Title: Abiotic manganese oxidation by peroxyl radicals generated from the reaction between hydroxyl radicals and their alcohol scavengers

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Abstract: Environmentally ubiquitous manganese (Mn) oxides play important roles in geochemical element redox cycling. They can be formed by both biotic and abiotic Mn^{2+}(aq) oxidation processes. We recently observed photochemically-assisted abiotic oxidation of Mn^{2+}(aq) to δ-MnO_2 nanosheets during nitrate photolysis. Mn^{2+} was mainly oxidized by superoxide radicals, while hydroxyl radicals (•OH) contributed little to Mn oxidation. However, unexpected abiotic Mn^{2+} oxidation was observed in the presence of *tert*-butyl alcohol (TBA) that was added to scavenge •OH. TBA, one of the most common •OH scavengers, has been thought to be able to completely scavenge •OH, leaving less reactive products that do not participate in further redox reactions in the system. However, we discovered that TBA was not an inert agent in scavenging •OH. Secondary peroxyl radicals (ROO•) were produced from the chain reactions between TBA and •OH, facilitating the oxidation of Mn^{2+} to MnO_2(s). These findings can also be applied to other alcohol scavengers, such as methanol, ethanol, and propanol. In addition, ROO• can be produced by the reaction between •OH and unsaturated organic matter in natural environments. This study helps understand the occurrences of Mn oxides in the environment, and it provides new insights into the oxidation pathways of other heavy metals ions (Fe^{2+}, As^{3+}, and Cr^{3+}) by ROO•.