Soluble Mn(III)–L complexes are abundant in oxygenated waters and stabilized by humic ligands

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Abstract

Dissolved Mn (dMn_T) is thought to be dominated by metastable Mn(II) in the presence of oxygen, as the stable form is insoluble Mn(IV). We show, for the first time, that Mn(III) is also stable as a soluble species in the oxygenated water column, when stabilized by organic ligands as Mn(III)–L complexes. We measured Mn(III)–L complexes in the oxygenated waters of a coastal fjord and a hemipelagic system where they make up to 86% of the dMn_T. Although Mn(III) forms similar complexes to Fe(III), unlike most of the analogous Fe(III)–L complexes, the Mn(III)–L complexes are not colloidal, as they pass through both 0.20 μm and 0.02 μm filters. Depending on the kinetic stability of the Mn(III) complexes and the microbial community of a given system, these Mn(III)–L complexes are capable of donating or accepting electrons and may therefore serve as both reductants or oxidants, can be biologically available, and can thus participate in a multitude of redox reactions and biogeochemical processes. Furthermore, sample acidification experiments revealed that Mn(III) binding to humic ligands is responsible for up to 100% of this complexation, which can influence the formation of other metal complexes including Fe(III) and thus impact nutrient availability and uptake. Hence, humic ligands may play a greater role in dissolved Mn transport from coastal areas to the ocean than previously thought.

1. INTRODUCTION

Manganese (Mn) is ubiquitous in the global ocean, where it is an essential trace nutrient in the electron transfer processes of several metallo-enzymes – notably in photosystem II for photosynthetic organisms. In its solid oxidized form, it serves as an electron acceptor in the bacterial decomposition of sedimentary organic matter and acts as an important scavenger for many trace elements and radionuclides. The chemical speciation of Mn in marine systems governs its diverse functions and is ultimately controlled by the redox conditions of the environment and the microbial community. The favorable oxidation state of Mn in oxic waters is Mn(IV), and thus Mn in oxygenated waters is primarily bound to oxygen as solid Mn(III/IV)-oxides (MnO_x). However, soluble Mn(II) is metastable in oxygenated waters because the oxidation of $Mn(H_2O)_6^{2+}$ to MnO_x by O_2 in a one electron transfer is thermodynamically unfavorable and the two electron transfer is kinetically slow (Luther, 2010), unless facilitated by microbes, surface

catalysis or superoxide-promotion (Stumm and Morgan, 1996).

In the last decade, soluble manganese (dMn_T) speciation has been re-evaluated to include soluble Mn(III) bound to ligands (Mn(III)–L complexes) in low oxygen environments. Mn(III)–L complexes have been measured in the suboxic porewaters of the St. Lawrence Estuary (Madison et al., 2013), the suboxic waters of the Black Sea (Yakushev et al., 2007, 2009; Trouwborst et al., 2006) and the Baltic Sea (Dellwig et al., 2012) as well as the anoxic bottom waters of the Chesapeake Bay (Trouwborst et al., 2006; Oldham et al., 2015). Because Mn(III)–L complexes can donate or accept electrons, they can potentially have a profound impact on the redox chemistry of a given environment. In addition to their reactivity, Mn(III)–L complexes can affect the uptake of other metals due to metal–ligand competition reactions (Luther et al., 2015). For example, the siderophore pyoverdine from the Mn(II)-oxidizing *Pseudomonas putida* GB-1 has a higher affinity for Mn(III) than for Fe(III) (Parker et al., 2004). Likewise, kinetic experimentation, using known laboratory ligands (desferrioxamine-B, pyrophosphate, to name two) and suboxic porewater samples from the St. Lawrence Estuary also indicate that Mn(III) may bind more strongly than Fe(III) to the same ligands (Luther et al., 2015). These findings are important given that many microorganisms use Fe(III)-binding ligands for Fe uptake. However, the impact of this ligand competition is poorly described because the presence of Mn(III)–L has not yet been documented in oxygenated marine environments as dMn_T concentrations in these environments are typically lower than the detection limits of current speciation methods (50 nM, Madison et al., 2011). Consequently, thus far, dMn_T speciation in oxygenated systems has been thought to be dominated by Mn(II) (e.g. Landing and Bruland, 1986).

Using a modification of the UV–Vis method of Madison et al. (2011), we show for the first time that, like Fe(III)–L complexes which account for up to 99.9% of dFe_T (e.g. Gledhill and van den Berg, 1994) in oxygenated marine waters, Mn(III)–L complexes are present in the oxygenated waters of both a coastal fjord and in the hemipelagic waters of the St. Lawrence Estuary, the largest enclosed estuary in the world. These Mn(III)–L complexes account for most of the dMn_T, but, unlike most Fe(III)–L complexes (Schlosser et al., 2013), are not colloidal (operational size class between 20 and 200 nm). Finally, our findings indicate that binding to humic ligands is responsible for up to 100% of the Mn(III)–L in these waters.

2. MATERIALS AND METHODS

2.1. Water column sample processing

Water column samples were collected in September 2014 from two sites in the St. Lawrence Estuary (Fig. 1; Station 23 [~350 m depth]: 48°42.29′N, 68°38.83′W; and Station SAG-30 [~260 m depth]: 48°21.72′N, 70°23.71′W) into 12 × 12 L Niskin PVC bottles mounted on the CTD-rosette. Contamination was avoided by sampling through a trace metal clean tube into clean 50 mL polypropylene
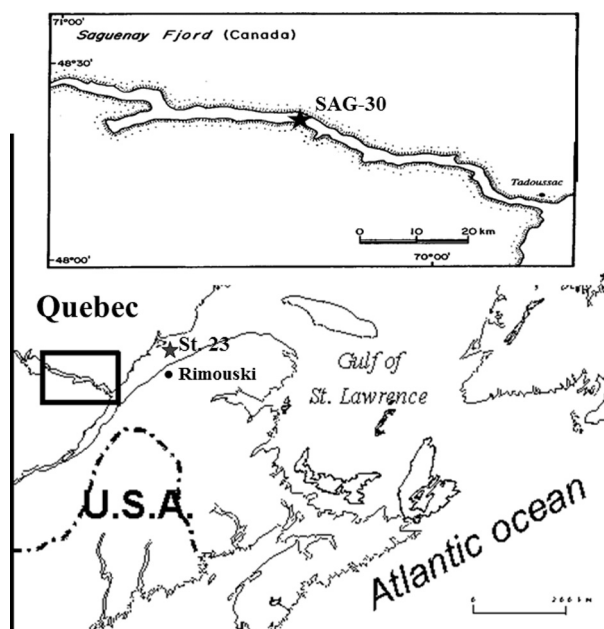

Fig. 1. Map of the two study sites in the St. Lawrence Estuary.

centrifuge tubes (Falcon), which were overflowed three times before filling. Water samples were immediately filtered through 0.20 μm syringe filters (Nylon, Whatman), in a fume hood aboard the R/V Coriolis II, into new 50 mL centrifuge tubes, and were kept in the dark until analysis. Aliquots were frozen at −20 °C in 50 mL centrifuge tubes for future analyses.

To obtain true bottom-water samples, undisturbed sediment multi-cores were recovered at Station 23 using a Bowers & Connelly Multicorer and 10-cm diameter clear plastic barrels. The overlying water at the sediment–water interface was withdrawn from the barrels with a trace metal clean polypropylene syringe, filtered and handled as above. The water analyzed is termed overlying sediment-core water and its composition, relative to waters above it, provides insights on the direction and magnitude of the flux of chemical species across the sediment–water interface.

2.2. Dissolved Mn speciation

All samples were analyzed for soluble Mn speciation within two hours of collection following the addition of a soluble porphyrin ligand [α, β, γ, δ-tetrakis(4-carboxyphenyl)porphine (T(4-CP)P)], according to the method described by Madison et al. (2011). The method allows for the subsequent spectrophotometric determination of both Mn(II) and Mn(III)–L_{weak} (Mn(III)–L_{weak} can be outcompeted by the added porphyrin ligand, and has $\log K_{cond}$ <13.2; Oldham et al., 2015; Luther et al., 2015) using the differential kinetics of the reaction between Mn and the added porphyrin which is initially complexed to Cd(II). The Mn(II) displaces the Cd(II) and reacts rapidly with the porphyrin, forming a Mn(III)-porphyrin complex as Mn(II) oxidizes in the presence of oxygen, whereas the Mn(III)–L_{weak} undergoes a ligand substitution reaction