

Applying Stable Isotopes for Source Fingerprinting of Dissolved Organic Nitrogen in Groundwater

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Project Goals: ENIGMA -Ecosystems and Networks Integrated with Genes and Molecular Assemblies use a systems biology approach to understand the interaction between microbial communities and the ecosystems that they inhabit. To link genetic, ecological, and environmental factors to the structure and function of microbial communities, ENIGMA integrates and develops laboratory, field, and computational methods.

In this project, we aim to: 1) differentiate the multiple sources of dissolved organic nitrogen (DON) in FRC contaminated groundwater via isotopic and elemental analysis; 2) quantify the contributions of DON in FRC contaminated groundwater during four successive seasons using stable isotope analysis in R (SIAR) mixing model; 3) verify the impact of source on labile fractions of DON in groundwater.

Abstract

DON constitutes a major pool of dissolved N in many aquatic ecosystems, playing an important role in biogeochemical cycling of both carbon (C) and N. Our recent work on natural organic matter at FRC indicated that dissolved organic nitrogen (DON) contributes to more than 50% of dissolved N pool in uncontaminated sediments, serving as an important source of C and N for microbes when labile C is limiting. Although considerable research has been carried out on dissolved inorganic N (DIN) transformation at FRC, the role of DON is largely unknown and has been overlooked thus far. Variations in source determine the quantity and quality of DON, therefore greatly affecting the microbial turnover of DON, and resultant microbial community structure. Stable isotope signature at natural abundance is a powerful tool in source fingerprinting of bulk C and N in soil and sediment, as well as nitrate in aquatic environments. However, only a handful of studies have been reported on isotopic survey of DON in marine, lake, and soil environments, none available for groundwater.

To obtain baseline information of DON in Oak Ridge FRC groundwater, we investigated the quantity and quality of dissolved organic matter (DOM) in groundwater during an ENIGMA 2-month sampling campaign, carried out in spring 2019 (mid March to mid May) at both FRC uncontaminated background area and nitrate contaminated area. Both DON and DOC content in nitrate-contaminated wells during late campaign period (mid April to mid May) was significantly lower ($p < 0.05$) than those during early campaign period. This suggests the existence of a

temporal fluctuation of DON quantity in FRC groundwater especially at nitrate-contaminated area, and the fluctuation can likely be explained as dilution by water from melting existing snowpack on ground. DOM quality in groundwater changed during this period as well. We used the ratio of ON to OC (ON/OC) as an indicator of DOM quality. During late campaign period (mid April to mid May), the ON/OC decreased in nitrate-contaminated groundwater, indicating that water input from melting snowpack potentially introduces different types of DOM (N-poor molecules) to groundwater.

Following up on these observations we are developing a reliable analytical method to measure N isotope signature of trace level of DON in groundwater. Currently, there is no well-established method for directly measuring $\delta^{15}\text{N}$ -DON in environmental water sample. We are testing solid-phase extraction based methods to concentrate trace level of DON from groundwater and to eliminate inorganic N such as nitrate and ammonium. We are testing different sorbents, and will apply Elemental Analyzer-Isotope Ratio Mass Spectrometry (EA-IRMS) for measuring $\delta^{15}\text{N}$ -DON in the solid sorbents.

This material by ENIGMA- Ecosystems and Networks Integrated with Genes and Molecular Assemblies a Scientific Focus Area Program at Lawrence Berkeley National Laboratory is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Biological & Environmental Research under contract number DE-AC02-05CH11231