Rewriting the Redox Paradigm: Dynamic hydrology shapes nutrient and element transformations 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 (E_h), but process measurements often deviate from predictions based on the thermodynamic "redox tower" paradigm. We hypothesize that poorly measured, granular scale 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 will combine empirically measured traditional biogeochemical indicators with newly developed electrochemical approaches to determine how fluctuating hydrology shapes redox regimes and processes. Specifically, our objectives are to (1) relate dynamic hydrology in a freshwater terrestrial aquatic interface wetland (Old Woman Creek, OH) to redox regimes; (2) determine how redox heterogeneity drives elemental cycling at multiple scales, and; (3) assess the sensitivity of process-based models to the inclusion of fine-scale variability in redox conditions. We will use zero resistance ammetry (ZRA) to exploit redox disequilibria among discrete zones to detect the distributions, extents, and kinetics of biogeochemical processes. ZRA can measure electrical current that arises from microbially-induced redox disequilibrium. In winter 2021-2022, we worked to refine a paired ZRA and Eh multi-sensor system that will detect electrochemical signals across the sediment-water interface at nested scales (sub-millimeter to decimeter) at a shallow location (< 10 cm surface water) in the Old Woman Creek wetland. In summer 2022, we will deploy these sensors and collect concurrent data on dissolved oxygen dynamics, surface and pore water nutrient concentrations, greenhouse gas fluxes (chamber measurements), and soil geochemistry. We will then use those data to demonstrate the feasibility of integrating microsite electrochemical and redox variability to the ecosys ecosystem scale model for improved representation of soil redox processes in spatially variable and temporally fluctuating systems.