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# Elemental composition, distribution and control of biogenic silica in the anthropogenically disturbed and pristine zone inter-tidal sediments of Indian Sundarbans mangrove-estuarine complex

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ABSTRACT

Spatial distribution and interrelationship among organic nutrients – silica and carbon – and various lithogenic elements were investigated in the surficial sediments of Matla estuary and Core Zone of Indian Sundarbans Reserve Forest using spatial analysis and multivariate statistics. Biogenic silica (BSi), an important parameter for coastal biogeochemistry, was measured using Si-time alkaline leaching method. BSi concentration ranged from 0.01% to 0.85% with higher concentrations in upstream region of Matla estuary and attenuated values towards the bay, seemingly due to changes in hydrodynamics and land use conditions. Spatial distribution of BSi did not exhibit significant correlation with sediment parameters of organic carbon (OC), elemental composition and clay content. However, it showed significant contrasting trends with total phosphorus (TP) and total silica of human influenced Matla estuary sediments as well as the dissolved silica (DSi) of its surface waters. Anthropogenic influence on sediment geochemistry is discernable with the presence of higher concentrations of organic and inorganic elements in Matla estuary than in Core Zone sediments. Spatial variation trends are often challenging to interpret due to multiple sources of input, varying energy and salinity conditions and constant physical, chemical and biological alterations occurring in the environment. Nonetheless, it is certain that anthropogenic activities have a substantial influence on biogeochemical processes of Sundarbans mangrove-estuarine complex and potentially the coastal ocean.


## 1. Introduction

Coastal areas represent almost 10% of the oceanic area and yet 77% of the totals economic value of the biosphere, representing their disproportionately high contribution to global marine primary production (Martinez et al., 2007). As much as 16% of the riverine and estuarine silica input to oceans is biogenically derived (Conley, 1997). Biogenic silica (BSi) in the surface sediment reflects the contribution of plant phytoliths and siliceous phytoplankton like diatoms to the primary productivity of the coastal seas (DeMaster, 2002). BSi accumulation and dissolution dynamics has been extensively studied worldwide in the coastal and open seas, and especially in the deep sea sediments, due to its close association with the carbon cycle (DeMaster, 1981; Kamatani and Oku, 2000; Ragueneau et al., 2001; Krause et al., 2011; Martin et al., 2013; Chase et al., 2015). Recently, the fate of silica and carbon at estuarine boundaries has come to the focus of biogeochemists due to the importance of these two elements for the global climate (Conley, 2002; Ragueneau et al., 2006; Struyf and Conley, 2009). However, no consensus exists on the factors ultimately controlling BSi dissolution and preservation in various sedimentary environments (Ragueneau et al., 2001) and little quantitative information is known about the distribution and cycling of silica in the coastal tropical mangrove ecosystems (Jennerjahn and Ittekkot, 2002). Highly productive coastal ecosystems at the land-sea interface of tropical regions are rich in plant phytoliths and thus likely to be a key regulator in biogenic silica preservation and mobilization (Derry et al., 2005; Zang et al., 2016).

Mangroves play an influential role in the coastal diatom distribution and the subsequent oceanic export of organic matter, owing to internal processes of silica cycling as well as external factors of hydrodynamics and geomorphology (Jennerjahn and Ittekkot, 2002; Dittmar et al., 2006). The Ganges-Brahmaputra river system is responsible for the world's largest sediment input to the ocean (Milliman and Meade, 2013). The river system discharges large amounts of dissolved silica into the Bay of Bengal, the amount of which accounts for approximately 5% of global river inputs (Unger et al., 2003). The Sundarbans, the largest single tract of mangrove forest in the world, are a massive source of organic matter and nutrients within the Ganges-Brahmaputra river system. Such fringing mangroves not only act as a biogeochemical filter by removing inorganic and organic nutrients, and pollutants from tidal water, but also modify substance speciation (Lin and Dushoff, 2004).

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Their morphology favors deposition of fine particles normally enriched with metals, biogenic matter and minerals; the interrelationships among which are influenced by various environmental variables.

>50% of the world mangroves have been lost since the 1950s, 35% in the last two decades, due to human influence and sea level rise (Feller et al., 2010). The Sundarbans are no exception to this trend (Sarkar et al., 2016). Over the last decade, human influence in the Sundarbans has perturbed the cycles of nitrogen (N) and phosphorus (P) through habitat destruction for aquaculture and coastal development, altered hydrology, and nutrient enrichment (Dadhwal, 2010; Manna et al., 2010); subsequently resulting in eutrophication and increased turbidity. This in turn, fosters decreased retention, and increased mobility and availability of nutrients to marine ecosystems (Smith, 2006; Rabalais, 2002; Ragueneau et al., 2002). The increased growth of silicate-utilizing diatoms due to N and P induced eutrophication, and the subsequent removal of fixed BSi via sedimentation out of the water column are thought to explain DSi limitation and shift to non-siliceous phytoplankton in estuaries (Ittekkot et al., 2000).

The Matla drainage basin is severely contaminated with huge organic load and metal pollution due to rapid industrialization, urbanization, unplanned tourism and agricultural runoff (Sarkar et al., 2004; Kumar and Ramanathan, 2015). Reduced freshwater and sediment discharge have also profoundly impacted the physical, biogeochemical and biological environment of the Sundarbans ecosystem (Rahman et al., 2011; Sarkar et al., 2016). Geochemical reactions occurring at the sediment-water interface affect estuarine fluxes of nutrients and trace elements; hence, they can be used to infer sources of pollution (Salomons and Förstner, 1980). At the sediment-water interface, rates of physical and biological processes drive large gradients of chemical potential across the surface; this electrolytic gradient affects processes such as retention-release, precipitation-dissolution, flocculation-deflocculation, and resuspension of organic matter and mineral elements (Santschi et al., 1990). A number of recent studies in the region have used sediment profiles to describe the degree of contamination in the Sundarbans sediments (Sarkar et al., 2004; Chatterjee et al., 2007; Silva Filho et al., 2011; Banerjee et al., 2012; Kumar and Ramanathan, 2015). Whereas Chatterjee et al. (2007) studied the vertical organic carbon distribution and noted that factors such as marine sedimentation and mixing processes, microbial processes and mud fraction in sediments played an influential role in organic carbon dynamics, little information is available on the distribution and accumulation of biogenic silica that would shed light on its dynamics under variable environmental conditions. The provenance of BSi in Sundarbans sediments, its spatial and temporal variations, and the corresponding environmental significance of this variation has not been well studied. On the basis of this gap in knowledge, an improved understanding of silica cycling in mangrove systems is critical. Diatoms dominate the phytoplankton community in Sundarbans (Manna et al., 2010) and the associated silica cycle could be an important dynamic that has been overlooked whilst documenting the shifting biogeochemistry of this stressed ecosystem. The motivation for this study was to better understand what determines the production and export of biogenic silica in the mangrove environment. We take an empirical approach to investigate the impact of environmental variables on biogenic and organic matter distribution and use surface sediments as a recorder of "recent" BSi and OC burial.

Thus, the objective of the present study was (I) to explore the spatial distribution and variability of biogenic silica, organic carbon and total phosphorus in surface sediments of human influenced Matla estuary and the pristine Core Zone, and (II) to elucidate the possible controls on the spatial distribution of biogenic matter in the region.

## 2. Material and methods

### 2.1. Study area and sampling methods

Encompassing the southernmost part of Ganga-Brahmaputra delta bordering the Bay of Bengal, Sundarbans mangrove-estuarine ecosystem is the world's largest monsoonal, macro-tidal delta-front halophytic mangrove forest (Chatterjee et al., 2013; Kumar et al., 2016). The land-ocean boundary at Sundarbans is highly irregular and traversed by numerous rivers and waterways that bring abundant nutrients to the bay and support it high primary productivity (Mandal et al., 2009). The present work refers to the region lying between 21°38′20.69″N and 22°19′50.25″N latitude and 88°35′31.84″E and 89°5′60.00″E longitude covering an area of 3950 $km^2$ in the active tidal delta (Fig. 1). The western part of the study area constitutes the Matla-Bidya estuarine system while the eastern part belongs to the core area of Sundarban Reserve Forest and is traversed by the Gosaba-Haribhanga river systems.

The subtropical monsoon climate of the area is characterized by an average rainfall of 1600–1800 mm (Gopal and Chauhan, 2006). Apart from monsoons, considerable precipitation is also received during pre-monsoon (March–June) and post-monsoon (October–February) from depressions and cyclones that form and move in from the Bay of Bengal (Chatterjee et al., 2013). The climate is warm humid type with average humidity maintained at 82% throughout the year. Mean sea level (MSL) in Sundarbans is about 3.3 m and the mean highest water level (MHWL) and mean lowest water level (MLWL) are 5.94 and 0.94 m respectively (Untawale, 1986). The tide is predominantly semi-diurnal with a vertical tidal range varying from 5.2 m in spring and 1.8 m during neap period at the mouth (Mukhopadhyay et al., 2006). The circulation in the Matla-Bidyadhari channel system is mainly driven by tidal currents. This is because the channel is fully deprived of freshwater flow from Himalayan river systems due to heavy siltation and clogging in the late 15th century (Chaudhuri and Choudhury, 1994). Strong tidal mixing in the shallow Matla estuary results in a nearly homogenous vertical profile in the water column.

Although the region predominantly exhibits productive mangrove vegetation, increasingly saline conditions have induced stunted growth and reduced the growth of freshwater mangrove species such as *Heretiera fomes*, *Nypa fruticans* and *S. apetala* in Matla estuary (Mitra et al., 2011a, 2011b). In the upstream region of Matla river (Sites M1 and M2), *Avicennia marina* and *Avicennia alba* constitute the dominant mangrove species; while further down, the Jharkhali mixed mangrove forest (Sites M6, M8, M10 and M11) comprises various mangrove species including *Nypa fruticans, C. nucifera, Ceriops decandra, Sonneratia griffithi, Acacia auriculiformis, Porteresia coarctata* and *Avicennia alba*. Sites M14, M16 (Bonnie Camp) lie in the downstream stretch of the estuary and M20 (Halliday Island) faces the mouth of the estuary to the bay. These are areas of pristine forest with luxuriant growth of *Avicennia, P. coarctata, Ceriops tagal and Rhizophora apiculata*. The Core Zone of Sundarbans Reserve is considered to be predominantly pristine. It is dominated by *Excoecaria agallocha* and *Ceriops* species in the upper reaches and a mixed mangrove forest towards the bay (Giri et al., 2014).

Surface sediments were collected from the Matla estuary and the Core Zone of Sundarbans Tiger Reserve. The funnel-shaped coastal plain estuary of Matla River lies adjacent to the Sundarban Tiger reserve but is notably affected by urbanization and development along its banks. The lower part of the estuary is an exception to this and is associated with dense mangrove patches. The sampling sites were chosen along the entire stretch of Matla estuary considering distance from the sea and variable degree of human interference. Sites M1 (Canning) and M2 (Basanti) in the upstream region are significantly affected by anthropogenic activity and effluent discharge. The width of the channel here is narrow with maximum tidal amplitude. The Jharkhali mixed mangrove forest is intermediate between pristine and anthropogenic stresses. The contrast in terms of human influence between the two study areas was significant in terms of this study because it allowed direct comparison between two environments affected by similar geology, climate, soil type and vegetation but with different extents of anthropogenic stresses. The sampling strategy was to study the spatial variability and anthropogenic influence in sedimentary parameters. A total of 26 surface sediments were collected (15 from the Core Zone of