Characterization of Natural Organic Matter in Low Organic Carbon Environments: Approaches and Implications for Reactivity

Patricia M. Fox[1][*], Peter S. Nico[1], Zhao Hao[1], Benjamin Gilbert[1], Malak Tfaily[2], and Jashvina Devadoss[1]

[1]Lawrence Berkeley National Laboratory, [2]Environmental Molecular Sciences Laboratory (EMSL)
[*]presenting author

Sediment-associated natural organic matter (NOM) is an extremely complex assemblage of organic molecules with a wide range of sizes, functional groups, and structures, which is intricately associated with mineral particles. The chemical nature of NOM may control its' reactivity towards metals, minerals, enzymes, and bacteria. Organic carbon concentrations in subsurface sediments are typically much lower than in surface soils, posing a distinct challenge for characterization. As a part of the Genomes to Watershed LBNL SFA 2.0 we investigated NOM associated with shallow alluvial aquifer sediments in a floodplain of the Colorado River in Rifle, Colorado, USA. Total organic carbon (TOC) contents in these subsurface sediments are typically around 0.1%, but can range from 0.03% up to approximately 1.5%. Total organic carbon content is largely correlated with sediment texture, which is highly heterogenous in this aquifer, with the highest TOC contents associated with naturally-reducing zones. 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, representing a large pool of carbon that may potentially be mobilized or degraded under changing environmental conditions. The goals of this study were to characterize the sediment-associated NOM and determine the degree to which it varies across different biogeochemical regimes present within the Rifle aquifer.

We have characterized the sediment-bound NOM from two locations within the floodplain with differing physical and geochemical properties. One location has relatively low organic carbon (<0.2%) and is considered suboxic [dissolved oxygen is low or absent, but no dissolved Fe(II) observed], while the other is a naturally reducing zone (NRZ) with higher organic carbon (0.2-1.5%) and Fe(II)-reducing conditions. A NOM extraction scheme was developed using a combination of sequential extraction [water and sodium pyrophosphate (pH 10)] and purification (dialysis and solid phase extraction) in order to isolate different fractions of sediment-associated NOM. Analysis of these different NOM fractions was then carried out by FTIR and ESI-FTICR-MS to allow for comparison of NOM structure and composition both across sites and across fractions for a single location. Using this combination of analytical techniques we can probe the variation in NOM chemical composition and mineral association across different biogeochemical regimes and assess the potential reactivity of various NOM pools. In combination with targeted field and laboratory experiments, this information can be used to determine key NOM characteristics to consider in modeling the biodegradation, transformation, and flux of carbon under changing conditions.