Molecular-Scale Characterization of Natural Organic Matter From A Uranium Contaminated Aquifer and its Utilization by Native Microbial Communities

Rifle IFRC (Principal Investigator: Philip Long)

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The availability and form of natural organic matter (NOM) strongly influences rates of microbial metabolism and associated redox processes in subsurface environments. This is an important consideration in metal-contaminated aquifers, such as the DOE's Rifle Integrated Field Research Challenge (IFRC) site, where naturally occurring suboxic conditions in groundwater may play an important function in controlling contaminant mobility, and therefore the long-term stewardship of the site. Currently, the biophysiochemical processes surrounding the nature of the aquifer and its role in controlling the fate and transport of uranium are poorly understood. Using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) with electrospray ionization (ESI), we characterized dissolved organic matter (DOM) chemistry for three surface and groundwater sources at Rifle and assessed microbial utilization in batch anaerobic incubation experiments. FT-ICR-MS uniquely offers ultrahigh mass measurement accuracy and resolving power for polar organics, in addition to enabling elemental composition assignments of these compounds.

Samples were collected from the Colorado River, a shallow groundwater aquifer adjacent to the river, and a spring/seep discharge point upgradient from the aquifer. DOM was concentrated and purified from each source and analyzed using FT-ICR-MS with ESI. We identified between 6,000 and 7,000 formulae at each location, with the river sample having the smallest and the spring sample having the largest number of identified peaks. The groundwater and spring samples contained DOM with a large percentage of formulae containing nitrogen and sulfur species, while the river sample was dominated by carbon, hydrogen, and oxygen species. Unsaturated hydrocarbons, cellulose, and lipids were rapidly utilized by indigenous bacteria during a 24-day incubation period, and presumably transformed to more recalcitrant lignins and protein-type molecules. Indeed, inoculation induced a shift in NOM composition from one with unique signatures to one with a larger percentage of shared formulae, suggestive of incipient conversion to the uniform chemical signature reflective of relatively recalcitrant NOM exported to river and marine systems. These findings indicate that FT-ICR-MS with ESI is an effective method for characterizing molecular-scale differences in DOM from complex environments. We also provide preliminary evidence that certain DOM fractions are more efficiently utilized by indigenous microbial communities and likely play an important role in controlling reducing conditions in heterogeneous subsurface environments.