediment, organic matter and metals within an estuary is regulated by changing tides, waves, winds, resulting in changes in salinity, pH, radox potential and other physico-chemical parameters with space and time. The metals are transformed from one phase to the other due to changes in physico-chemical conditions asthese phases are sensitive to changes in pH and Eh. The sediment associated biota, bioaccumulatethe metals available in solution and bioavailable phases (exchangeable, carbonate, Fe-Mn oxide, organic/sulfide). The edible sediment associated biota with metal bioaccumulation is consumed by the fish eating coastal human population. Regular consumption of these biota can affect the health of coastal population. On the other hand, mangroves are known for biomagnification of metals and help in remedial measures to control the quality of coastal waters. The awareness campaign to the coastal population on the effect of eating metal bioaccumulated biota and use of mangroves in bioremediation is recommended.

Introduction

The central west coast of India constitute the coasts of Maharashtra, Goa and northern Karnataka and it represents region of small rivers and pocket beaches, bays, rocky cliff and estuaries.Estuaries are transition zones between land and sea wherein fresh water mixes with sea water thereby alters the salinity and pH of resulting water and favours high rate of sedimentation. Distribution of sediments within estuaries is often classified on the basis of grain size which in turn helps in understanding the hydrodynamic conditions prevailing in the area. The metals get adsorbed onto the suspended particulate matter and are transported through the water column which finally gets incorporated into the sediments. Estuarine sediments retain large quantity of finer sediments and organic matter and act as sink for a wide range of metals which show high affinity for fine grained sediments. Fairbridge (1980), definedestuary as "an inlet of sea reaching into a river valley as far as the upper limit of tidal rise", usually being divisible into three sectors(Fig. 1.1): a) a marine or lower estuary, which has free connections with open sea; b) a middle estuary subjected to strong salt and freshwater mixing; c) fluvial or an upper estuary, characterized by freshwater but subjected to tidal action. However, the boundaries or the transition zones between these sectors shift according to constantly changing tides and river discharge.

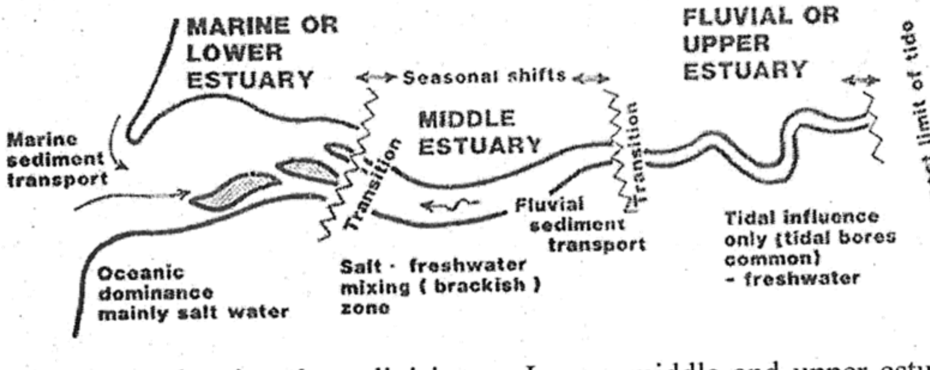

Fig. 1.1 Estuary showing three divisions – Lower, middle and upper estuary: The boundaries are the transition zones that shift according to season, weather and tides (After, Fairbridge, 1980).

The sediments brought to the estuaries may settle either within the channel or along the bank as intertidal flats. Intertidal flats within the estuaries vary from sandflat in the lower estuary to mudflat in the middle estuary. According to Bates and Jackson (1987), these are sandy to muddy depositional systems along estuarine shores that are submerged and exposed in the course of the rise and fall of the tide at regular intervals. These are the sites of sediment deposition where silts and other finer sediments accumulate in the shallow water in quieter areas within estuaries. The changing physico-chemical properties of water are responsible for binding clay particles together in estuaries. These clay grains aggregate and form large particles that sink through the water column. Therefore, clay deposition is more in estuaries where there is mixing of seawater and freshwater, in the presence of organic matter having strong chemical binding properties. Fine grained mud, due to its stickiness can resist being re-suspended and transported by moving water which is capable of transporting larger, non-cohesive sands and gravels.

Mangroves begin to grow as far seaward as mean high water neaps while mudflats often continue to form below the level of low water spring tides, (McCann, 1980). Sea-level changes and effects of anthropogenic input are very well recorded over mudflat and mangrove sedimentary environment. Mangrove environments are generally found in tropical coastal areas and also in sub-tropical region. Mangroves are one of the productive ecosystems (Kathiresan, 2003) and cover a large area on a global scale (Spalding et al., 1997). The physical, chemical and biological processes involve in mixing, changing the redox conditions, remobilise and finally release the metals into the overlying water column through the processes of bioturbation, early diagenesis, dredging, and erosion(Deng et al., 2010; Filho et al., 2011;Pande and Nayak, 2013).When the abundance of metals is considered, major concentrations (99%) of metals are stored in sediments whereas a minor fraction (about 1%) is available in the dissolved form. Therefore, sediments are considered as the major sinks for metals. However, as they involve in persistence, bioavailability, metal toxicity, bio-accumulation and may get transferred to the overlying water column thereby entering into the food chain (Nemati et al.,2011;Díaz-de Alba et al., 2011). Therefore, it is essential to determine the metals with different geochemical phases. Sequential extraction provides adequate information related to the occurrence, origin, transport of metals, biological/physicochemical aspects, and their mobilization, though the procedure is complicated and lengthy (Passos et al., 2010). Further, it providesinformation on role of degradation of organic matter, redox potential and pH on the mobilization and retention of the metals in the aquatic ecosystems (Tessier et al., 1979; Saleem et al., 2015).

Methodology

A sample is a small portion that is representative of an area or environment. Sample preservation after collection is important in order to avoid alteration of chemical components in the sediment which may lead to erroneous results. Sediment core samples collected representing mudflat and mangrove environments were sub-sampled at 2 cm interval and investigated for various parameters like sand, silt, clay(Folk, 1968), organic matterby Walkley-Black method (Walkley, 1947),clay minerals(Biscaye, 1965)and metals in bulk (Jarvis and Jarvis, 1985) as well as in different chemical phases (Tessier et al., 1979)using standard methods and sophisticated instruments like XRD Analyzer and Atomic Absorption Spectrophotometer (AAS). The metal phases include"exchangeable", "carbonates", "Fe/Mn oxides", "organic/sulphidic" and "residual" (Tessier et al. 1984). Metals were also studied in mangrove pneumatophores and soft tissues of benthic organisms. Al, Fe, Mn, Cr, Co, Ni, Cu and Zn were studied for total sediment, speciation and bioaccumulation. The data obtained was processed using statistical techniques and computed pollution indices including Sediment Quality Values (SQV) following Screening Quick Reference Table (SQUIRT) and the Risk Assessment Code (RAC) as proposed by Perin et al. (1985).Selected sediment cores were dated using lead dating method.

Results and Discussion

Along the central west coast of India, rainfall decreases from South to North, while the tidal range is in the micro-tidal scale in Karnataka, meso-tidal in Goa and meso to macro tidal in Maharashtra.Our studiescarried out on the estuaries along central west coast of India (Singh and Nayak, 2009; Fernandes et al., 2011; Singh et al., 2013a; Volvoikar and Nayak 2013, 2015; Fernandes and Nayak, 2015) have revealed significant results. We also studied the bioaccumulation and bioremediation potential in an estuary(Noronha e D'Mello and Nayak, 2016; Dias and Nayak 2016). The rainfall, river runoff,construction of dams, geomorphology of the estuaries and anthropogenic activities have considerably influenced the depositional environment. We observed that there is a strong transition in the estuarine environment from fresh water dominated in the past to marineinundated in recent years. These changes are related tothe rainfall pattern, decrease in runoff due to the construction of dams in recent times, rise in sea level and so on. Due to these changes, the mixing processes were affected leading to increased flocculation and deposition of fine grained sediments in the recent years. Further, anthropogenic activities in the catchment areas like mining, transportation of ores and agricultural practices have added considerable amount of material in to the estuaries.The main sediment source of an estuary is from terrigenous material from the catchment area. The distribution of the sediments within an estuary is regulated by interactions between the available sediments and flow hydrodynamics.The interaction among cohesive sediments (mud) is different from that of non-cohesive sediments (sand). Cohesive sediments may aggregate, forming flocs by the flocculation process caused by chemical or biological interaction. Flocculation increases the settling velocity of sediment particles. Mangroves are known for being sites of sediment deposition and are associated carbon and nutrients. The mangroves trap sediment by their complex aerial root structure and are an important sink for suspended sediments and. Mudflats are usuallysituated adjacent to mangroves and consists of mainly of fine particles. The intertidal mudflats support communities characterized by polychaetes, bivalves and oligochaetes and large numbers of birds and fish.

The distribution and accumulation of metals within estuarine sediments are influenced by the sediment texture and mineralogical components. The metals get assimilated in the sediment along with organic matter, Fe/Mn oxides, sulphide,and clay and thus undergo changes in their speciation due to geochemical modifications. The physico-chemical factors such as pH, redox conditionsand salinity determine metal sorption and precipitation processes. In addition, sediment grain size substantially influences the metal concentration in the estuarine sediments as the clay fractions that have a high specific surface area, favor adsorption processes.The organic matter content in the sediments leads to relatively higher metal accumulation.

The chemical speciation of metals in sediments provides information on the potential availability of metals to biota under various environmental conditions. The metals in the exchangeable fraction are likely to be affected by sorption-desorption processes such as weaklybound to clays, hydrated oxides of iron and manganese and humic acids.The metals in the carbonate fractions can be associated with sediment carbonates and this fraction is susceptible to changes of pH. The exchangeable and carbonate fractions are together called as the labile fraction. The metalsbound to iron and manganese oxides are excellent scavengers for trace metals and are thermodynamically unstableunder anoxic conditions. The trace metals bound to various forms of organic matter such as detritus, humic and fulvic acids etc, form complexation and peptization phenomenon. The residual fraction of the sediments constitutes of primary and secondary mineralswhich may retain trace metals within their crystal structure and are not released easily into solution (Nayak and Noronha-D'Mello, 2018).The first four fractions are considered as the bioavailable fraction as they exhibit mobility and are potentially available for uptake by organisms. The mobile fractions introduced through anthropogenic activities remain bound to the exchangeable andthe carbonate phases. The sediment-associated metals due to their mobility and bioavailability, affects both ecosystems and life through a process of bioaccumulation and biomagnification, respectively. Marine organisms can accumulate metals in their tissues that may threaten the health of organisms higher in the food chain. The ecological risk posed by metal-contaminated sediments depends strongly on the sediment characteristics, specific chemical forms of the metals, influencing their availability to aquatic organisms (bioavailability) and the ability of these organisms toaccumulate (bioaccumulation) or remove metals. Various accumulation patterns havebeen described regulating the uptake of metals defined by the balance between uptake and excretion rates and by detoxification processes usually involving proteins such as metallothioneins (Nayak and Noronha-D'Mello, 2018). Mangrove pneumatophores also bio-accumulate metals and retain metals and therefore help in bioremediation.

Conclusion

Study carried out on estuarine mudflats and mangroves sub-environments along central west coast of India revealed that rainfall, river runoff, construction of dams, geomorphology and anthropogenic activities have influenced the depositional environment. The bioavailability of metals in sediments have direct relation with bioaccumulation of metals in benthic biota. Mangrove pneumatophores bio-accumulate metals and can help in remedial measures.

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