

## Verified Carbon Tetrachloride and Chloroform Transformation via Biotic, Abiotic, and Reactive Iron Sulfide Mechanisms

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**Background/Objectives.** Although significant progress has been made in elucidating the mechanisms and pathways contributing to the degradation of chlorinated methanes, knowledge of the interplay of microbially-mediated reactions with abiotic processes contributing to carbon tetrachloride (CT) and chloroform (CF) transformation remains limited to date, hindering the application of combined biotic-abiotic remedial approaches at field sites. With the availability of novel tools to characterize mineralogical data and active microbial community members and a focus on in situ engineered bioremediation practices that couple biotic-abiotic processes, significant opportunities exist to advance microbial remedies to tackle chlorinated methane contamination.

**Approach/Activities.** Targeted in situ injections involving the direct-push delivery of EHC™, a combined zero valent iron (ZVI) and organic carbon substrate, were completed at a site impacted with CT (~15,000 ug/L) and CF (~8,000 ug/L) in groundwater. The selected injection approach was designed to: (a) chemically reduce CT and CF via direct contact with ZVI, (b) enhance microbial CT and CF transformation via addition of organic carbon, and (c) exploit the naturally elevated concentrations of iron and co-disposed sulfur compounds to catalyze the biologically-mediated formation of reactive iron sulfide minerals capable of abiotically transforming CT and CF. The phased injection program included installation of 17 temporary monitoring wells, baseline sampling of wells within and downgradient of the EHC™ injection areas, direct-push injection of almost 300,000 pounds of EHC™ into more than 320 locations at an average of three depth intervals each, confirmatory soil borings to evaluate the distribution of EHC™ in the subsurface, and post-injection performance monitoring. The effectiveness of EHC™ injection was evaluated using multiple lines of evidence: (a) changes in field parameters during injection, (b) declining concentrations of CT and CF, (c) geochemical analysis to verify reducing conditions, (d) soil core sampling to collect mineralogical data, (e) Min-Traps™ – a passive sampling device that is deployed within a monitoring well – to verify the formation and persistence of reactive iron sulfide minerals in situ, and (f) microbial community investigation.

**Results/Lessons Learned.** Injection results indicate that EHC™ delivery is highly effective for treatment of CT and CF impacts in groundwater. Where EHC™ was distributed in the subsurface, strongly reducing geochemical conditions were formed and enhanced biotic and abiotic (complete) degradation of CT and CF were observed. Post-injection performance monitoring is ongoing through December 2018. Characterization of reactive iron sulfide minerals formed within both Min-Traps™ and confirmatory soil boring samples will be conducted using scanning electron microscopy-energy dispersive X-ray spectroscopy and acid volatile sulfide and chromium extractable sulfide techniques in September 2018. At the same time, assessment of the microbial community via QuantArray®-MIC (microbially induced corrosion), will also be performed. The Min-Trap™ and QuantArray®-MIC data, along with geochemical and CT/CF transformation trends, will further our understanding of the role of coupled biotic-abiotic processes in the in situ transformation of chlorinated methanes.