# Chapter 5
# Long-Term Performance Evaluation of Groundwater Chlorinated Solvents Remediation Using Nanoscale Emulsified Zerovalent Iron at a Superfund Site

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## ABSTRACT

*This chapter addresses a case study of long-term assessment of a field application of environmental nanotechnology. Dense Non-Aqueous Phase Liquid (DNAPL) contaminants such as Tetrachloroethene (PCE) and Trichloroethene (TCE) are a type of recalcitrant compounds commonly found at contaminated sites. Recent research has focused on their remediation using environmental nanotechnology in which nanomaterials such as nanoscale Emulsified Zerovalent Iron (EZVI) are added to the subsurface environment to enhance contaminant degradation. Such nanoremediation approach may be mostly applicable to the source zone where the contaminant mass is the greatest and source removal is a critical step in controlling the further spreading of the groundwater plume. Compared to micro-scale and granular*

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*counterparts, NZVI exhibits greater degradation rates due to its greater surface area and reactivity from its faster corrosion. While NZVI shows promise in both laboratory and field tests, limited information is available about the long-term effectiveness of nanoremediation because previous field tests are mostly less than two years. Here an update is provided for a six-year performance evaluation of EZVI for treating PCE and its daughter products at a Superfund site at Parris Island, South Carolina, USA. The field test consisted of two side-by-side treatment plots to remedy a shallow PCE source zone (less than 6 m below ground surface) using pneumatic injection and direct injection, separately in October 2006. For the pneumatic injections, a two-step injection procedure was used. First, the formation was fluidized by the injection of nitrogen gas alone, followed by injection of the EZVI with nitrogen gas as the carrier. In the pneumatic injection plot, 2,180 liters of EZVI containing 225 kg of iron (Toda RNIP-10DS), 856 kg of corn oil, and 22.5 kg of surfactant were injected to remedy an estimated 38 kg of chlorinated volatile compounds (CVOC)s. Direct injections were performed using a direct push rig. In the direct injection plot, 572 liters of EZVI were injected to treat an estimated 0.155 kg of CVOCs. Visual inspection of collected soil cores before and after EZVI injections shows that the travel distance of EZVI was dependent on the method of delivery with pneumatic injection achieving a greater distance of 2.1 m than did direct injection reaching a distance of 0.89 m. Significant decreases in PCE and TCE concentrations were observed in downgradient wells with corresponding increases in degradation products including significant increases in ethene. In the pneumatic injection plot, there were significant reductions in the downgradient groundwater mass flux values for chlorinated ethenes (>58%) and a significant increase in the mass flux of ethene (628%). There were significant reductions in total CVOCs mass (78%), which was less than an estimated 86% decrease in total CVOCs made at 2.5 years due to variations in soil cores collected for CVOCs extraction and determination; an estimated reduction of 23% (vs.63% at 2.5 years) in the sorbed and dissolved phases and 95% (vs. 93% at 2.5 years) reduction in the PCE DNAPL mass. Significant increases in dissolved sulfide, volatile fatty acids (VFA), and total organic carbon (TOC) were observed and dissolved sulfate and pH decreased in many monitoring wells. The apparent effective destruction of CVOC was accomplished by a combination of abiotic dechlorination by nanoiron and biological reductive dechlorination stimulated by the oil in the emulsion. No adverse effects of EZVI were observed for the microbes. In contrast, populations of dehalococcoides showed an increase up to 10,000 fold after EZVI injection. The dechlorination reactions were sustained for the six-year period from a single EZVI delivery. Repeated EZVI injections four to six years apart may be cost-effective to more completely remove the source zone contaminant mass. Overall, the advantages of the EZVI technology include an effective "one-two punch" of rapid abiotic dechlorination followed by a sustained biodegradation; contaminants are destroyed rather than transferred to another medium; ability to treat both DNAPL source zones and dissolved-phase contaminants to contain plume migration; ability to deliver reactants to targeted zones not readily accessible by conventional permeable reactive barriers; and potential for lower overall costs relative to alternative technologies such as groundwater pump-and-treat with high operation and maintenance costs or thermal technologies with high capital costs. The main limitations of the EZVI technology are difficulty in effectively distributing the viscous EZVI to all areas impacted with DNAPL; potential decrease in hydraulic conductivity due to iron corrosion products buildup or biofouling; potential to adversely impact secondary groundwater quality through mobilization of metals and production of sulfides or methane; injection of EZVI may displace DNAPL away from the injection point; and repeated injections may be required to completely destroy the contaminants.*

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