

## Quantification and Molecular Characterization of Mineral Associated Organic Carbon as Influenced by Redox Oscillations

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In redox-dynamic wetlands, the onset and oscillation of anoxic and oxic events induces biogeochemical processes and the composition of mineral-associated-organic carbon (MOC). It may become more significant for colloidal particles (1-1000 nm) due to their very large specific surface areas, high reactive site densities, and mobility. Shifts in pH and dissolution of metal oxides resulting from redox oscillations have profound influence on the mobilization of MOC. Despite the significance of wetland in global carbon (C) cycling, MOC remains poorly understood at the molecular level. In this study, soil samples were suspended in 2.0 mM NaCl electrolyte solution and allowed to undergo three oscillation events in the laboratory. MOC was investigated in different size fractions (1000-450 nm, 450-100 nm, 100-2.3 nm and < 2.3 nm). Size fractionated samples were analyzed for changes in surficial elemental composition by K $\alpha$  x-ray photoelectron spectroscopy (XPS) and for alterations in isotopic composition ( $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ ) by isotope ratio mass spectroscopy (IRMS). Deconvolution of C spectra for different size fractions confirms the existence of aliphatic and aromatic C<sup>[0]</sup> (C-C, C=C, C-H), ether and alcoholic C, C located mostly in polysaccharides, C<sup>[+1]</sup> (C-O, C-N) and carbonyl C<sup>[+2]</sup> (C=O, C(O)N) and the relative atomic % was 44-58, 28-34 and 12-23, respectively. Results also show that “nano-sized” MOC (2.3-100 nm) is mostly depleted in C-C/C-H but enriched in C=O and C-O/C-N functional groups, has the highest surficial atomic % of C, N and higher Mg/Al but lower C/N ratio. Cumulative oscillation events decreased the atomic % of C-C/C-H and increased C=O groups. IRMS analysis further revealed that SOM was depleted in heavier isotopes ( $\delta^{13}\text{C}$ ) and therefore, more enriched in recalcitrant C species at smaller sizes. However, the MOC becomes more recalcitrant with increasing oscillation events. Such size dependent heterogeneity in C species and their bonding with mineral phases can yield diverse assemblages of MOC, which can influence their fate and reactivity in redox-dynamic wetlands in response to changing climatic conditions.