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Recent Contributions to The Geochemistry and Sedimentology of Estuaries, Mangroves, and Mudbanks Along the Indian Coast: A Status Report

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In the last four years, significant progress has been made in biogeochemical/ geochemical and sedimentological studies of the coastal sediments along the east and west coasts of India. The present review highlights the research output in sediment dynamics, biogeochemical processes like sulfate reduction/ nitrogen cycle and metal enrichment/contamination in the coastal sediments in three distinct depositional milieus like estuaries, mangroves, and mudbanks. These depositional regimes are not only highly dynamic owing to tidal currents and waves, but also highly productive. Both biodiversities as well as water/sediment compositions of the coastal regions are very much susceptible to anthropogenic input.

Estuaries

Estuaries are unique and complex environments where a river or a stream opens into the sea (Bhaumik *et al*., 2016). Salinity in estuaries varies from 0 to 35 psu (brackish water) due to the mixing of seawater and riverine freshwater (Nagvenkar, 2014). Flocculation and deposition of river-borne fine particulates result in the effective sedimentation of clay and silt in estuaries. However, the nature of sediment may change significantly with the upstream decrease in salinity. Salinity in the estuaries may vary considerably over the day owing to tidal influence. Estuaries are one of the most productive regions both in terms of fisheries and deposition of highly fertile silt, supporting cultivation. The high fertility of the estuarine sediments may be attributed to nutrient storage and the recycling properties. Estuaries are a buffer zone between coastal catchments and the marine environment. Owing to insignificant wave action, estuaries provide a quiet shelter for the survival of numerous aquatic species. The productive nature of estuaries makes the coastal zone around them thickly populated. On the other hand, anthropogenic activities like industrialisation, tourism, dredging, land reclamation, over-exploitation of fish stock and coastal construction contribute to accumulation of toxic metals, organic pollutants, microplastics (Sruthy and Ramasamy, 2017), hydrocarbons (Ramzi *et al*., 2017) and construction debris etc. which significantly damage the fragile ecosystem. India is blessed with 14 major, 44 medium and 162 minor rivers draining into the sea through various estuaries (Fig. 1; Kumar and Sarma, 2018). Most of India's major estuaries occur on the east coast. In contrast, the estuaries on the west coast are smaller. Two typical examples of estuaries on the west coast are the Mandovi and Zuari estuaries.

Estuarine Sediment Dynamics

An observational study (Vinita *et al*., 2017) of sediment dynamics in the Cochin Estuary reveals the mechanics of variation in suspended sediment concentrations (SSC) at intertidal, fortnightly and seasonal time scales. Tide, current, hydrography (vertical profile) and turbidity data indicate the influence of hydrodynamic processes (resuspension, mixing, advection) driven by the river runoff and spring-neap fluctuations on the SSC. These observations are vital in the development and

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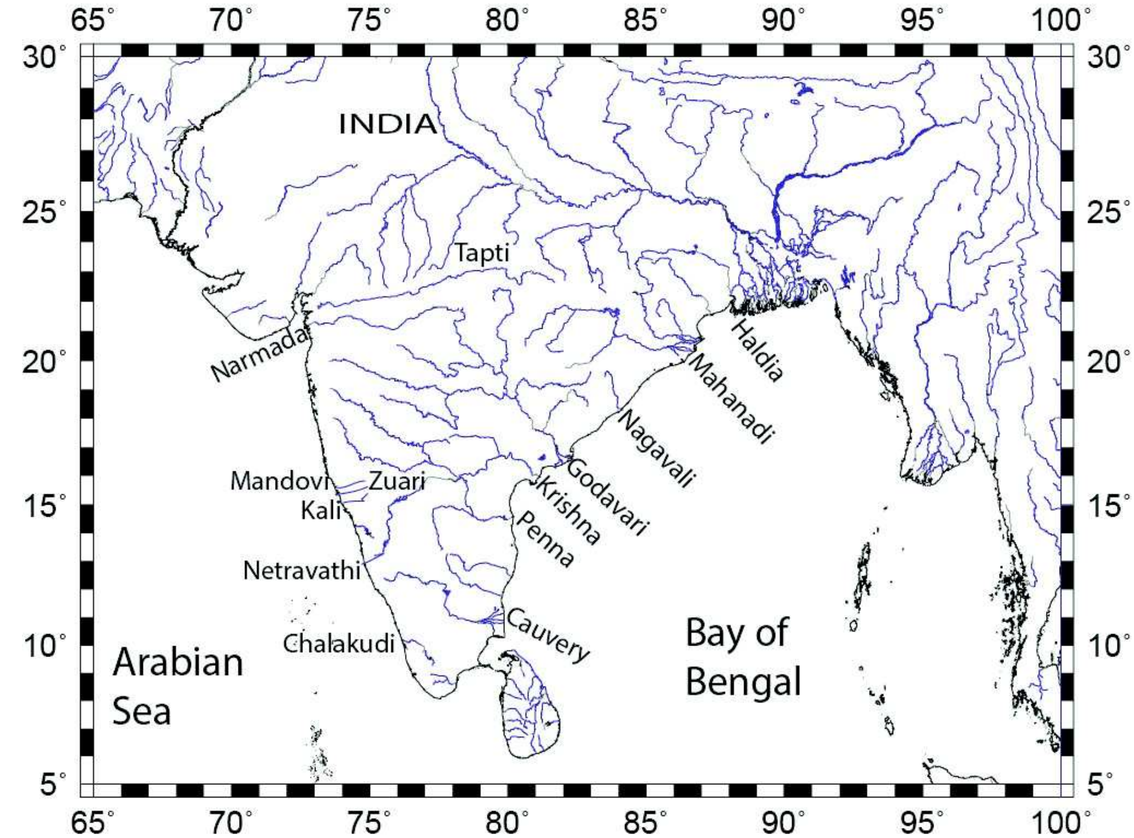

Fig. 1: The major rivers and estuaries of India

protection of harbors situated close to the inlet of estuaries and for the efficient implementation of an integrated coastal management program. Estuarine turbidity maximum (ETM) is an important feature at the mouth of estuaries. Fernandes et al. (2018) studied the spatio-temporal variations in suspended particulate matter (SPM) in two meso- (Mandovi and Zuari) and four micro- (Terekhol, Chapora, Sal, and Talpona) tidal estuaries of Goa. They attributed the origin of ETM to gravitational circulation as well as flocculation at the seawater-freshwater interface during the wet season and the impact of tidal and wind-induced currents at the river mouths during the dry season. Saha *et al*. (2018) reported highly variable mixing of sediments along the Gulf of Khambhat estuary. The Tapti and Sabarmati Rivers supply basaltic (from Deccan province) and granitic rock fragments respectively to the Khambat estuary. Saha *et al*. (2018) showed that the proportion of mixing varies systematically from the outer to the inner estuary depending on the interaction of fluvial currents and tidal flows. The felsic:mafic ratio is 40:60 in the outer estuary, 65:35 in the central estuaries and 90:10 in the fluvial-dominated inner estuaries. Thus, provenance interpretation from estuarine sediments should take care of the depositional setting.

Biogeochemistry of Estuarine Sediments

Some recent studies on estuarine biogeochemistry shed light on the nitrogen and sulfur cycles in estuarine sediments. Salahudeen *et al*. (2018) measured denitrification rates in Ashtamudi estuarine sediments and showed significant spatio-temporal variations. The results suggested that denitrification in the Ashtamudi estuary is not driven by nitrate from agricultural runoff but from the NO_3-N produced *in situ* in the sediment. Apparently, the sediment temperature and total organic content point to coupled nitrification-denitrification as an important microbial activity in the sediment. Studies on the nitrogen biogeochemistry of the Mandovi and Zuari estuaries by Ahmed *et al*. (2019) indicated significant N_2 fixation rates, ranging between 0.1 and 34 micro molNm^{-3}d^{-1}. The significant variation between the two adjacent estuaries was attributed to variations in turbidity caused by various factors, including mining, winds/ navigation, and fishing activities.

A comparison of the dissolved methane (CH_4) concentrations in the west and east coast estuaries of India by Rao and Sarma (2016) showed significantly higher CH_4 concentrations (wet period: 113±40 nM and dry period: 88±15nM) in estuaries along the west coast compared to those measured in estuaries along the east coast (wet period: 27±6 nM and 63±12 nM,). The results also highlighted the significantly lower methane flux into the atmosphere from Indian estuaries compared to that from European estuaries. Studies on CH_4 emission from the Mandovi and Zuari estuaries show significant increase towards the freshwater end (Araujo *et al*., 2018). The concentrations varied from 6 to 901 nM (saturation: 300-46,000 %) in the Mandovi estuary and from 8 to 1022 nM (saturation: 400-41,000%) in the Zuari estuary. The high concentrations of CH_4 were attributed to contributions from mangrove swamps, sedimentary input, and river runoff.

The studies on organic carbon degradation and sulfate reduction along the salinity gradient of Mandovi estuary (Naik *et al*., 2019) showed significant variability in sulfate reduction rates (SR). The maximum SR was recorded within the mangrove domain. Pyrite content (3.45-12.9 mg/g) was the highest at the marine end and decreased towards the freshwater end. Sulfate reduction was the dominant pathway of organic carbon (OC) mineralization in the mid-salinity region, accounting for over half of the OC mineralization, whereas, at other locations, Fe(III) and Mn(IV) possibly played an important role in organic carbon mineralization.

Metal Contamination in the Estuaries

In the last four years, concentrations, mobility and retention metals in the estuarine system have been the major focus of research on estuaries. Bakshi *et al.* (2017) described the micro-spatial variation of elemental distribution in estuarine sediment and the bioaccumulation of those elements in different mangrove species of the Indian Sundarbans. Their data reflect a higher concentration of elements, including Al, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, and Pb, in the sediment. Various sediment quality indices suggest that surface sediments are moderately contaminated and undergoing progressive deterioration. Copper, Cr, Zn, Mn, and Ni show higher values of enrichment factors (0.658-1.469), contamination factors (1.02-2.7), and geo-accumulation index (0.043-0.846). Studies on the distribution of Co, Cr, Cu, Fe and Zn along with sediment properties from the Hooghly-Matla estuarine system (Ghosh *et al*., 2019) showed enrichment of Co, Cu, and Zn in the intertidal sediments. The values of geo-accumulation index (Classes II & III) and pollution load index were higher than unity (1.6-2.1), suggesting Co and Cu as the major contributors to sediment pollution, followed by Zn, Cr, and Fe. The authors suggested multiple parameters, including discharge pattern and exposure to industrial effluent, domestic sewage, stormwater, agricultural run-off and fluvial dynamics of the region, as possible causes of metal enrichment.

Studies on the speciation as well as sediment quality values (SQV)/risk assessment code (RAC) of Fe, Mn, Ni, Co, and Cr carried out on the mudflat sediments of Mandovi and Sharavathi estuaries (Nasnodkar and Naik, 2017) showed adsorption of Fe, Mn, Co and Cr on fine-grained sediments and organic carbon, which also indicates bioavailability of Mn and Co. Mercury speciation studies reveal the significance of particulate-associated Hg (Hg_{SPM}) in increasing the bioavailability of Hg in the Mandovi estuarine system during the dry season (Chakraborty *et al.*, 2019).

Based on the sedimentary metal concentration data from the Cochin backwaters, George *et al.* (2016) showed significant variations in the concentrations of Fe (15517-90885 μg/g), Mn (122.5-970.9 μg/g), Co (6.9-41.9 μg/g), Ni (12.9-62.9 μg/g), Cu (15.9-56.8 μg/g), Zn (58.7-888.7 μg/g), Cd (0.9-14.5 μg/g), and Pb (12.7-46.8 μg/g) during the monsoon, post-monsoon, and pre-monsoon periods. The data may play an important role in identifying the sources of contaminants and for tracking the dispersal pathways of contaminants in estuarine environments. Studies on the Cr, Cu and Ni concentrations in sediments from Uppanar estuary situated at Cuddalore showed the association of trace metals with Fe and Mn, indicating their adsorption on Fe-Mn oxyhydroxides (Kalpana *et al.*, 2016). Based on geo-accumulation index and enrichment factors, the sediment was classified as unpolluted to moderately

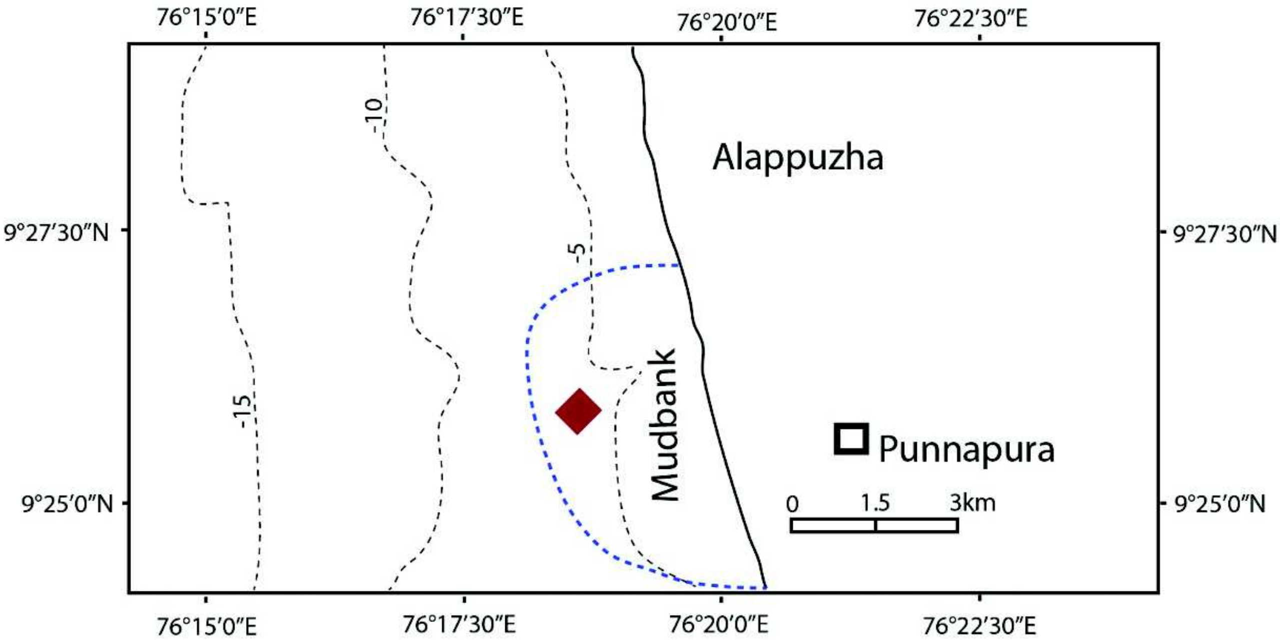

Fig. 2: The Alappuzha mudbank in the SW coast of India. Note: The outer boundary of the mudbank is shown by the blue broken line and the sampling station by the brown square. Water depth contours are in meters below sea level

polluted with respect to Fe, and Cu and moderate to considerable with respect to Pb and Co. Two simultaneous studies on metal concentrations in oysters from Chikalim and Chapora estuaries (off Goa) showed significant seasonal variations in metal concentrations and higher-than-safe level of concentrations of Cu and Cd in edible oysters, which may pose a threat to human health (Chakraborty *et al*., 2016 and Shenai-Tirodkar *et al*., 2016). These authors showed that bioaccumulation of Cd in oyster (*Crassostrea* sp.) depends not on the total Cd concentration in the sediments but on the speciation of Cd in the system.

Mudbank

Mudbanks are unique depositional milieu exclusively appearing along the Kerala coast (Prasanna Kumar *et al*. 2018). They are best developed off Alappuzha and appear every year during the SW monsoon. Mudbanks are considered unique also because of the high stock of plankton and fish catch. Mudbanks of Kerala form in a calm area of the sea amidst high waves due to a special property of dampening and dissipation of wave energy. The formation of mudbank is commonly attributed to the coastal upwelling associated with the SW monsoon (Shynu *et al*., 2017; Kumar *et al*., 2018; Jyothibabu *et al*., 2018). On the other hand, significantly cold, hypoxic and nitrate-rich waters surfacing near the coast via upwelling fuel the exceptionally high phytoplankton stock. Apparently, except at points close to the sea bottom, turbidity level in the Alappuzha Mudbank is below the critical level to inhibit the plankton stock (Jyothibabu *et al*., 2018). The suspended sediments could be attributed to vertical spurts due to the disturbance of the bottom fluid mud layer.

Through a high-frequency, long time-series observation (7-month long weekly time-series observation) at Alappuzha, Muralidharan *et al*. (2018) highlighted the role of strong winds and high amplitude waves associated with the southwest monsoon as the key factor responsible for the formation of mudbanks. The prevailing onshore upwelling current during the southwest monsoon, while propagating from the deep to shallow water region, transports the fluid mud through depression channel network towards the coast. The accumulated fluid mud, on the other hand, acts as a wave damper for high monsoon waves, leading to the formation of a tranquil mudbank region. Based on ground-penetrating radar (GPR) data, Loveson *et al*. (2016) indicated the presence of buried paleo-channels and established their role as a conduit

Fig. 3: Typical mangrove vegetation of Chorao Island, Mandovi River showing tangled prop roots (after Forest Department of Goa: https://www.forest. goa.gov.in/mgr/)

for the transportation of clay particles during monsoon. Muralidharan *et al*. (2017) questioned the subterranean fresh-water concept by experimentally demonstrating the analytical artifact in measuring the salinity at high mud contents.

Studies on the magnetic properties and grain size distribution by Badesab *et al*. (2018) suggested a linkage between enrichment of silt-sized magnetic particles and formation processes of mudbank along the Alappuzha coast. The coarse magnetic particles settle to the bottom sediments, while the finer magnetic particles remain suspended in the water column as long as supported by the prevailing energy conditions. The spatial distribution of SSC and particle size distribution, using a laser interferometer (LISST 100X), in and around the Allapuzha mudbank (Santosh Kumar and Manimurali, 2018) helped in delineating the periphery of the mudbank. The concentration of clay near the sea bottom at the three measurement stations ranges from increases from 20 mg/l to 250 mg/l.

Studies on the seasonal distribution of benthic foraminifera in mudbanks showed a low diversity during both pre-monsoon and monsoon seasons, pointing to a stressed environment (Dubey *et al*., 2018). *Ammobaculites dilatatus* and *Ammobaculite sexiguus* are the dominant agglutinated benthic foraminiferal species, suggesting carbonate undersaturation under the fresh-water influence.

Mangrove

Mangroves are dense thickets or forests (Fig. 3) that grow along tidal estuaries, in salt marshes, and along muddy coasts in tropical and subtropical latitudes (Kathiresan, 2018). Shrubs and trees in mangrove forests belong mostly to families Rhizophoraceae, Acanthaceae, Lythraceae, Avicineacea, Meliaceae, Combretaceae, and Arecaceae. They are characterized by a dense tangle of prop roots (exposed, supporting roots) which slow down the movement of tidal waters, causing sediments to settle out of the water and build up the muddy bottom. The tangled roots allow the trees to handle the daily rise and fall of tides. The very high organic matter flux and the fine-grained nature of the sediments prevent oxygen diffusion deep into the mangrove sediments, resulting in anaerobic conditions a few centimeters below the sediment surface. The aerial roots or pneumatophores that extend out of the water and take in oxygen from air during low tide (Srikanth *et al*., 2015). Mangroves are extremely important to the coastal ecosystems as they buffer coastal communities against extreme weather events such as hurricanes, stabilize coastlines and reduce soil erosion. India has a vast aerial coverage (4921 km^2; ISFR Report, 2017) of mangrove forests, occupying 3.2 % of the global mangrove forest. In terms of the percentage of aerial coverage of individual mangrove forests relative to total area of Indian mangrove forests, Sundarbans (44%) has the largest mangrove cover, followed by Gujarat (23%), Andaman & Nicobor (13%), Andhra Pradesh (7,7%), Orissa (4.8%), Maharastra (4.7%), Tamil Nadu (0.9 %), Goa (0.5%), Kerala (0.8%), Karnataka (0.06%), Daman & Diu (0.06%) and Puduchery (0.04%). Common mangrove species reported along Indian coast include *Rhizophora mucronata, Rhizophora apiculate, Bruguiera gymnorrhiza, Bruguiera cylindrical, Ceriops tagal, Kandelia candel (K. rheedi), Avicennia officinalis, Avicennia marina, Sonneratia alba, Acrostichum aureum, Sonneratia caseolaris, Aegiceras corniculatum, Excoecaria agallocha, Acanthus illicifolius, Lumnitzera racemose.*

Some recent advances in mangrove biogeochemistry and metal accumulation are summarised below:

Manju *et al.* (2016) reported concentrations of biochemical components like carbohydrates, lipids and proteins, TOC/TN ratio and $\delta^{13}C_{TOC}$ data for sediments collected from five mangrove ecosystems along the Kerala coast. The $\delta^{13}C_{TOC}$ values (–29.2 to –23.9 ‰ VPDB), TOC/TN ratio of 11.39 to 24.14 and protein/carbohydrate ratio of < 1 in the entire study region indicate a large content of aged organic matter in mangrove sediments. On the other hand, organic geochemical data (n-alkane, n-alkene, hopanes) reported by Resmi *et al*. (2016) indicate marked seasonal variations (pre-monsoon, monsoon, and post-monsoon) in contribution from bacterial biomass, phytoplankton, and terrestrial/ mangrove-derived litter. The presence of hopane biomarkers was attributed to the *in situ* activity of the bacterial community, using carbon sources of mangrove origin. The hopane biomarkers may be correlated with the periodic anoxic events in the study region. Diagenesis of the mangrove-derived organic matter produces pore-water NH_4^+. Fernandes *et al*. (2016) indicated that nitrification/ denitrification in mangrove sediments is driven by an enhanced NH_4^+ availability in porewater due to the degradation of organic litter.

Dutta *et al.* (2017) reported a very high efflux of CH_4 from the Sunderban mangrove sediments. They reported 53.4 times high supersaturation of CH_4 in sediment pore water than in adjacent estuarine waters. This resulted in a significant CH_4 efflux from sediments to estuarine waters via advective and diffusive transport.

Ranjan *et al.* (2018) reported enrichment (EF > 1) of trace metals like Co, Cr, Cu, Fe, Ni, Pb and Zn from the surface sediments of Sundarban mangrove ecosystem, suggesting anthropogenic contamination. Based on the temporal variations in the contents of metals (Fe, Mn, Cu, Zn, Cr and Co), organic carbon, grain size distribution (sand, silt, clay) in six sediment cores collected from one of the largest mangrove-associated mudflats of Mandovi estuary, west coast of India, Nayak *et al.* (2018) suggested past changes in tidal energy conditions, freshwater inflow and anthropogenic activities over the past few decades as possible reasons.

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