

## Chemical Characterization and Release Dynamics of Sediment Associated Organic Matter at the Rifle, Co Field Site

Patricia Fox, Ruth Tinnacher, Xiu Yuan, Jim Davis, Benjamin Gilbert, Peter S. Nico; Lawrence Berkeley National Laboratory, Berkeley, CA, 94720, USA

**Patricia Fox**, Lawrence Berkeley National Laboratory, Berkeley, CA, United States

Sediment-associated natural organic matter (NOM) is an extremely complex assemblage of organic molecules. The chemical nature of NOM may control its' reactivity towards metals, minerals, enzymes, and bacteria. Total organic carbon (TOC) contents are typically around 0.1% (posing a distinct challenge for characterization), but can range from 0.03% up to approximately 1.5%. Even at the typical TOC values of 0.1%, the mass of sediment-associated OC is approximately 5000 times higher than the mass of dissolved OC (assuming typical DOC values of 1-3mg/l). The goals of this study were two-fold: first, to understand how the chemistry of sediment associated organic matter varied with location across the site, depth relative to water table, and different functionally defined reactive fractions; second, to understand the capacity for mineral associated organic matter to buffer DOC concentrations under varying chemical conditions.

We have characterized sediment-bound NOM from two locations. One location has relatively low organic carbon (<0.2%) and is suboxic [dissolved oxygen is low or absent, but no dissolved Fe(II) observed], while the other is a naturally reducing zone with higher organic carbon (0.2-1.5%) and Fe(II)-reducing conditions. Different NOM fractions [water soluble (MQ-SPE), pyrophosphate–acid soluble (PP-SPE), and pyrophosphate–acid insoluble (PP >1kD)] were extracted and isolated from the sediments and analyzed by a variety of techniques, including UV-Vis, FTIR, and ICP-MS. Each NOM fraction was chemically distinct, with the MQ-SPE and PP-SPE fractions being relatively more similar and distinct from the PP >1kD fraction. The MQ-SPE fraction appears to be more aliphatic and the PP fractions more aromatic as evidenced by both FTIR and UV-Vis data. The MQ-SPE fractions varied more widely across samples than the other fractions, indicating that this represents a much more dynamic pool of sediment-associated NOM.

To understand the DOC buffering capacity of the sediment associated organic matter, aquifer sediments were brought into contact with fresh, organic-carbon free groundwater solutions, at natural or reduced CO<sub>2</sub> concentration levels, in lab-scale batch experiments. During the repeated exchange of solutions at two temperature settings (room-temperature and 4 °C), solution pH and metal and organic carbon concentrations were monitored. Preliminary results for 20 exchanges of groundwater solutions over 50 days, showed an ongoing ability of the sediment associated organic matter to buffer DOC concentrations ~0.4-1mg/L through repeated release of low concentrations of organic carbon (~0.5-2 mg C/g sediment; ~0.05-0.2% of sediment-associated organic carbon) without any apparent depletion in the overall source term during the experiment.