Organic Matter and Electron Acceptor Chemistry Jointly Determine Soil Carbon Decomposition Pathways *in situ*

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Soil organic carbon (SOC) decomposition is driven by microbial metabolisms and often modeled via Michaelis-Menten kinetics or empirically derived rate terms. However, SOC decay models that include these processes do not reliably predict SOC dynamics. Here we demonstrate that the thermodynamics of microbial respiration additionally regulate SOC decomposition rates. Organic carbon will only be respired if the available electron acceptors yield sufficient energy for microbial growth when metabolically coupled to SOC oxidation. We used dual pore domain reactors in which water flows over chemically uniform packed soil, allowing oxygen to diffuse through the soil and establishing a redox gradient, to examine thermodynamic constraints on carbon mineralization. The soil developed typical redox zonation with depth: after oxygen was depleted, nitrate, Mn, Fe, and sulfate served as electron acceptors. Dissolved OC (DOC) increased by 150% between the soil surface and at depth, and addition of electron acceptors (nitrate, sulfate) resulted in less DOC production and greater respiration at depth. When combined with carbon chemistry data obtained from X-ray absorption spectra and high-resolution ion cyclotron resonance mass spectrometry, our findings indicate that the thermodynamic potential of an electron donor (organic substrate) and an electron acceptor differentially impact respiration rates under redox conditions spanning aerobic to sulfate reducing.

This work highlights how thermodynamic constraints within specific redox metabolic zones of soils and sediments constrain microbial respiration and, thus, SOC decomposition. An improved understanding of these energetic limitations is critical to predict SOC dynamics under changing hydrology (e.g. saltwater intrusion, permafrost melting), temperature, and other factors impacting microbial respiration energetics.