

# Biogeochemical Dynamics of Aqueous Fe and Mn in Soil Pore-Waters and Stream with Respect to Dissolved Organic Matter (DOM) Quantity and Quality

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Iron (Fe) and manganese (Mn) oxides, hydroxides and oxyhydroxides are well known redox-sensitive and reactive mineral components of environmental systems. Soil horizons with abundant Fe and Mn oxides/hydroxides have high mineral surface area and thus a high capacity to complex carbon (C), reducing susceptibility of C to microbial degradation. At the same time, Mn and Fe oxides are strong oxidizing agents under anaerobic conditions and could facilitate the microbial degradation of organics and formation of humic compounds.

The National Science Foundation (NSF) Critical Zone Observatory program is a system of six environmental observatories in the USA within a growing network throughout the world. The Christina River Basin-Critical Zone Observatory (CRB-CZO), located in the Piedmont region of Southeastern Pennsylvania and northern Delaware, is a partnership between the University of Delaware and the Stroud Water Research Center. At the White Clay Creek Watershed (WCCW) of the CRB-CZO we study how biogeochemical dynamics of Fe- and Mn- along redox gradients affect the C cycle within a floodplain forest.

We investigated the composition of soil pore-waters and stream over a 9 month-period with respect to the concentration of dissolved organic carbon (DOC) and the quality of dissolved organic matter (DOM) coupled with aqueous Fe and Mn, pH, temperature, alkalinity, conductivity, major anions, major cations,  $\delta D$ , and  $\delta^{18}O$ . DOM quality was characterized using UV-visible absorbance and fluorescence metrics such as absorption coefficient at 254nm ( $a_{254}$ ), specific-UV absorbance ( $SUVA_{254}$ ), slope ratio ( $S_r$ ), humification index (HIX), fluorescence index (FI), protein-like and other indices obtained from PARAFAC modeling of fluorescence excitation-emission matrices (EEMs). The biogeochemical approach above was combined with an advanced in-situ monitoring of biogeochemical parameters including redox, soil moisture and temperature. The sensors are being used to characterize geochemical gradients and how they change over time, and to enable targeted sampling at hot spots and during hot movements.

Our preliminary results demonstrated a significant redox gradient across the interface between anoxic wetland soils and valley-bottom gravel layers within a floodplain forest. Variations in redox gradients near the streambed may drive changes in Fe- and Mn-oxide precipitation and dissolution affecting C complexation or destabilization. DOM quality fluctuated in time and space indicating the existence of humic, microbial, or protein regions depending on the redox environment.