Hydrologic Controls on Losses of Individual Components of Crude Oil

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Background/Objectives. Source zone natural attenuation in the shallow subsurface is the subject of an ongoing study of a terrestrial crude oil spill. The study site, located near Bemidji, Minnesota, was contaminated in 1979 when a pipeline rupture spilled ~1.7 million liters of light crude oil. The initial clean up removed ~75% of the oil and the remaining ~25% infiltrated the sand and gravel glacial outwash formation forming three main source zones (SZ). This study is based on the largest SZ, with an area of ~2,500 m^2, oil saturations of 20-65% and an estimated SZ oil volume of 147,000L. Average annual recharge is ~12 cm/y and the water table depth in the SZ is 6-8 m.

Approach/Activities. In 2010 oil samples were bailed from 13 wells in the SZ and stored in the freezer. Oil samples from five of these wells had been collected in 1987, 1989, 2005 and 2008. Concentrations of volatile constituents were determined by solid-phase microextraction-gas chromatography/ mass spectrometry (SPME-GC/MS). The volatile constituents measured were C_6-C_{12} *n*-alkanes, cyclic hydrocarbons including cyclohexane, methyl- and ethylcyclohexane, and aromatic hydrocarbons including BTEX (benzene, toluene, ethylbenzene, xylenes), C_3- and C_4-benzenes (tri- and tetramethyl benzenes and isopropyl- and n-propylbenzenes), naphthalene and methyl-, ethyl- and dimethylnaphthalenes. Composition data for individual compounds were compared with water table depth and oil saturations measured at 25 locations. A 13-month laboratory experiment with SZ sediments was conducted to determine if benzene degrades in the SZ.

Results/Lessons Learned. The analyses show that losses of the oil compounds from the source are controlled by susceptibility to degradation under methanogenic conditions and solubility. Compounds that do not degrade under methanogenic conditions at the study site include benzene, ethylbenzene and *m*- and *p*-xylene. Losses of these compounds from the oil correlated with water saturation and effective solubility, consistent with dissolution as the loss mechanism. A laboratory microcosm study confirmed that benzene does not degrade in sediments from the SZ. In 2010, 31 years after the spill, benzene concentrations ranged from 5% to 42% of those in the original oil. Compounds that degraded under methanogenic conditions include toluene, *o*-xylene, and the *n*-alkanes. Losses of these compounds correlate better with location in the oil body than with water saturation, with greater losses below a topographic depression where focused recharge occurs, potentially providing greater fluxes of nutrients and electron acceptors to facilitate degradation. Normalization to a relatively persistent compound 1-methyl-napthalene indicates total oil losses by 2010 of 19-46% across the SZ with a saturation-weighted average of 32% (equivalent to 649 gallons/acre/year). Mass-balance modeling based on surface carbon dioxide efflux data indicates oil mass decreased ~14%. Reasons for the discrepancy will be discussed as well as implications of the study results for remedial strategies and SZ depletion monitoring.