

# Sulfate Enhanced In Situ Biodegradation of MTBE and TBA in Fractured Bedrock for Source Area Treatment and Downgradient Risk Mitigation

**Naren Babu** (naren.babu@stantec.com) (Stantec, Walnut Creek, CA USA)  
David Collins, PE (david.collins@stantec.com)  
Kyle Waldron (kyle.waldron@marathon.com)

**Background/Objectives.** Historical releases of gasoline and pure phase MTBE due to the failure of a former aboveground storage tank fill line resulted in dissolved MTBE and TBA concentrations ranging up to 12,000,000 µg/L and 1,100,000 µg/L, respectively. The site is characterized by a steep topographic decline and complex geologic structure. The uplands in the source area consist of fill and marginally lithified/indurated claystone, siltstone, and sandstone with varying degrees of weathering and fracturing and the downgradient wetlands consist of bay peats and muds. The orientation and varying hydraulic conductivities of the more lithified strata have resulted in the transport of fuel oxygenates beyond the existing hydraulic control features. The steep topography, low permeability lithologic materials, and high fuel oxygenate concentrations have resulted in a broad MTBE plume with low mass flux that limits the effectiveness of typical mass removal technologies. Previous studies at the site utilized multiple lines of evidence including physicochemical, microbial, and isotopic analyses to demonstrate MTBE and TBA biodegradation. Results showed that the source area is primarily methanogenic and downgradient areas have sulfate reducing conditions. Given the complex hydrogeologic setting and anoxic conditions, a pilot study was implemented to evaluate enhancing the in situ anaerobic biodegradation of MTBE and TBA via sulfate reduction to treat the source area and mitigate transport beyond the hydraulic control.

**Approach/Activities.** A 60,000 mg/L solution of magnesium sulfate was gravity fed into the saturated zone in six wells in the source area and four temporary boreholes in the downgradient study area. Continuous reading AquaTroll meters with data loggers were deployed to assess amendment arrival and collect monthly snapshot water quality data by measuring total dissolved solids (TDS), specific conductivity, pH, and oxidation-reduction potential. Pre- and post-injection groundwater samples were collected on a quarterly basis and evaluated for chemical concentrations, geochemical parameters, compound specific isotope analysis (CSIA) of MTBE <sup>13</sup>C and <sup>2</sup>H and sulfate <sup>34</sup>S, and microbial analysis.

**Results/Lessons Learned.** Baseline microbial analytical results showed moderate levels of biomass and the presence of sulfate reducing bacteria. Post-injection TDS and sulfate concentrations showed steady increases in the nearest downgradient monitoring wells providing clear evidence of amendment arrival. Redox conditions became more reduced providing evidence of sulfate consumption. MTBE and TBA concentrations varied. In some cases, a clear trend of the degradation of both compounds was observed, and in others a decrease in MTBE coupled with an increase in TBA was observed, both indicative of biodegradation. And in some wells MTBE and TBA increased, which is potential evidence of MTBE biodegradation to TBA and back diffusion of MTBE from the bedrock matrix. While clear trends in the enrichment of MTBE <sup>13</sup>C and <sup>2</sup>H were not observed, sulfate <sup>34</sup>S enrichment was observed in the nearest downgradient well in the source area, providing a confirming line of evidence of sulfate consumption for contaminant biodegradation. Overall, pilot study results confirmed the effectiveness of EISB via sulfate reduction in both areas of the site leading to the design of a full-scale EISB remedy.