# The Role of Hydroxyl Radicals in Iron Biogeochemical Cycling under Redox Dynamic Conditions

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Iron (Fe) redox transformation in soils and sediments plays an essential role in the biogeochemical cycling of associated nutrients and elements. It is documented recently that hydroxyl radicals (•OH) can be produced upon oxygenation of Fe(II)-bearing minerals in soils and sediments. As •OH induces serious oxidative stress to microbes, it is likely that •OH produced upon Fe(II) oxygenation inactivates the coexisting dissimilatory iron-reducing bacteria and subsequently impacts Fe redox transformation. This hidden interplay between Fe species transformation and •OH production in soils and sediments during anoxic-oxic cycles remains unexplored. In this study, a field sediment was incubated with *Shewanella oneidensis* strain MR-1 and treated for six anoxic-oxic cycles. Fe species transformation, •OH production and MR-1 activity variation were measured throughout the six cycles. Fe in the sediments prior to anoxic-oxic cycles mainly existed in Fe-bearing silicates and Fe (hydr)oxides. For the anoxic periods, a portion of Fe(III) in sediments was either reduced to structural Fe(II) in (hydr)oxides and silicates or reductively dissolved to aqueous $Fe^{2+}$. Total Fe(II) produced from Fe(III) bio-reduction increased in the first two anoxic periods but decreased in the following four anoxic periods. For the oxic periods, Fe(II) was oxidized along with a production of •OH, and the cumulative •OH concentrations were around 31 μM in the first three periods but decreased to 6.3 μM in the subsequent three periods. MR-1 was inactivated by about 0.6 order of magnitude in the first two oxic periods, and the inactivation became insignificant for the later oxic periods. A strong interplay between Fe species transformation and •OH production occurred in anoxic-oxic cycles. Fe(III) bio-reduction by MR-1 in anoxic periods determined the content and speciation of Fe(II), which governed •OH production in the subsequent oxic periods. The generated •OH affected MR-1 activity in oxic periods, which further controlled Fe(III) bio-reduction in anoxic periods. The hidden interplay identified herein improves our understanding of the cycling of Fe and associated elements under redox fluctuating environments.