Soluble manganese(III) is ubiquitous in natural waters and sedimentary pore waters

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In previous work, we documented the presence of significant concentrations of soluble ($<0.2\mu$m) manganese(III) in the suboxic waters of the Black Sea, the Chesapeake Bay and sedimentary pore waters. Recently, we showed that soluble Mn(III) is kinetically stable in the anoxic waters of the Chesapeake Bay when its concentration is greater than or equal to the sulfide concentration, and that the ligands stabilizing Mn(III) appear to be of humic origin with catecholate functional groups. Here, we demonstrate that soluble Mn(III) is also found in fully oxygenated waters ranging from those of a coastal waterway (salinity ranging from freshwater to 31) bordered by wetlands and salt marshes to the water column of the St. Lawrence Estuary. Soluble Mn(III) comprises up to 50% of the total manganese in these oxic waters. Our results reveal that soluble Mn(III) is ubiquitous, and, as such, is a key redox species in the global sedimentary cycles of carbon, oxygen, iron and sulfur.

The spectroscopic porphyrin method we use for manganese oxidation state analysis, provides kinetic information on the actual weak and strong complexes binding soluble Mn(III). The reaction rate constants permit an estimate of the conditional stability constants of the weak and strong complexes. Weak Mn(III)L complexes are those that react with the porphyrin competitive ligand. Strong Mn(III)L complexes are those that do not react with the porphyrin and have K_{COND} (M′L) values $> 1.6 \times 10^{13}$ M^{-1} (log $K_{COND} > 13.2$). The ligands responsible for the Mn(III) complexes are ubiquitous and originate from metabolic processes in the sediment, in the water column as well as runoff from wetland and terrestrial systems.