An Alternative Hypothesis of the Nature of Dissolved Organic Carbon in Groundwater at Petroleum Release Sites

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Background/Objectives. A plume of oxygen-containing organic compounds often extends beyond the plume of hydrocarbons in groundwater at petroleum release sites. Our group has been using two-dimensional gas chromatography with time of flight mass spectrometry (GCxGC-TOF-MS) to identify these compounds. This work has been based on a biochemistry-focused hypothesis that the compounds are components of petroleum degradation pathways. Recent findings suggest that many of the compounds may not be degradative intermediates, but are the result of microbial growth, secondary production, and carbon cycling. Based on such a microbial ecology-focused hypothesis, the nature of dissolved organic carbon (DOC) in groundwater plumes would be consistent with that of other natural aquatic systems. The purpose of this presentation is to describe and evaluate this updated hypothesis.

Approach/Activities. GCxGC-TOF-MS was used to tentatively identify compounds (TICs) in over 100 groundwater samples collected from over 20 petroleum release sites. The samples were collected from wells upgradient of the petroleum release, within the source zone, and downgradient of the dissolved hydrocarbons but within the oxygen-containing organic compound plume. The specific compounds and number of times they were detected were compared across the various types of well locations. Principal component analysis was used to evaluate the complexity of chemical mixtures in samples collected from the various types of wells. To compare the TICs to compounds found naturally in the biosphere, their structures and chemical formulas were matched to those listed in a metabolic database.

Results/Lessons Learned. About 60% of the most commonly-detected compounds in downgradient wells were also detected in upgradient wells. A majority of these were fatty acids or fatty acid esters with structures that should be readily degradable. Such acids are known to be ubiquitous components of DOC in aquatic systems. Few of the TICs were branched or cyclic compounds that would suggest incomplete degradation of recalcitrant hydrocarbons. Principal component analysis indicated a continuum of biodegradation between the source area and downgradient samples with the latter becoming more consistent with upgradient samples. Approximately 98% of the TIC's chemical formulas were matched to those in the metabolic database. Using the more specific chemical structure, about 24% of the downgradient TICs and 43% of upgradient TICs were in the database. Compounds known as phthalates were found about as frequently in upgradient samples as in downgradient samples, indicating that these are not related to the petroleum source.

High-definition mass spectrometry methods, such as Orbitrap electrospray ionization (ESI-MS) or Fourier-transform ion cyclotron resonance (FTICR-MS), are increasingly being used to evaluate the fate of naturally occurring organic compounds in aquatic systems. Irrespective of the growth substrates, microbial communities generate a complex but generally consistent chemical mixture measured as DOC. Application of these methods to groundwater samples collected from petroleum release sites has been initiated and the results will be discussed.