Bioremediation and Sustainable Environmental Technologies—2017. Fourth International Symposium on Bioremediation and Sustainable Environmental Technologies (Miami, FL; May 2017). ©2017 Battelle Memorial Institute, Columbus, OH, www.battelle.org/biosymp. A. Barton and S. Rosansky (Chairs)

Use of Diagnostic Tools to Assess the Efficiency of Sulfate Land Application to a Petroleum Hydrocarbon Plume

Violaine Ponsin, Daniel Hunkeler, Daniel Bouchard (University of Neuchatel, Neuchatel, Switzerland)
Eugene L. Madsen, Chris DeRito (Cornell University, Ithaca, NY, USA)
Neil R. Thomson (University of Waterloo, Waterloo, ON, Canada)
Kammy Sra, Tim Buscheck, Ravi Kolhatkar, Eric Daniels (Chevron, San Ramon, CA, USA)

Background/Objectives. Biodegradation of petroleum hydrocarbons in groundwater is frequently limited by the availability of electron acceptors. During engineered remediation, gaseous or dissolved oxidants are injected into the subsurface to increase the biodegradation rate. Land application of sulfate-bearing salts at the ground surface is an attractive alternative that does not require the installation of expensive treatment systems. Furthermore, sulfate is highly soluble, and has a high capacity to accept electrons. However, it is a thermodynamically less favorable oxidant compared to oxygen or nitrate. It is therefore important to verify that sulfate reduction occurs and in particular that compounds of concern such as benzene are degraded. The aim of this study was (i) to test different diagnostic tools that can be used to track the intended remediation process and (ii) to assess if land application is effective in stimulating sulfate-reducing biodegradation of compounds of concern.

Approach/Activities. The study was carried out at a former refinery site operated until 1995 with petroleum hydrocarbon contamination in soil and groundwater. Agricultural gypsum ($CaSO_4$) was applied in a pilot test area, together with sodium bromide (NaBr) as a tracer to track solute transport across the vadose zone. Two types of diagnostic tools were tested: (i) tools that indicate the occurrence of sulfate-reduction such as $^{34}S/^{18}O$ in sulfate and ^{13}C in dissolved inorganic carbon (DIC) and (ii) tools that provide information on the degradation of compounds of concern including compound-specific isotope analysis (CSIA) and biomarkers (metabolites, mRNA). Water samples were taken from long-screened and multilevel wells to evaluate if the spatial scale of sampling influences the diagnostic tool response. Furthermore, soil cores were taken to assess the fate of applied sulfate in the vadose zone.

Results/Lessons Learned. The applied sulfate reached the shallowest part of the plume where BTEX concentrations were highest. ^{34}S in SO_4^{2-} indicated that sulfate-reduction was occurring. Biomarkers confirmed that BTEX were biodegraded under anaerobic conditions. Dual carbon and hydrogen isotope plots ($\delta^{13}C$ vs $\delta^{2}H$) for benzene and toluene showed that these compounds were undergoing biodegradation under sulfate-reducingconditions. The soil cores revealed approximately half of the land-applied sulfate mass remained in the vadose zone 16 months after land application, while sulfate was completely consumed in groundwater after several months. Thus, biodegradation was limited by the rate of transport of sulfate across the vadose zone rather than the applied amount of gypsum and could be potentially increased by continuing irrigation. In conclusion, the diagnostic tools provide detailed insight into the occurrence of key remediation processes and thus help to verify that resources for remediation are spent effectively.