Title: Photolytic reaction of dissolved organic matter and bromide ions promote the formation of manganese oxides

Authors: Zhenwei Gao[1], Jing Liu[1], Charlie Skurie[1], Yaguang Zhu[1], and Young-Shin Jun[1,] *

[1]*Department of Energy, Environmental and Chemical Engineering, Washington University in St. Louis, St. Louis, Missouri 63130, United States*

*ysjun@wustl.edu

Manganese (Mn) oxide solids widely exist in nature, serving as both electron donors and acceptors for a variety of redox reactions. Previous studies have highlighted the adsorption of dissolved organic matter (DOM) on Mn oxides, as well as the reduction of Mn oxides by DOM. Here, we show the underappreciated roles of photolytic reactions of DOM in Mn^{2+}(aq) oxidation and its consequential formation of Mn oxide solids. During the photolysis of DOM, reactive intermediates including excited triplet state DOM ($^3DOM^*$), hydroxyl radical ($^{\bullet}OH$), superoxide radical ($O_2^{\bullet-}$), hydrogen peroxide (H_2O_2), and singlet oxygen ($^1O_2$) can be generated. Among them, we found that $O_2^{\bullet-}$ was responsible for Mn oxidation. In addition, in the presence of bromide ions (Br^-), the photolytic reactions between DOM and Br^- formed reactive bromide radicals and facilitated the oxidation of Mn^{2+}(aq) to Mn oxide solids. Moreover, the composition of DOM affected its oxidative capability. When DOM contained more aromatic functional groups, we observed more oxidation of Mn^{2+} to Mn oxides. These new findings advance our knowledge of natural Mn^{2+} oxidation and Mn(III/IV) oxide formation, as well as the hitherto overlooked oxidative role of DOM in the oxidation of metal ions in surface water under sunlight illumination.