The temporal variability of Mn speciation in the Chesapeake Bay and St. Lawrence Estuaries

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The speciation of soluble Mn (dMn) has been reevaluated in the last decade to include soluble Mn(III)-L complexes, where previously speciation was limited to dMn(II) and solid Mn(III/IV) oxides. These complexes make up to 100 % of dMn in oxic surface waters, and can also dominate suboxic and anoxic waters. Data from August 2014 and 2015 in the seasonally anoxic Chesapeake Bay indicate that the cycling between the three oxidation states of Mn is rapid, with oxidation occurring at the suboxic-oxic interface and reduction at the suboxic-anoxic interface, both resulting in the stabilization of Mn(III)-L. Our speciation results from the St. Lawrence Estuary (SLE) in May 2014 and September 2016 indicate that spring and fall blooms result in the stabilization of Mn(III)-L in the mid-waters of the lower estuary. In contrast to the Chesapeake Bay, the SLE is oxygenated with dO_2 decreasing in the bottom waters. Low dO_2 corresponds to high dMn, indicating that Mn oxides are more readily dissolved at low O_2. We find that Mn(III)-L complexes are transported in surface waters of the St. Lawrence Estuary from terrestrial sources, different in origin from the Mn(III)-L in the middle of the water column, indicating diverse pathways for Mn(III)-L formation. Given that both the Chesapeake Bay and St. Lawrence Estuary represent sites with multiple formation pathways for Mn(III)-L, Mn cycling in seawater needs to be evaluated on shorter timescales and using reaction kinetics to separate diverse processes.