## Soil Respiration Rates under Natural Attenuation versus Enhanced Biodegradation

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**Background/Objectives.** Groundwater and soil at a petroleum industry site contains benzene, toluene, and total petroleum hydrocarbons in the gasoline range (TPH<sub>g</sub>). A treatability study was performed to evaluate potential treatment alternatives that had the potential for future application at the Site as part of a planned corrective action for soil and groundwater impacts. Active stimulation of biodegradation was compared to natural attenuation to determine whether active stimulation provided a significant advantage over natural processes.

Natural attenuation is a remedial approach that relies on natural subsurface mechanisms that are classified as either destructive or nondestructive. Biodegradation is the most important in situ destructive mechanism, while non-destructive mechanisms include sorption, dispersion, dilution, and volatilization. However, natural attenuation has its inherent limitations and can be slow, making the time frame for completion relatively long.

**Approach/Activities.** Enhanced biodegradation, both aerobic and anaerobic, and natural attenuation were evaluated using groundwater and soil from the Site. Microcosms were prepared using varying doses of different amendments to evaluate enhanced biodegradation for the treatment of benzene, toluene, and TPH<sub>g</sub>. Amendments tested included, oxygen, nutrients, sulfate and microbial inocula. A second set of microcosms was prepared without the use of any amendments to evaluate the existing natural attenuation occurring at the Site.

Compound-specific isotope analysis (CSIA) was performed on groundwater samples collected from the Site. The results of the CSIA were used to determine whether natural attenuation could be demonstrated to be occurring.

**Results/Lessons Learned.** The data suggest that natural attenuation would occur at the Site over time; however, natural attenuation rates would be slow, therefore treatment by natural attenuation would require an extended time period. Low microbial populations currently present in soil would also limit natural attenuation in the vadose zone. Natural attenuation could be applied at the Site if an extended time period was available for monitoring.

Enhanced biodegradation appeared to increase soil respiration at the Site and was expected to increase biodegradation rates over time. More biodegradation of benzene, toluene, and TPH<sub>g</sub> were observed when aerobic conditions were enhanced than when anaerobic conditions were enhanced; therefore, enhanced aerobic biodegradation was the recommended technology, although anaerobic biodegradation would also be effective.

CSIA results showed that samples with higher benzene concentrations had higher  $\delta^{13}$ C values. This suggested that biodegradation was occurring at a low rate in the source areas where benzene concentrations were highest but that the lower concentrations outside the source areas were caused by dilution rather than biodegradation and that there was less biodegradation occurring outside the source areas.

No relationship between  $\delta^2 H$  values and benzene concentration was observed, which suggested that biodegradation was primarily occurring by the breakage of carbon-carbon bonds

rather than carbon-hydrogen bonds. This is consistent with the known benzene biodegradation pathway.