Sulfate Delivery Methods for Enhancing Biodegradation of Petroleum Hydrocarbons

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Background/Objectives. Elevated concentrations of petroleum hydrocarbons (benzene, toluene, ethylbenzene, and xylene [BTEX], or total petroleum hydrocarbons) typically persist in groundwater either due to the presence of residual hydrocarbon source mass (in the form of light non-aqueous phase liquid [LNAPL] of refined products or crude oil) and/or low concentration of electron acceptors (e.g., dissolved oxygen, nitrate, or sulfate). Natural biodegradation of petroleum hydrocarbons in subsurface under sulfate reducing conditions is ubiquitous and leads to depleted concentrations of sulfate in an impacted subsurface. Addition of sulfate to enhance biodegradation of hydrocarbons like BTEX is a cost-effective and viable remedial technology at many sites and offers the potential to reduce the timeframe of groundwater monitoring required prior to site closure. However, appropriate sulfate delivery and distribution in the subsurface remain the primary challenges in implementing and sustaining enhanced biodegradation over time, particularly when using liquid or slurry injection approaches.

Approach/Activities. To overcome these challenges, cost-effective delivery mechanisms that achieve a stable, uniform sulfate concentration were developed to improve effectiveness of sulfate-enhanced biodegradation strategies. Based on site characteristics including distribution of contaminants, geology, remedial objectives, four solid-based delivery methods are outlined for use at environmental sites. These include:

- Sulfate land application involving spreading of gypsum on ground surface followed by precipitation or irrigation-facilitated sulfate dissolution and infiltration to impacted subsurface.
- 2. <u>Permeable filled borings</u> involving placement of gypsum in a transect of borings to promote sulfate dissolution and delivery into impacted groundwater.
- 3. <u>Permeable filled conduits</u> involving placement of gypsum in borings ending above smear zone and supported by trickle irrigation to promote sulfate dissolution and delivery into impacted vadose and saturated subsurface.
- 4. Excavation backfill involving mixing of gypsum into the backfill so that gypsum acts as a continuous source of sulfate into the underlying impacted subsurface.

Performance of sulfate delivery methods was studied using groundwater analytical data: standard geochemical parameters, dissolved inorganic carbon (DIC), BTEX, and advanced diagnostic tools such as compound-specific isotope analysis for BTEX, and stable isotope analysis for sulfate and DIC.

Results/Lessons Learned. Results demonstrated sustained delivery of sulfate into impacted subsurface and enhanced biodegradation of BTEX which corresponded with sulfate reduction and with complete mineralization of hydrocarbons. Results confirmed viability of sulfate delivery to enhance hydrocarbon biodegradation and led to beneficial site outcomes (e.g., optimized excavation footprint needed for mass removal, expedited site closure). These findings helped define site conditions and key considerations for application of an appropriate sulfate delivery method.