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Humic Substances Affect Iron-Driven Hydroxyl Radical Production

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Hydroxyl radical (•OH) is the most reactive oxidant, which plays important roles in the biogeochemical cycle of elements and the attenuation of contaminants in the environment. In recent years, the redox reaction of iron in soils was found to produce •OH naturally, even in dark conditions without the presence of exogenous hydrogen peroxide. However, the effect of mineral-associated soil organic matter (SOM) on the process are not well understood. This study used fulvic acid (FA), humic acid (HA), and humin (HM), components of humic substances operationally separated from soil, to evaluate the influence of SOM characteristics on iron redox processes. High electron exchange capacity of FA and HA promoted the microbial iron reduction process under anoxic conditions, while HA with high electron donating capacity inhibited the yield of •OH under oxic conditions. Using the scavengers of possible intermediate involved in •OH production, different pathways for •OH production in SOM-containing system were established. The one-electron transfer process dominated the •OH production in the FA-containing system, while both one- and two-electron transfer processes were present in HA- and HM-containing systems. Microbially mediated iron redox processes changed the properties of dissolved fractions of SOM. The aromaticity of dissolved fraction of HA decreased due to its high reactivity with •OH. Combined with the high resolution transmission electron microscope and X-ray diffractometer, ferrous secondary minerals formed and SOM inhibited its transformation to higher stable and crystalline iron oxy(hydr)oxides. This work advances the understanding of SOM-involved iron redox processes and •OH production. As humic fertilizer has become a common soil amendment, this study provides valuable information for its potential impact on the behavior of both nutrients and pollutants.