The Use of Advanced Characterization Tools in Combination Improve Our Understanding of Biodegradation at Crude Oil Release Sites

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Background/Objectives: We studied the chemical composition of oxygen containing compounds (OCCs) found in groundwater upgradient, within, and downgradient of several crude oil releases to understand differences and similarities between the structural classes of OCCs detected under different redox conditions. Our hypothesis is that many OCCs found in background groundwater are found downgradient from the studied crude oil releases with similar redox conditions. OCCs closer to the hydrocarbon source can be related to petroleum biodegradation processes.

Approach/Activities: Groundwater and crude oil samples collected from several crude oil releases were analyzed using gas chromatography mass spectroscopy (GC-MS), GC flame ionization detection (GC-FID), non-targeted two-dimensional gas chromatography time-of-flight mass spectroscopy (GCxGC-TOF-MS) and high resolution mass spectroscopy (HRMS). Tentatively identified compounds (TICs) were detected and classified by their molecular formula and structural class. Total petroleum hydrocarbons (TPH) were quantified with and without silica gel cleanup to understand contribution from OCCs to the TPH analysis. Geochemical data was collected to understand redox conditions for each well location. Results were compared to known biodegradation pathways under aerobic and anaerobic conditions.

Results/Lessons Learned: An evaluation of OCCs found at several crude oil release sites indicates many TICs found downgradient from petroleum releases are also found in upgradient wells and can be found in background groundwater with similar redox conditions. While a number of TICs may be petroleum biodegradation intermediates, others are consistent with components of dissolved organic carbon found in unimpacted aquatic systems. Each analytical method has strengths and limitations. GC-MS and GC/FID provide quantitative data for compounds of interest from a biodegradation perspective. GCXGC-TOF-MS is a powerful analytical tool for evaluating chemical structural class but, as a non-targeted method, cannot provide quantification (i.e., concentration data) for each chemical detected. HRMS provides molecular data that includes compounds which cannot be analyzed by GC; but cannot provide structural class information. Overall, results demonstrate that advanced analytical methods, when used in a complementary combination, allow for a more complete and robust analysis of OCCs at petroleum release sites.