Natural Attenuation Rates of Benzene and Total Petroleum Hydrocarbons (TPH) at Petroleum Release Sites

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Background/Objectives. Recent studies have shown that natural attenuation of total petroleum hydrocarbons (TPH) in light non-aqueous-phase liquid (LNAPL) source areas at petroleum release sites can, in certain cases, rival TPH mass removal rates via engineered remediation. Such information is being used as technical justification for terminating hydraulic recovery after primary hydrocarbon plume containment has been established. Other remedial endpoints, such as predicting whether risk-based standards can be met within a reasonable timeframe, require additional information on natural attenuation rates of key constituents of potential concern (COPCs). Further knowledge of the spatiotemporal variability of natural attenuation rates is also required to understand key factors that affect natural attenuation (i.e., guide data collection efforts) and improve plume longevity predictions.

Approach/Activities. Natural attenuation rates of benzene and total petroleum hydrocarbon (TPH) were estimated by calibrating a vapor transport model (BioVapor) to soil-gas concentration data contained in the US EPA Office of Underground Storage Tanks petroleum vapor intrusion database. The database was filtered such that only soil-gas data associated with LNAPL sources were evaluated. The resultant database consisted of 266 soil-gas samples collected from 55 soil-gas probe locations at 35 UST sites across the US and Australia. Hydrocarbon vapor transport was simulated assuming gaseous-phase diffusion according to Fick's Law, site-specific estimates of the effective diffusion coefficient, and 1^{st}-order oxygen-limited reaction kinetics.

Results/Lessons Learned. Median natural attenuation rates for TPH and benzene were 240 and 0.13 gal/acre-yr, respectively. The rates determined for TPH are consistent with natural source-zone depletion rates reported in the literature measured using surface flux chambers and carbon traps. The natural attenuation rates of benzene are also reasonable considering that the vast majority of vapor sources (LNAPL) were likely gasoline containing <1 % wt/wt benzene. TPH and benzene rate estimates were not sufficiently correlated to infer meaningful estimates of COPC attenuation rates from NSZD and LNAPL composition data. Natural attenuation rates were more sensitive to spatial (proximity to source, source concentration, and soil type) rather than temporal factors (seasonality). Mean aqueous-phase 1^{st}-order rate constants for benzene (0.15 hr^{-1}) determined by model calibration are ~5x less than those reported in the literature and increase slightly during summer (April – September) months. The reason for the discrepancy between model calibrated and literature rates is uncertain but may relate in part to assumptions regarding the effective diffusion coefficient. Although the methodology invoked in this study is not new, the analysis sheds light on key factors that affect attenuation rates and helps promote a simple approach for improved risk-based decision making at petroleum release sites.