Composition of Extractable Organics in Groundwater at Biodegrading Crude Oil Release Sites

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Background/Objectives. Crude oil releases, like refined petroleum fuel releases, undergo biodegradation in the environment. During these processes the constituents are transformed from the original hydrocarbons into oxygen-containing (polar) biodegradation metabolites, which can be measured as extractable organics in groundwater at these sites. We have studied the detailed composition of extractable organics plumes at multiple biodegrading fuel release sites using targeted and non-targeted gas chromatography (GC) based methods, and have published those results (Mohler et al., 2013 DOI 10.1021/es401706m; Zemo et al., 2016 DOI 10.1002/ieam.1848). There is little data in the scientific literature on the detailed composition of the complex mixture of polars actually present in groundwater at biodegrading crude oil sites, and there is uncertainty about the potential polar compounds that could be formed at these sites as compared to those that are formed at fuel release sites. Differences could occur due to the composition (i.e., PAHs and cyclic biomarkers) and complexity of crude oil. Recently, we have begun studying the polar compounds detected as extractable "diesel-range" and "oil-range" total petroleum hydrocarbons at crude oil release sites using the same GC-based methods employed in our previous work as well as expansion to electrospray ionization mass spectrometry (ESI-MS).

Approach/Activities. Upgradient, source area and downgradient groundwater samples have been collected and extracted with methylene chloride. Extracts were analyzed using targeted (GC-FID, GC-MS) and non-targeted (GC-MS, and comprehensive two-dimensional gas chromatography with time of flight mass spectrometry [GCXGC-TOFMS]) analytical methods. The compounds in each sample extract were tentatively identified by GCxGC using the same criteria (e.g., mass spectral similarity of 750 or higher) and database (NIST, 2005) as our previous work. The extracts were also analyzed on an Orbitrap (ESI-MS) in both negative and positive ion mode to gain insight into material that might not be detected by GC-based methods.

Results/Lessons Learned. The GCxGC tentatively identified extractable compounds with boiling points up to approximately 496°C, which is equivalent to nC36. Results to date indicate that the nature and distribution of the polar compound molecular classes present in downgradient wells at crude oil sites are quite consistent with those from downgradient locations at biodegrading fuel release sites, with the n- and alkyl- organic acids/esters dominating the percentage of tentatively identified compounds. Naphthenic (saturated cyclic) acids were only detected in two source zone wells to date. The specifics on the analytical approach, the results from one (or more) biodegrading crude oil releases, and a comparison to the results from multiple fuel release sites will be presented. Preliminary results obtained by the Orbitrap will also be presented.