

Subsurface Hydrologic Limitations on Crude Oil Biodegradation

BARBARA BEKINS¹, MARY JO BAEDECKER²,
ROBERT P. EGANHOUSE², FRANCES D. HOSTETTLER¹,
DINA M. DRENNAN³, WILLIAM N. HERKELRATH¹,
EAN WARREN¹, GEOFF DELIN⁴
AND ISABELLE M. COZZARELLI²

¹USGS, 345 Middlefield Rd., Menlo Park, CA 94025, USA

²USGS, 12201 Sunrise Valley Dr., Reston, VA 20192, USA

³Colorado School of Mines, Golden, CO 80201, USA

⁴USGS, Denver Federal Center, Lakewood, CO 80225, USA

In a crude oil contaminated aquifer near Bemidji, Minnesota, USA, hydrologic processes limit oil weathering rates in two ways: (1) relative permeability for water moving through the oil controls dissolution rates; and (2) recharge from the land surface transports limiting growth nutrients unequally to different locations. The oil contaminated zone is 75m x 25m centered on the water table at a depth of 6-8m. Gas and water concentrations and microbial community data show that methanogenic conditions prevail in this zone. Volatile compounds in the oil, including alkylbenzenes, naphthalenes, cyclohexanes and C₆-C₁₂ *n*-alkanes, show that loss rates of individual compounds are controlled by relative solubility and susceptibility to methanogenic biodegradation. Benzene and ethylbenzene persist under methanogenic conditions at this site, such that dissolution is the primary loss mechanism from the crude oil. Losses are linearly correlated with pore space oil saturations and consistent with the relative solubilities of these compounds. A 13-months microcosm study confirmed persistence of benzene under methanogenic conditions.

Compounds susceptible to methanogenic biodegradation include the *n*-alkanes, toluene, and *o*-xylene. There is extreme spatial dependence in the degradation rates such that the *n*-alkanes are mostly degraded in the upgradient end, but are nearly unaltered in the downgradient end. Surface hydrologic properties controlling groundwater recharge at this site have a large effect on the biodegradation rates in the subsurface. Recharge rates estimated in 2002 using moisture probes show that the more degraded end received over twice the recharge of the less degraded end. Real-time qPCR data show that the average methanogen concentrations are 37 times greater in the more degraded end of the oil body suggesting that a growth nutrient is supplied by recharge. In summary, these results indicate that biodegradation is tightly coupled to the physical processes of permeability and recharge.