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Dynamics of carbonate system vis-à-vis its controlling factors at land-ocean continuum: a case study in a tropical monsoonal estuary

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Carbonate dynamics in the fluvio-marine transitional zone is driven by complex interactions of hydrological and biogeochemical processes. Rapid fluctuations in pH and alkalinity due to variations in intensity of fresh- and saline- water mixing, and mechanisms such as carbon fixation, remineralization and respiration cause shifts in carbonate saturation states and aqueous chemistry. These changes have the potential to largely impact the global carbon cycle by altering air-water CO_2 exchange, marine biogenic calcification and blue carbon storage. However, carbonate dynamics in estuarine systems remains poorly explored. Therefore, the current study aims to understand the carbonate chemistry in a tropical monsoonal estuary by interlinking spatio-temporal variability of saturation indices (SI) with physicochemical parameters - salinity, pH, temperature, total alkalinity (TA), dissolved inorganic carbon (DIC), dissolved oxygen saturation (DO%) and pCO_2. This investigation was conducted during summer, monsoon and winter season in the Devi river estuary, which is formed by the Mahanadi river draining into the Bay of Bengal on the east coast of India. The SI of calcite, aragonite and dolomite ranges from -1.73 to 0.98, -1.87 to 0.83 and -2.84 to 2.68, respectively. Spatially, SI values increase towards estuarine mouth in all seasons. Although carbonate precipitation is predominant during summer due to relatively higher temperature and pH, the estuary remains mostly under-saturated in winter and monsoon. Inverse correlations between SI and pCO_2 (r = -0.51 to -0.30) indicate influence of pCO_2 on carbonate precipitation/dissolution processes. However, dolomite shows lower susceptibility to changes in pCO_2 and pH. Decreasing SI values with reducing pH accompanied by lowering of DO% suggest coupling of precipitation/dissolution processes with organic matter degradation, a primary controlling process for pCO_2. Precipitation is further induced by removal of pCO_2 due to large CO_2 efflux associated with higher wind speed and temperature during summer season. Conversely, the carbonate dynamics plays an important role in governing TA and DIC within the estuary. Hence, the present study demonstrates heterogeneous nature of carbonate system with respect to the rapidly changing physicochemical parameters in an estuarine environment. Findings of this study have significant implication for assessing the impact of climate change on ocean carbonate chemistry.