Insight into the Composition and Structure of Petroleum Metabolites Not Identified by Standard Methods of Analysis

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Background/Objectives. Biodegradation at the National Crude Oil Spill Fate and Natural Attenuation Research Site near Bemidji, MN produces partially-oxidized water-soluble metabolites that partition from the oil into the aquifer. This petroleum-derived dissolved organic matter (DOM) undergoes continuous biodegradation as it is transported away from the crude oil source by groundwater to the Unnamed Lake. Regulators from federal and state agencies utilize standard methods of analysis to determine if crude oil and fuel spill sites are contaminated with toxic hydrocarbons, but these methods require extraction of polar DOM compounds with dichloromethane (DCM), and subsequent analysis by gas chromatography-based methods that are designed for analysis of volatile and semi-volatile compounds. The result is that potentially toxic oxyhydrocarbons are selectively excluded during extraction and/or analysis.

Approach/Activities. Here we utilize extraction and complementary analytical methods that are designed to determine the source, processing and fate of polar, non-volatile dissolved organic carbon. Water samples were collected along a linear transect of the oxyhydrocarbon plume at the research site. The DOM obtained from these samples was characterized by excitation-emission matrix spectroscopy (EEMs), ultrahigh resolution mass spectrometry (UHR MS), and nuclear magnetic resonance (NMR) spectroscopy. Additionally, samples were screened for acute toxicity by Microtox®.

Results/Lessons Learned. DOM solubilized from the crude oil is comprised of relatively aliphatic compounds with a small number of oxygen-containing functional groups. This is evidenced by blue-shifted fluorescence, an abundance of compounds with H:C > 1.5 and O:C < 0.5 identified by UHR-MS, and NMR spectra that reveal compounds depleted in carboxyl, aromatic, aliphatic C-O, and non-methyl alkyl carbons. As the DOM is transported away from the source, either biodegradation produces degradation products comprised of relatively aromatic, highly oxygenated compounds or these are selectively preserved in the plume. This is apparent from systematic enrichment in the classes identified by NMR spectroscopy, shifts to relatively low H:C and high O:C by UHR MS, and red-shifted fluorescence. Finally, a component identified by parallel factor (PARFAC) analysis created from EEMs spectra of petroleum-derived DOM shows a strong positive correlation with Microtox® results. In-situ screening of acute toxicity at spill sites and the structure/chemical composition of toxic compounds will be discussed.