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Seasonality and sunlight dependency of manganese oxide formation and cycling in surface waters of a meromictic pond

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Manganese (Mn) oxide minerals are strong oxidants, as well as sorbents of contaminants and nutrients. Consequently, understanding Mn oxide formation and dissolution mechanisms has implications for a number of other biogeochemical cycles. Typically, Mn oxides do not persist in the photic zone because photoreduction rates are thought to exceed Mn oxidation rates. In contrast, accumulation of Mn oxides has been observed in the surface waters of Siders Pond, a Mn-rich meromictic kettle hole pond on Cape Cod (Massachusetts, USA). Little is known about the spatial and temporal distribution of these Mn oxides, or the underlying processes responsible for their accumulation.

We use a field study to understand the cycling and formation of Mn oxides in Siders Pond. Seasonal variation in Mn oxide formation and composition in Siders Pond was investigated from July to November of 2020. Despite being permanently stratified, data demonstrate a dynamic Mn cycle. We observe seasonal variations in surface Mn oxide concentrations varying from <100 nM up to 2 µM. Using X-ray absorption spectroscopy, we find a number of Mn oxide minerals, including δ-MnO2, triclinic birnessite, and feitknechtite, and the ratios of these minerals change over the course of the season.

Furthermore, we use incubation experiments to determine mechanisms of Mn oxide formation and dissolution. We observe photoreduction in sunlight-exposed sterilized control incubations, However, we see either no net reduction or net Mn oxide formation in sunlight-exposed live incubations. This latter observation highlights the importance of biological activity in Mn oxidation and indicates that, under some conditions, light-dependent Mn oxidation rates can exceed photoreduction, giving rise to Mn oxide accumulation. Additionally, Mn oxide mineralogy differs in light and dark incubations. While dark incubations produce mostly δ-MnO2, light incubations generally yield lower oxidation state Mn oxides like triclinic birnessite and feitknechtite, likely due to photoreduction of precipitated oxides. These results improve our understanding of how light plays a key yet currently misunderstood role in Mn oxide formation, cycling, and mineralogy in the environment.