

Dynamic Hydrology Shapes Microbially Mediated Redox Processes in a Great Lakes Coastal Estuary

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The propensity for redox processes to occur is sometimes predicted by measured or assumed redox potential, but process measurements often deviate from predictions based on the thermodynamic “redox tower” paradigm. In coastal wetlands, dynamic hydrology, rhizosphere processes, and bioturbating animals contribute to heterogeneous soil redox conditions. We hypothesize that poorly measured soil heterogeneity causes apparent departures from thermodynamic exclusion principles at bulk scales, with consequences for biogeochemical cycling which are not currently resolved in ecosystem, regional, or global scale models. We combined empirically measured traditional indicators with novel electrochemical approaches to reveal redox regimes in a Great Lakes coastal wetland. Specifically, we paired zero resistance ammetry (ZRA) measured with polymer-conductive carbon electrodes with traditional redox potential measurements using platinum electrodes to detect both the potential for and actual transfer of electrons due to microbial activity. ZRA can measure electrical current that arises from microbiological activities under contrasting redox regimes, and thus can detect the distributions, extents, and kinetics of biogeochemical processes. We co-located ZRA and redox potential sensor arrays with surface water, pore water, sediment, and greenhouse gas sampling to capture short- and long-term responses to frequent flooding and drying in a shallow cove of the Old Woman Creek wetland (Old Woman Creek National Estuarine Research Reserve, Huron, OH). In 2023, soil redox potential regimes responded to transient wetting and draining events as expected, but ZRA sensors revealed highly dynamic and heterogeneous microbial conditions at fine spatial and temporal scales when other tools suggested stable and homogenous conditions. Soils became oxidizing following a predictable vertical pattern during low water levels as moisture was lost from the soil surface and into deeper layers and converged at all depths to reducing conditions (~ -200mV) during and immediately after precipitation-driven rewetting

events. ZRA, conversely, revealed highly variable and active microbial redox transfers between multiple soil layers, even zones within 2 mm of one another, during the time periods when redox potential indicated stable and homogenous reducing conditions. Traditional indices of biogeochemical processes including greenhouse gas fluxes, pore water chemistry, and sediment characteristics, indicate the consequences of heterogeneous redox regime shaped by dynamic hydrology.