

## From Molecular- to Field- Scale Investigation of Iron Biogeochemistry in Marine and Freshwater Coastal Environments

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Hydrological fluctuations in coastal terrestrial-aquatic interfaces impact the behavior of redox-sensitive elements such as iron (Fe), which is directly involved in the biogeochemical cycles of carbon, nutrients, and contaminants. As part of the Coastal Observations, Mechanisms, and Predictions Across Systems and Scales - Field, Measurements, and Experiments project, this study aims to understand Fe cycling across coastal ecosystems and improve the predictions of soil biogeochemical responses to hydrological disturbances. We combined spatially resolved X-ray Absorption Spectroscopy, X-ray diffraction, Scanning Electron Microscopy, 16S rRNA sequencing and solid/pore water chemistry analyses to investigate Fe biogeochemistry along undisturbed soil cores collected across upland to shoreline gradients in the Western Lake Erie Basin and the Chesapeake Bay regions. We show that Fe occurs mainly in its oxidized form, Fe(III), in cores collected from unsaturated upland and transition locations, with variable proportions of Fe(III)-oxyhydroxide, Fe(II,III)-phyllosilicate, and Fe(III)-organic species depending on the soil characteristics (e.g., mineral and organic carbon contents). In water-saturated soils (i.e., wetlands and some upland-wetland transition zones), varying Fe(III)/Fe(II) ratios and reduced Fe(II) species revealed diverse redox and biogeochemical conditions. At the Lake Erie wetlands, Fe reduction was identified as a dominant process that resulted in the release of Fe(II) to the pore waters. However, the extent of Fe(III) reduction was limited by the presence of recalcitrant Fe(III) in phyllosilicates. In the Chesapeake Bay wetlands and one transition site, the pore water sulfide concentrations and the abundance of pyrite (FeS<sub>2</sub>) indicate that

Fe cycling is also controlled by sulfur-driven redox dynamics. In contrast, some transition sites at both Lake Erie and Chesapeake Bay contained predominantly oxidized Fe(III) despite water-saturated conditions. At these sites, the pore water chemistry was indicative of little to no reduction of Fe(III) and of sulfate, suggesting water inputs that may have impacted microbial redox processes. These results demonstrate the advantages of combining classic solid and pore water analyses with advanced techniques such as X-ray absorption spectroscopy for determining elemental speciation across various scales and improving our understanding of biogeochemical cycling in coastal environments.