

Title: Photochemically-assisted Formation of Manganese Oxide Solids in the Presence of Dissolved Organic Matter and Bromide Ions

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Dissolved natural organic matter (DOM) is a complex matrix of organic matter that is ubiquitous in natural aquatic environments. So far, substantial research has been conducted on the DOM adsorption on Mn oxides as well as the reduction processes of Mn oxides by DOM. However, little is known about the oxidative roles of DOM in oxidizing $\text{Mn}^{2+}(\text{aq})$ to Mn(III/IV) oxide solids. Sunlight-driven processes can initiate the degradation of DOM accompanied by the formation of photochemically produced reactive intermediates, including excited triplet state DOM ($^3\text{DOM}^*$), hydroxyl radical ($^{\bullet}\text{OH}$), superoxide radical ($\text{O}_2^{\bullet-}$), hydrogen peroxide (H_2O_2), and singlet oxygen ($^1\text{O}_2$). Further, in the presence of halide ions, reactive halogen species can be generated by reactions between $^3\text{DOM}^*$ and halide ions, and by reactions between $^{\bullet}\text{OH}$ and halide ions. In this study, we found that the solution pH controlled the oxidation of $\text{Mn}^{2+}(\text{aq})$ to Mn oxide solids during photolysis of DOM. Among the reactive oxygen species, $\text{Mn}^{2+}(\text{aq})$ was found to be oxidized to Mn oxide solids mainly by $\text{O}_2^{\bullet-}$. The DOM with different quantities of aromatic functional groups affected its oxidative capability. With the addition of bromide ions (Br^-), $\text{Mn}^{2+}(\text{aq})$ oxidation was promoted further by formation Br radicals, which can also oxidize $\text{Mn}^{2+}(\text{aq})$ to Mn oxide solids. These findings can help us better understand the oxidative role of DOM in the formation of Mn oxide solids in organic-rich surface water. In addition, this study assists in comprehending the impacts of the photolytic reactions between DOM and halide ions and their resulting reactive oxygen and halogen species on the oxidation and reduction processes of other transition metal oxides in the environment.