

A kinetic method to assess the chemical species of Mn during photochemically-assisted abiotic oxidation

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Manganese exists widely in the terrestrial environment and plays an important role in the geochemical cycle of Fe, C and other elements. Soluble Mn(III) was generated as an intermediate product during bio-oxidation and photosynthesis, which can potentially serve as both oxidant and reductant. However, this species is frequently overlooked as a major component of Mn cycling, since it could disproportionate to soluble Mn(II) and particulate Mn(IV)O₂ rapidly. By applying a spectrophotometric kinetic method, we compared the photochemical oxidation product in solution containing Mn(II) and nitrate at low and high pH values. At low pH value, all Mn species remain soluble, and a fraction of Mn(III) was observed, accounting for 1-2% of total Mn, even though strong metal-binding ligand was not included. Formation of colloidal Mn(IV)O₂ was observed at a pH higher than 6, and the amount of soluble Mn(III) decreased significantly once Mn(IV)O₂ was formed. Despite low concentration, the soluble Mn(III) shows higher reactivity toward organic carbon degradation compared to the same amount of particulate Mn(IV)O₂. Therefore, the important role of soluble Mn(III) in the redox cycle of Mn should be considered.