

Oxidation-reduction cycling of manganese in lacustrine environments: A case study in Lake Biwa

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Manganese (Mn) is one of the redox-active elements involved in complex reaction cascade that occurs in the redox-boundary layer (RBL) of aquatic environments. Mn exists as highly mobile Mn^{2+} in the reduced zone of RBL and can freely diffuse up to the oxic zone, where it is oxidized into stable oxyhydroxides of Mn(III) and Mn(IV), which are insoluble and precipitate back to the reduced zone. Consequently, the redox cycle of Mn turns over very effectively. Mn^{2+} is stable even in well-oxygenated waters so that spontaneous oxidative precipitation of Mn^{2+} does not proceed at any significant rates, unless some specific microorganisms accelerate the reaction. On the other hand, reductive dissolution of Mn oxides proceeds as direct chemical reactions with HS^- and Fe^{2+} that are produced in deeper region of RBL, and also as biochemical reactions mediated by heterotrophic bacteria that use Mn oxides as respiration substrates. When the redox cycling of Mn is restricted within the bottom sediments as seen in Lake Biwa, a dark-brown layer of oxidized Mn is formed at a specific depth near the sediment surface. Since important redox reactions of nitrogen (N) such as nitrification and denitrification occur at similar depths to those of Mn, the redox cycles of Mn and N may interact to each other. In fact, it has been known that the nitrification product NO_2^- reacts with Mn oxides and is oxidized into NO_3^- . The Mn-oxide layer may also provide convenient habitats for nitrifiers, denitrifiers and methane-oxidizing bacteria.

Microorganisms that mediate oxidative precipitation of Mn^{2+} in aquatic environments can be classified into (1) sheathed filamentous bacteria *Leptothrix*, (2) some fungi, and (3) microbially produced, ill-defined filamentous structure called *Metallogenium*. While all these Mn^{2+} -oxidizing microorganisms have been detected from Lake Biwa, the most important agent for the lacustrine Mn cycle is presumably *Metallogenium*. We have succeeded in establishing stable enrichment cultures of *Metallogenium* from lake water, using a viscous medium containing Mn^{2+} , HCO_3^- and malt extract. They contained mixed populations of heterotrophic bacteria and/or fungi. While *Metallogenium* was produced with fungi from the initial growth stage, it was not produced until the stationary phase in bacterial cultures. Physiological role of Mn^{2+} oxidation for the fungi and bacteria is unknown. Whether or not *Metallogenium* contains cellular structure has not been confirmed yet. The production of *Metallogenium* associated with bacterial rather than fungal populations is presumably relevant to Mn^{2+} removal in natural lacustrine environments.

In Lake Biwa where the whole water column is always well-oxygenated, RBL is restricted within the sediment, and the occurrence of *Metallogenium* had previously been confined within some special area where an anoxic water mass was artificially formed by dredging. However, it has been reported in the last decade that the oxidation reaction of Mn^{2+} mediated by *Metallogenium*, which comprises the topmost part of the RBL, often occurred within the hypolimnion of the lake in late stagnant periods. Although exact mechanism for this uplifting event of the Mn cycle is currently unknown, it may imply (i) activation of reductive reactions within the sediment as a result of elevated organic inputs from the watershed, (ii) increase of anthropogenic SO_4^{2-} that enhances sedimentary HS^- production, resulting in higher efflux of Mn^{2+} to the overlying water, and (iii) stabilization of thermal stratification due to the global warming and decrease in O_2 supply to the hypolimnion and the sediment. The hypolimnetic anoxia, if occurs, must result in drastic changes in the whole biogeochemical processes in this lake. Therefore, careful continual monitoring is being conducted on hypolimnetic chemical processes in this lake.