



ZVI and Enhanced Bioremediation at a 1,1,1-TCA & PCE Site

Site Type: Contaminated groundwater (chlorinated ethenes and chlorinated ethanes) in Indiana

Project Type: Full-scale CSIA and Gene Assays (qPCR)

PROJECT SUMMARY

Location: Indiana

Client: Confidential

Contaminants: Chlorinated ethenes and chlorinated ethanes

Project Practice Area: ZVI and Enhanced Bioremediation

Products Supplied: ZVI ironGEL™ and enhanced bio (EDS-ER™ (EVO), EDS-Activator™, Substrate Shuttle™, Nutrimens® nutrient blend and KB-1® Plus chloroethane enhanced dechlorinating culture)

Our Contribution:

- Effectively remediated a complex contaminant mixture in a challenging geologic setting.
- Developed and implemented tool to distinguish the remedial contributions of ZVI and bioremediation.
- Utilized adaptive management to time second injection based on aquifer response, establishing a much higher assimilative capacity.

Highlights:

Contaminants: Chlorinated ethenes and chlorinated ethanes

State: Indiana

Remediation Technologies: ZVI ironGEL™ and enhanced bio (EDS-ER™ (EVO), EDS-Activator™, Substrate Shuttle™, Nutrimens™ nutrient blend and KB-1 Plus chloroethane enhanced dechlorinating culture)

Site description: 4-5 sentences; Historical source; Geologic setting; Very brief remedial history and setting; Intro. to map, brief mention of major features (map in Figure 3)

Remedial Approach:

Timeline (see Figure 4): Need to file for closure in 1- 3 years

Project field events consisted of:

- Two Injection events
- A baseline sampling event that included regular VOC concentration analyses, CSIA, and Gene Assays
- Six regular VOC concentration analyses
- Four regular VOC concentration analyses combined with CSIA and Gene Assays

Technology: Combine ISCR (via ZVI in ironGEL™) with enhanced bioremediation; Provided rapid contaminant destruction of contaminants already in groundwater; Established robust bioremediation to destroy sorbed contaminants

Reference to map in Figure 3

Investigative Technology:

CSIA

- Provided evidence of compound degradation during the project
- Demonstrated that “rebound” was desorbing contaminants

Gene Assays showed when bioremediation started to thrive.

Detailed concentration analyses at the end of the project showed remaining exceedances to be the final portion of a predicted progression to complete remediation.

Conserved resources by studying CSIA and gene assays:

- At four strategically located wells
- Five times throughout the course of the 2.5-year project
- Combined with regular quarterly sampling

Collected and analyzed regular quarterly concentration measurements in addition.

Challenges:

Baseline sampling showed slow degradation with no evidence of VC formation and 11-DCE concentrations much greater than 11-DCA concentrations, both indicators of very slow reductive dechlorination. The remediation timeline was 1-5 years, but the client wanted to see some progress rapidly. While a bioremediation solution was possible at this site, between the lag and the typical rates achieved by bioremediation, bioremediation alone did not seem an appropriate remedy.

The low hydraulic permeability in this aquifer produces low groundwater seepage velocities, despite the relatively steep hydraulic gradient. This was confirmed by a tracer test that failed to produce quantitative results in the allotted time. Additionally, the plume follows the hydraulic gradient and makes an almost 90-degree turn from its source to its distal end, further suggesting hydrogeologic complexity and heterogeneity. The timeline suggested a remedy such as ISCR, but the complex hydrogeology and low permeability suggested that the stored contaminant mass in the aquifer would produce an apparent “rebound” as the contaminant mass desorbed.

It was decided that a combination of ISCR and enhanced bioremediation could meet the client’s goals and produce an effective and lasting remedy. However, justifying both the roles of the ISCR reagents and the bioremediation reagents posed a problem, as did the intricacies of trying to pursue bioremediation of both chloroethenes and chloroethanes. Additionally, there was a strong desire for immediate confirmation of the remedy’s effectiveness. All of these concerns were addressed by the addition of CSIA and Gene Assays to the analytical plan.

Approach:

Using the combined ISCR-biodegradation approach, ZVI (ironGEL™) was co-injected with an electron donor substrate mixture (EDS-ER™, EDS™ Activator, and Substrate Shuttle™) along with a bioaugmentation culture rich in *Dehalococcoides McCartyi* (Dhc, capable of fully degrading the PCE) and *Dehalobacter* (Dhb, capable of fully degrading the 1,1,1-TCA) bacteria (KB-1® PLUS). Since the goals are reduction and reductive dechlorination, a KB-1 Primer was also injected to eliminate any oxygen present.

In addition to regular monitoring of volatile organic compounds (VOCs) and geochemistry, compound-specific isotope analysis (CSIA) and gene assays were used to measure and document the impact of the injections and the progress of the remediation.

In the fourth quarterly monitoring after the first injection, there were signs of undegraded chemicals desorbing into the groundwater. This was fairly mild and was expected, and it triggered a second injection. This was the last planned injection.

Results:

Combined ZVI treatment and enhanced bioremediation provided initial chemical reduction of chlorinated solvents and established biological treatment capacity to address contaminants subsequently released through desorption from the aquifer matrix. CSIA and microbial gene assays provided evidence of contaminant degradation, documented the transition from chemical reduction to biological treatment, and helped guide the timing of the second injection.

There have been five quarterly monitoring events since the second and final injection. Twelve treated wells are regularly monitored, and currently, there are only exceedances in four of those wells. Those exceedances are detailed in Table 2, and the comments present multiple reasons to expect those exceedances to be transient.

Benefits of Approach:

- Combining ZVI and enhanced bioremediation produced a solution that both:
 - ✓ Produced immediate degradation
 - ✓ Prepared the aquifer to rapidly degrade desorbing contaminant in this complex aquifer matrix
- Using CSIA and Gene Assays allowed verification that each remedial step was working as planned.
- Combined technologies to get both immediate and longer-term results (see Figure 1)
- Used CSIA and gene assays to monitor remedial progress during project (see Table 1)
- Enabled the aquifer to assimilate contaminant “rebound” from post-ZVI desorption (see Figure 2)

Figures:

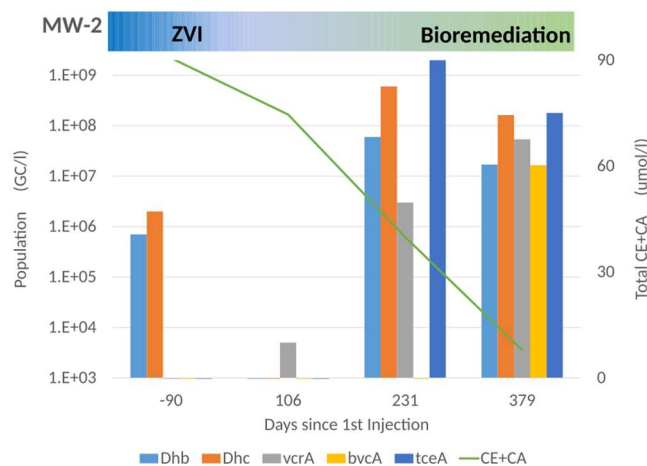


Figure 1. Graph combining Gene Assay results with total concentration results, showing the period when the remedial progress was dominated by ZVI and the progression toward the period when it was dominated by bioremediation.

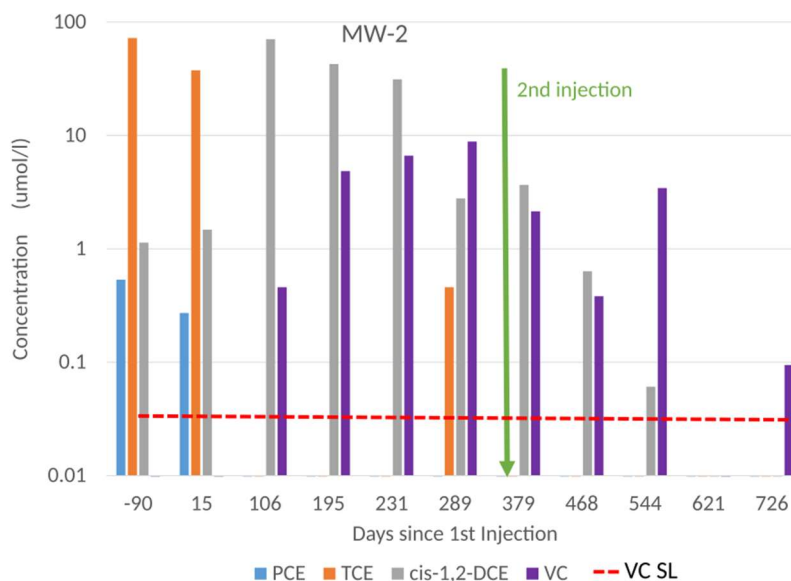


Figure 2. Concentration profiles of chloroethenes, showing TCE “rebound” 289 days after the first injection. That TCE was rapidly degraded, and another desorption must have occurred between day 468 and 544, but the aquifer was able to rapidly degrade that as well.

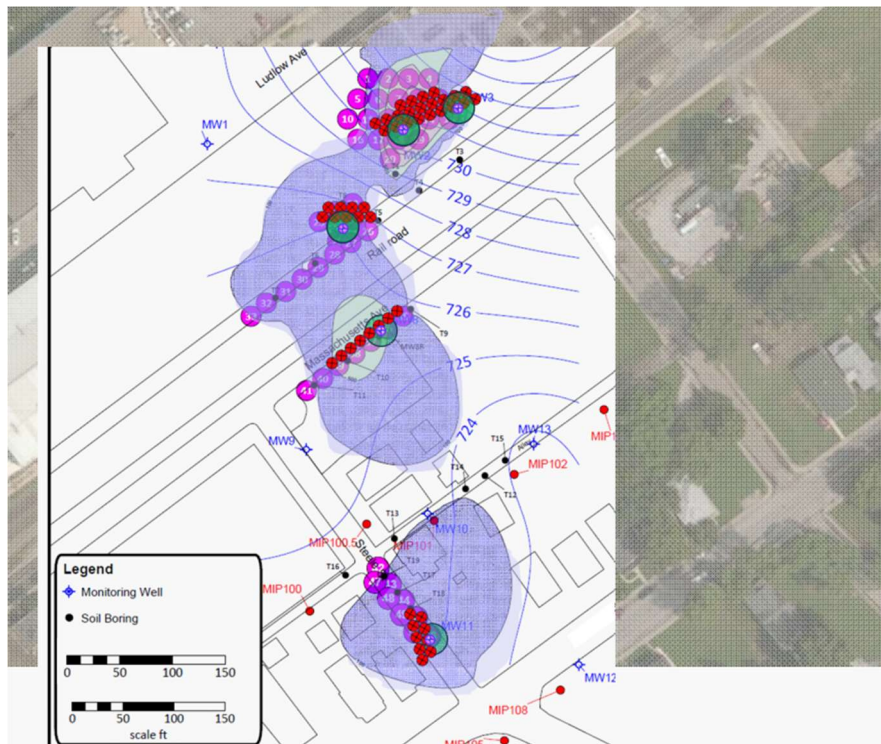


Figure 3. Site map showing groundwater elevation, PCE isocontours, the location of the first injections (red circles), the location of the second injections (purple circles), and the location of primary monitoring points (green circles)

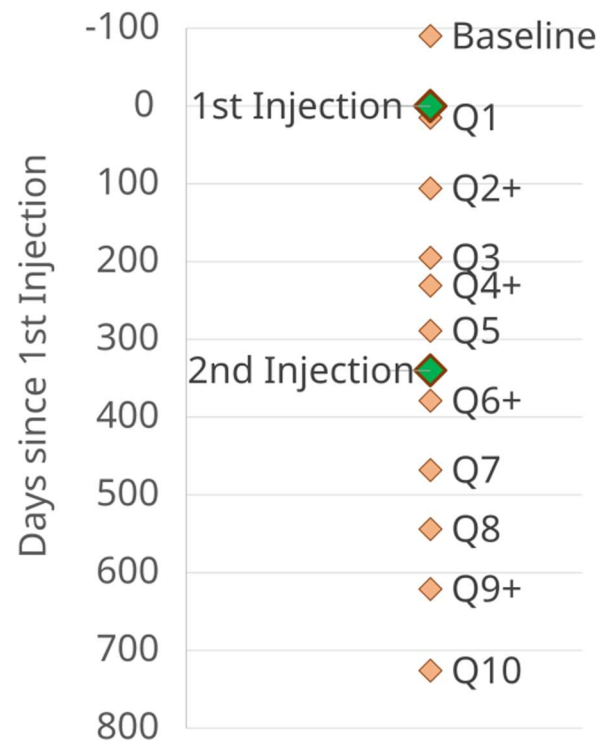


Figure 4. Timeline for field activities

Tables:

Table 1. Table showing CSIA values for cis-dichloroethylene (cis-DCE) and vinyl chloride (VC) along with their interpretation and the values those data were compared to make that interpretation.

	Days (1st)	cis-DCE	cis-DCE	VC	VC
	Days (1st)	$\delta^{13}\text{C}$ (‰)	degrading	$\delta^{13}\text{C}$ (‰)	degrading
MW-2	106	-26.0	?	-	-
MW-2	231	-14.7	✓	-34.8	?
MW-2	379	-25.4	✓	-25.3	✓
MW-3	621	-	-	-18.7	✓
MW-11	231	-25.5	✓	-	-
MW-11	379	+1.1	✓	-22.0	✓

Lightest PCE at site -27.7 ‰, lightest 1,1,1-TCA at site -28.3 ‰

Table 2. Observed exceedances five quarters after the second injection and the reasons those exceedances are expected to be transient

Sample Location	Specialized Monitoring	Exceedance (concentration, ug/l)	Exceedance (concentration, ug/l)	Exceedance (concentration, ug/l)	Comment
MW-2	Yes	11-DCA (98)	VC (5.9)		Declining trend Observed biodeg. product chloroethane (CA) $\delta^{13}\text{C}$ -VC is indicative of biodegradation Functional gene vcrA present at 5 X 107 on 12-28-2023 and 6 X 108 on 8-26-2024
MW-3	Yes	11-DCA (710)	TCE (7.1)	VC (53)	Observed biodegradation product CA Declining trend for 1,1-DCA $\delta^{13}\text{C}$ presents evidence of CA (and 11-DCA) biodegradation Presence of 11-DCA microbial degraders Presence of TCE & VC degraders Declining trend for VC. $\delta^{13}\text{C}$ VC presents evidence of VC destruction High presence of DHC
MW-4	No	None			-
MW-5R	Yes	VC (9.0)			Molar chloroethene mass is steadily decreasing VC concentration decreasing for 4 qtrs. Functional gene vcrA present at 5 X 106 on 12-28-2023 and 2 X 107 on 8-26-2024
MW-7	No	None			-
MW-8R	Yes	None			-
MW-9	No	None			-
MW-10	No	None			-
MW-11	Yes	None			-
MW-12	No	None			-
MW-13	No	None			-
MW-14	No	PCE (15)	TCE (34)		Profile shows expected sequential chlorinated ethene degradation Downgradient of treatment – impact expected