

Interplay between Iron Species Transformation and Hydroxyl Radicals Production in Sediments during Anoxic-Oxic Cycles

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Iron (Fe) redox transformation plays a major role in soil and sediment biogeochemical processes. Recent work documented that hydroxyl radicals ($\bullet\text{OH}$) could be produced when Fe(II)-bearing sediments were perturbed by O_2 . Since $\bullet\text{OH}$ could induce serious oxidative stress to microbes, $\bullet\text{OH}$ produced upon Fe(II) oxygenation would potentially inactivate the coexisting Fe(III)-reducing bacteria (FeRB) and subsequently impact Fe species transformation. However, the interplay between sediment Fe species transformation and $\bullet\text{OH}$ production in sediments during anoxic-oxic cycles remains unknown. Here we incubated sediments with 1×10^8 *Shewanella oneidensis* strain MR-1 under six cycles of anoxic-oxic treatments. The transformation of Fe species, the production of $\bullet\text{OH}$ and the variation in MR-1 activity were measured throughout the anoxic-oxic cycles. During the six anoxic periods, the total Fe(II) produced from Fe(III) reduction increased from 3.46 mM in the first period to 8.24 mM in the second periods and decreased to 0.09 mM afterwards. During the oxic periods, Fe(II) was oxidized with the production of $\bullet\text{OH}$, and the cumulative concentration of $\bullet\text{OH}$ produced in the first three periods was around 31 μM , but decreased to 6.3 μM in the sixth period. Around 0.6 orders of magnitude of MR-1 was inactivated by the $\bullet\text{OH}$ produced during the first two oxic periods, but the inactivation was insignificant from the third to sixth oxic periods. Our results indicated that Fe species transformation and $\bullet\text{OH}$ production interacts during anoxic-oxic cycles. The amount of $\bullet\text{OH}$ produced upon Fe(II) oxygenation was mainly controlled by the extent of Fe(III) reduction, which was controlled by the FeRB activity and Fe(III) bio-availability. Although the produced $\bullet\text{OH}$ inactivated FeRB, the increase in Fe(III) bio-availability and the residual reactivity of dead cells resulted in an enhancement of Fe(III) reduction for the first 2 cycles. However, the further inactivation of FeRB led to a slower Fe transformation and lower production of $\bullet\text{OH}$. After application of more cycles, the Fe species transformation and $\bullet\text{OH}$ production stabilized at a relatively low level. The interaction identified in this study improves our understanding of the cycling of Fe and associated elements under redox fluctuating environments.