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Effects of Changing Iron-to-Sulfur Ratios on Hydroxyl Radical Production in Wetland Sediments along an Estuarine Salinity Gradient

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Tidal wetlands are among the world's most productive ecosystems, playing a crucial role in sequestering "blue" carbon in their sediments, which is vital for global carbon storage. Around the world, tidal wetlands are impacted by salinization due to storm surges and sea level rise, and the impacts of salinization on the stability of organic matter (OM) in sediments are poorly understood. One impact of salinization is a change in iron (Fe)-to-sulfur (S) ratios in sediments as a result of seawater sulfate (SO_4^{2-}) inputs, with impacts on the speciation and reactivity of Fe in sediments. In this contribution, we investigate the effects of changing Fe/S ratios on the “dark” formation of hydroxyl radicals (·OH), a powerful non-selective oxidant of OM, during oxygenation of wetland sediments. Field measurements of ·OH in Hudson River tidal marsh sediment porewaters using the terephthalate (TPA) assay at low tide revealed up to four-fold greater ·OH concentration at a brackish site than a freshwater site, despite very low aqueous Fe(II) concentrations at the brackish site. This finding was attributed to high concentrations of mackinawite (FeS) in the brackish site, verified by synchrotron-based µXRF and µXANES analysis, and greater production of ·OH from oxygenation of FeS compared to aqueous Fe(II) or other reduced Fe minerals. Laboratory experiments with oxygenation of FeS synthesized with varying Fe(II):S(-II) ratios confirmed that FeS significantly boosts ·OH formation. Laboratory experiments with incubations of freshwater wetland sediments amended with 4 to 12 mM SO_4^{2-} further demonstrated that ·OH formation is coupled with oxidation of FeS and not aqueous Fe(II) or other reduced Fe minerals. These experiments also showed that the high chloride concentration typical in brackish systems could suppress over half of the ·OH production. Taken together, these results highlight the critical role of coupled Fe-S cycling in controlling ·OH production in tidal wetland sediments, with potential implications for OM mineralization.