Goldschmidt 2023 Abstract
https://doi.org/10.7185/gold2023.20384

Response of Ligand-Stabilized Manganese by Siderophores to Seasonal Hypoxia in the Northern Gulf of Mexico

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Widespread seasonal hypoxia on the Louisiana Shelf in the northern Gulf of Mexico has profound impacts on redox-active metals and nutrients. High concentrations of sulfides, ammonia, methane, and reduced metal species are typical of oxygen-depleted seawater. Manganese (Mn) is present as soluble Mn(II), soluble ligand-stabilized Mn(III), and insoluble Mn(III/IV) oxides in seawater, but increased dissolved Mn concentrations have been reported in hypoxic waters. The ligand-stabilized Mn(III) form is thought to be particularly important as it is the intermediate between the soluble and insoluble forms, but little is known about the identity of the organic ligands. Cathodic-stripping voltammetry (CSV) findings suggest Mn(III) binds weakly to terrestrially derived organic humic matter and strongly to microbially-produced siderophores. This study aims to investigate the role of siderophores, which are known to facilitate the uptake of iron by microbes but poorly understood as Mn ligands. Water column samples were collected from the Mississippi River and Louisiana Shelf for ligand analysis by liquid chromatography-electrospray ionization mass spectrometry (LC-ESI-MS). Sampling locations were chosen to provide salinity and oxygen gradients. Samples collected in March 2021 served as a baseline before the onset of hypoxia while those collected in August 2022 during the peak of seasonal hypoxia were used to assess the impact of low oxygen conditions. Increased complexation by known siderophore ligands was detected in samples collected during the summer in both hypoxic bottom waters and oxygenated surface waters. These dual trends suggest both a chemical and biological control on extent of complexation with known siderophores playing a greater role in Mn(III) complexation in the summer on the Louisiana Shelf.