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## Free radical-related mechanisms in soil and their relevance to the cycling, stabilization, and storage of carbon

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Plant residues in soil create temporal and spatial hotspots of extremely high microbial activities leading to very intensive greenhouse gas (GHG) fluxes that challenge our mechanistic understanding and predictive power. Using a series of well-controlled soil microcosm experiments, we examine how abiotic processes (e.g., iron reduction-oxidation cycling) at residue/soil interfaces contribute to hotspot dynamics. We quantify for the first time the contributions of microbially-initiated Fenton reactions, which produce strongly oxidizing hydroxyl radicals ( $\text{HO}\cdot$ ), to organic matter solubilization and mineralization in hotspots 0–3 mm from the litter surface. The concentrations of ferrous iron ( $\text{Fe}^{2+}$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and  $\text{HO}\cdot$  were 2.1–3.0, 3.0–9.0 and 2.6–2.8 times higher, respectively, at the straw-soil interface than in the bulk soil. Thus, iron minerals, especially in concert with microorganisms, produce a burst of hydroxyl radicals that explain extremely high GHG fluxes from soil hotspots. Our findings highlight how Fe minerals and microorganisms synergistically influence global carbon cycling and stability. Our findings highlight the relevance of free radical-related mechanisms in soil to the cycling, stabilization, and storage of carbon and also extend our mechanistic understanding of processes occurring within hotspots.