Importance of Fe-mediated processes in blackwater river estuarine sediments

Beckler, J.S.[1]*; Jones, S.T.[1]; O'brien, A.D.[1]; Taillefert, M.[2]; Milbrandt, E.[3]

*correspondence: jbeckler@mote.org
[1]Mote Marine Laboratory, Sarasota, FL, USA
[2]Georgia Institute of Technology, Atlanta, GA, USA
[3]Sanibel-Captiva Conservation Foundation, Sanibel, FL, USA

Estuarine sediments are subject to relatively high deposition rates of terrigenous materials such as organic carbon and oxidized minerals, and early diagenesis is therefore spatially and temporally dynamic and typically includes a full suite of heterotrophic respiratory processes. A growing body of evidence indicates that iron-mediated processes play a large role in controlling organic carbon remineralization pathways in the sediments of estuaries fed by blackwater rivers such as those commonly found in the southeastern USA. These processes in turn control nutrient and trace metal fluxes from sediments to the overlying waters of estuaries and, eventually, offshore. For example, a recent transect in the organic-rich Caloosahatchee Estuary (Florida, USA) revealed that a concentrated pool of highly reactive, poorly crystalline Fe (oxy)hydroxides accumulates over a relatively confined longitudinal distance (a few km) in the upper estuary with low water column salinities (between 0 and 5). Corresponding sediment profiles obtained with mercury/gold (Hg/Au) voltammetric microelectrodes revealed that dissimilatory Fe reduction was the most dominant biogeochemical process in the top 20 cm, but sulfate reduction dominated outside this Fe-rich region. Diffusive profiles of soluble organic-Fe(III) complexes detected by voltammetric sensors indicate a persistent flux of iron towards the water column that is apparently fed by reoxidation of Fe(II) near the sediment-water interface, and overlying estuarine bottom waters are enriched in truly soluble (< 20 nm) iron. Fe concentrations remain high at the mouth of the estuary (salinity = 25), suggesting that this river may impact estuarine primary production and even export dissolved iron to the continental shelf. In addition, macronutrient (N and P) cycling and fluxes are also significantly affected by this interplay between Fe and S. Given the dynamic nature of these systems and the ubiquity of blackwater rivers world-wide, hydrologic and seasonal controls of these Fe-driven processes should be assessed to

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better understand the influence of iron on estuarine and coastal primary production.