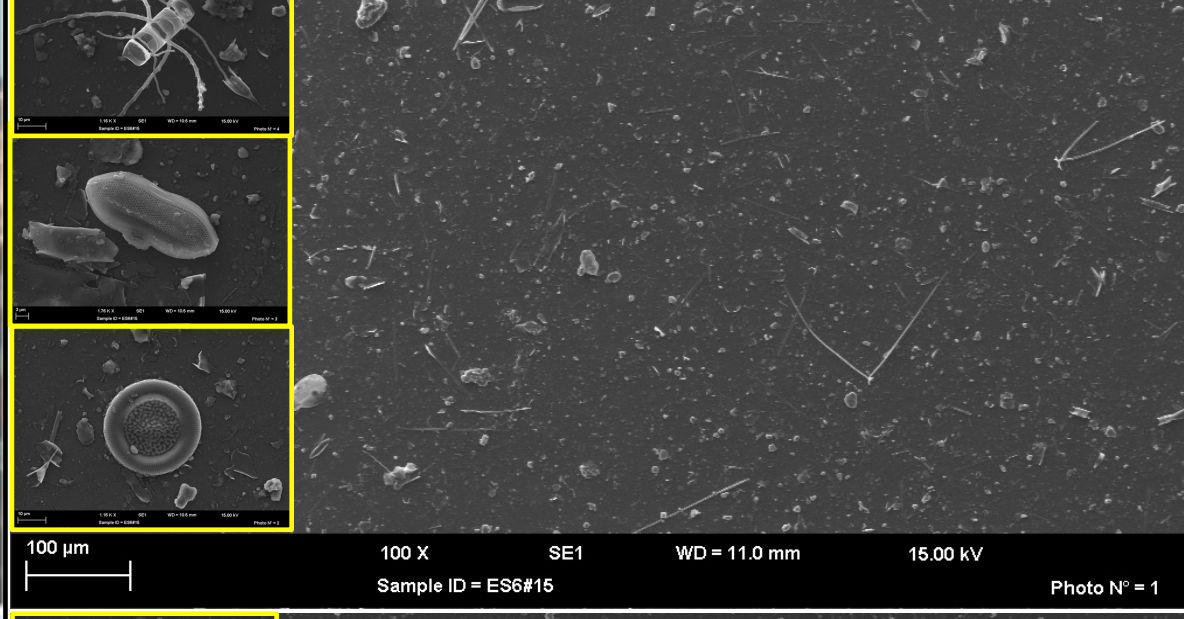

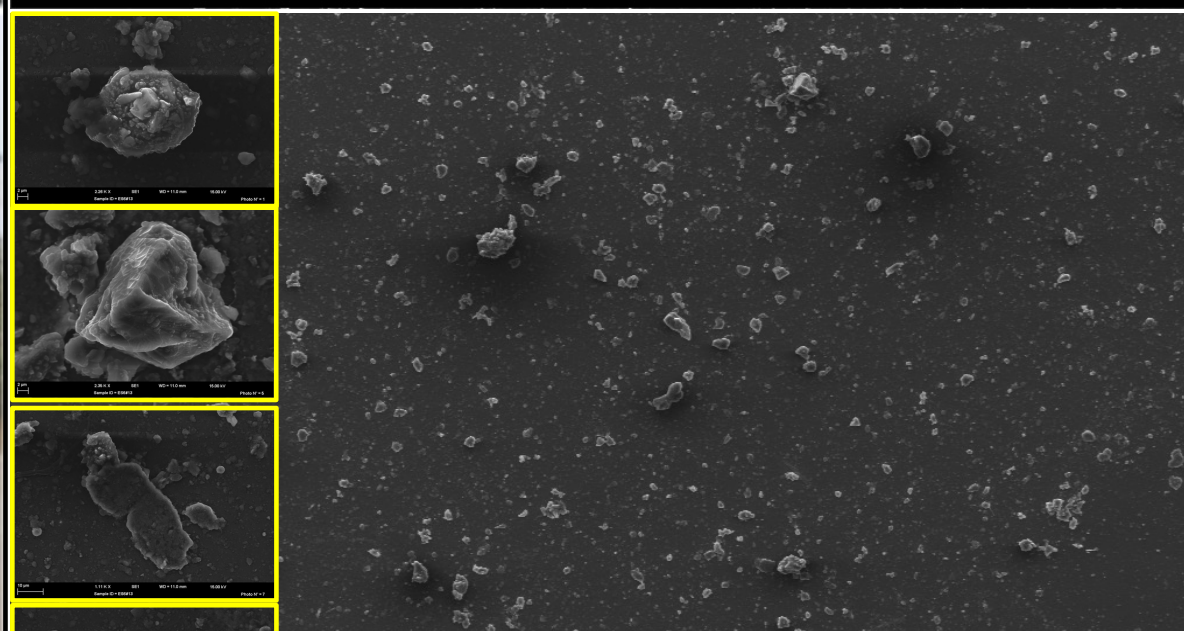

Estuaries as biogeochemical reactors; implications for Si and Ca transport across tropical monsoonal estuary

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Estuaries are highly dynamic transition zones between freshwater and seawater, exhibiting significant spatial and temporal variability depending on the extent of mixing and estuarine biogeochemical processes. The study investigated seasonal variability and major drivers of silicon (Si) and calcium (Ca) biogeochemistry in the largest monsoonal estuary in India, Godavari estuary. We observe a non-conservative mixing in dissolved silicon (DSi) between river water and seawater during dry season, with a 65±6% removal of riverine Si within the estuary and 1.0±0.4‰ enrichment in Si isotopes ($\delta^{30}Si$). The Si loss during dry season was primarily driven by diatom uptake, based on abundance of marker pigment fucoxanthin and Scanning Electron Microscope (SEM) observations of abundant diatom frustules in suspended matter. The retention of river flow by damming upstream limits discharge during dry season, forming a stable water column with high residence time, favoring diatom growth. Additionally, the non-conservative nature of water mass source tracers such as $^{87}Sr/^{86}Sr$ and $\delta^{18}O$ indicates active groundwater discharge into the estuary during dry season, with groundwater contribution ranging from 75% in upper to 6% in lower estuary.

The groundwater supply isotopically light Ca to the upper estuary (lower $\delta^{44/40}Ca$), while we observe signatures of carbonate precipitation in lower estuary (higher $\delta^{44/40}Ca$) compared to simple two endmember mixing. Monsoonal precipitation and the opening of dam gates lead to high river water influx during the wet season, resulting in low salinity (<0.2) and high suspended matter (175±50 mg/l) throughout the estuary. We observe high $^{87}Sr/^{86}Sr$ in monsoonal river water, resulting from water contribution of tributaries draining more radiogenic Archean-Proterozoic gneiss complexes in the middle-lower reaches of Godavari basin. The $\delta^{30}Si$ signature exhibit no variability along the estuary, primarily reflecting silicate weathering and formation of secondary clays in the river basin. The $\delta^{44/40}Ca$ composition of the estuary was relatively low during the monsoon, with a higher Ca/Sr ratio, indicating increased contribution from carbonate weathering due to high monsoonal discharge. Overall estuaries are biogeochemically active zones with complicated mixing dynamics and can act as a filter for riverine supply of solutes to the ocean.

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