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Reactive oxygen species in soil: Abiotic mechanisms of biotic processes and consequences for organic matter and nutrient cycling

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Although most organic matter (OM) in soil is mineralized by microorganisms, the nonmicrobial processes, e.g., Fenton reactions and photo-degradation, strongly contribute to OM decomposition and CO_2 emission and are the chemical background of many biotic transformations. Fenton oxidation is a catalytic reaction chain of hydrogen peroxide (H_2O_2) with ferrous iron (Fe(II)) and Fe (oxyhydr)oxides that generates highly reactive hydroxyl radicals ($HO^{\bullet}$) oxidizing OM to CO_2. Reactive Fe (oxyhydr)oxides store at least one quarter (~600 Gt) of organic C in soil, which may be subjected to Fenton reactions in which nano-sized Fe (oxyhydr)oxides act as nanocatalysts. The Fenton mechanisms depend on the sources of reactive oxygen species (ROS): $O_2^{\bullet-}$, H_2O_2 and $HO^{\bullet}$. Because microorganisms continuously produce ROS, biotic Fenton chemistry is ubiquitous in all soils, especially with strong UV radiation, fluctuating O_2 concentrations and redox, microbial hotspots such as rhizosphere and detritusphere, and high contents of Fe (oxyhydr)oxides. Charcoal and biochar catalyze ROS formation in soil as an electron shuttle or by electron transfer from the valence to the conduction band under UV irradiation. Despite the extremely short lifetime (from nanoseconds to a few days), ROS are continuously produced and sustain the ubiquity of chelators and Fe(III) reduction. For the first time we calculated the fundamental Eh-pH diagrams for ROS species and showed their relevance for Fenton reactions under soil conditions. $HO^{\bullet}$ as one of the most powerful oxidants (E^o = 2.8 V) provides the most energy release from Fenton reactions in soil. In some ecosystems (hot deserts; red soils in the tropics and wet subtropics) Fenton reactions contribute to OM oxidation to 30% and even exceed 50% of total CO_2 emissions. Fenton reactions are omnipresent and play a dual role for soil C cycling: stimulate OM mineralization (including the most stable pools) and facilitate long-term C stabilization due to the increased recalcitrance of remaining OM and organo-mineral complex formation. Summarizing, Fenton reactions and their effects on OM decomposition and formation are an emerging research field that explains the chemical background of many oxidative enzymatic processes, may crucially change our views on C, energy and nutrient cycling in soils.