

## **Addition of Divalent Iron to Electron Donor Mixtures for Remediation of Chlorinated Ethenes: A Study of 100 Wells**

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**ABSTRACT:** The objective of this study was to assess the effects of adding soluble dual valent iron (DVI) to emulsified electron donor mixtures to promote the biogeochemical destruction of four common chlorinated ethenes, perchloroethylene (PCE), trichloroethylene (TCE), cis-1,2-dichloroethylene (cis-DCE) and vinyl chloride (VC), as part of in situ bioremediation (ISB) treatments in groundwater. Twenty-four project sites were studied, comprising 100 performance monitoring wells across the US. Wells that received DVI treatment showed increased dechlorination rates, improved contaminant reduction, and limited daughter product formation relative to the wells that did not receive DVI treatment. Following injection of ISB and DVI, the average time required for a well to reach 90% reduction from a peak concentration was improved by 141 days for PCE, 63 days for TCE, 34 days for cis-DCE, and 11 days for VC relative to an approach using ISB alone. The total improvement in time to degrade chlorinated ethenes through VC was improved by 99 days from 394 days to 295 days. Daughter product formation was also significantly less for wells where DVI was added to the electron donor mixture. The cost to add a DVI amendment was less than \$3 per cubic yard as applied.

### **INTRODUCTION**

We have found that the addition of soluble DVI (also referred to as ferrous iron, or Fe[II]) to an electron donor mixture promotes biogeochemical destruction of common chlorinated ethenes such as PCE, TCE, cis-DCE and VC. An electron donor, and in most cases, a bioaugmentation culture, were used to promote biological reduction of these contaminants through reductive dechlorination (i.e., hydrogenolysis), which is a microbial-mediated, sequential substitution of hydrogen atoms for chlorine atoms. This process eventually leads to the formation of non-toxic end products, such as ethene, ethane, and chloride. Under these biotic conditions, DVI will form iron-based minerals in situ, including oxides, sulfides, and hydroxides. The iron-based minerals provide an abiotic pathway, allowing contaminants in this biogeochemical system to be degraded either biotically or abiotically. The abiotic, beta-elimination pathway allows parent chlorinated compounds (such as PCE and TCE) to be degraded through chloroacetylene and acetylene intermediates, which are rapidly degraded to ethene and ethane. Degradation via this beta-elimination pathway is beneficial because it reduces the formation of daughter species (e.g. cis-DCE and VC). Cis-DCE and VC are a common concern when utilizing an ISB approach due to their persistence and toxicity. For the purposes of this study, we refer to cis-DCE and VC as daughter species and PCE and TCE as parent species.

The study focuses on answering the following questions quantitatively:

- 1) Does the addition of DVI to an electron donor mixture allow the more rapid degradation of chlorinated ethenes?
- 2) Does the addition of DVI to an electron donor mixture reduce daughter product formation?
- 3) What is the relative cost of DVI?

## OBSERVATION WELL DATA SUMMARY

A total of 100 observation wells were included in the study. The observation wells were from 24 project sites located in the following states: CA, IN, IL, FL, MO, MN, NC, PA, WI. All wells, except one, were located at industrial or dry-cleaning facilities where spills of chlorinated solvents had impacted groundwater. Although in some cases other contaminants were detected in the wells, the study focused on the compounds PCE, TCE, cis-DCE and VC, which were the primary contaminants requiring remediation at these sites.

Starting concentrations in the observation wells spanned five orders of magnitude ranging from tens to hundreds of thousands of micrograms per liter ( $\mu\text{g/L}$ ). The four contaminants of concern had median and average total concentrations of 549  $\mu\text{g/L}$  and 19,229  $\mu\text{g/L}$ , respectively. Average and median concentrations for the data set, with n-values indicating number of occurrences, are shown in Table 1.

**TABLE 1. Median and average starting concentrations for PCE, TCE, cis-DCE and VC.**

Starting Concentration ( $\mu\text{g/L}$ )	PCE (n=49)	TCE (n=83)	cis-DCE (n=80)	VC (n=44)
Median-All Wells	323	103	120	4
Average-All Wells	6,364	7,340	4,610	915

$\mu\text{g/L}$  = micrograms per liter  
n=number of occurrences

The average monitoring period for the observation wells was 605 days with most wells represented by at least one year of data. The disparity between the median and average concentrations is due to several wells containing high concentrations of contaminants. For instance, five of the wells had concentrations greater than 100,000  $\mu\text{g/L}$ , and an additional five wells contained concentrations between 50,000 and 100,000  $\mu\text{g/L}$  at baseline.

Of the 100 wells, 69 were screened through predominantly coarse-grained soils (sands and gravels), and 31 were screened through predominantly fine-grained soils (silts, clays, fine-sand/silt/clay mixtures). All wells were within grid arrays of injection points, and direct push injection techniques were used for substrate delivery. Injection points were spaced every 100 to 300 square feet of surface area.

Eighty-nine of the wells were treated with a bioaugmentation culture containing *Dehalococcoides* sp. bacteria. Forty-six of the wells received DVI treatment.

## MATERIALS

The same electron donor was applied to all treatment areas to supply a sustained source of hydrogen. The electron donor was a micellar suspension which exhibits self-distributing properties through micellar diffusion after the initial displacement achieved from pumping. Dosing of total organic carbon (TOC) was determined on a total pore volume basis. Dosing ranged from 1.2 to 2 grams of TOC per liter of pore volume, with median dosing of 1.5 grams of TOC per liter of total pore volume (all approximate).

Eighty-nine of wells received treatment from a bioaugmentation culture which was applied at concentrations ranging from  $5 \times 10^6$  to  $1 \times 10^7$  cell copies per liter into the effective pore volume. Note that the total and effective pore volumes in most cases were estimated using literature values for similar soil types; in some cases, tested values were used.

The DVI substrate was a liquid form of ferrous gluconate, a common food additive. It was pH neutral and soluble, allowing for ease of mixing and transport in the treatment

zone. DVI dosing was on a mass-basis where the mass of DVI was 20% to 40% of the mass of electron donor. This formula supplied a minimum of 20 milligrams per liter of ferrous iron into the pore volume of the total treatment zone (TTZ). The DVI substrate was added directly to the electron donor mixture with minimal effort, and the application volume was essentially unchanged.

**METHODS**

Starting concentration data were organized for the wells as depicted in Figure 1. Performance was assessed at each observation well by measuring the time required for the contaminants to reach peak concentration and the time required for contaminants to show a 90% reduction from the peak concentration. The day that the injection occurred was defined as Day 0. The number of days between the injection date and the monitoring date was recorded. Next, the maximum (or peak) concentration for each constituent was logged. The day that a contaminant reached a 90% reduction relative to its peak concentration was also recorded.

An example is shown in Figure 1. The maximum concentration for PCE was observed at the baseline monitoring event dated 9/13/2011. The injection occurred on 10/15/2011, which is defined as Day 0. Concentrations on the injection date are assumed to be the same as baseline. A 90% reduction in PCE concentration was observed at 58 days (12/12/2011). For cis-DCE in the example below, the 90% reduction from peak was nearly attained at 285 days, and a 99% reduction was attained at 339 days. In this instance, the midpoint number of days between the two events, 312 days, was recorded as the time when a 90% reduction from the peak was attained for cis-DCE.

**FIGURE 1. Example observation well data depicting chlorinated ethene concentrations, days to reach peak concentrations and days to reach 90% reduction from peak concentrations (concentration values shown in micrograms per liter).**

10/15/2011 <--Injection Date = Day 0						
Well	Date	Days	PCE	TCE	DCE	VC
24i	9/13/2011	-32	357	53	1080	231
	<b>10/15/2011</b>	<b>0</b>	<b>357</b>	<b>53</b>	1080	231
	12/12/2011	58	10	10	1640	429
	1/31/2012	108	2	2	744	79
	3/12/2012	149	0.5	1	540	68
	4/19/2012	187	0.5	1	490	58
	6/12/2012	241	0.5	0.25	380	88
	7/26/2012	285	0.5	0.25	210	120
	9/18/2012	339	0.5	0.25	17	16
	10/24/2012	375	0.5	0.25	4.1	3
	12/10/2012	422	0.5	0.6	1	0.8
	1/28/2013	471	0.5	0.5	1	0.5
	3/21/2013	523	0.5	0.5	2	0.125
	5/13/2013	576	0.5	0.25	0.5	0.125
	6/24/2013	618	0.5	0.25	0.5	0.125
	<b>Days - Peak</b>		<b>0</b>	<b>0</b>	<b>58</b>	<b>58</b>
	<b>Days - 90% Red</b>		<b>58</b>	<b>108</b>	<b>312</b>	<b>339</b>

## RESULTS AND DISCUSSION

### Assessing Performance for All Wells

Following the analysis of the 100 observation wells, charts were developed showing both the number of days required to reach the maximum concentration of each contaminant and the number of days required to reach a 90% reduction of each contaminant relative to its maximum concentration. We define the contaminants as degraded once a 90% reduction in the peak concentration of VC is observed. A chart showing the average values for these metrics for all 100 wells is shown in Figure 2. Based on this analysis, we observed that it takes less than 1 year (358 days), on average, to degrade chlorinated ethenes utilizing one or more of: an emulsified electron donor (all 100 wells), dechlorinating bacteria (89 wells), and DVI (46 wells).

**FIGURE 2. Average number of days when maximum concentrations and 90% reductions were attained for PCE, TCE, cis-DCE and VC, all wells (n=100).**

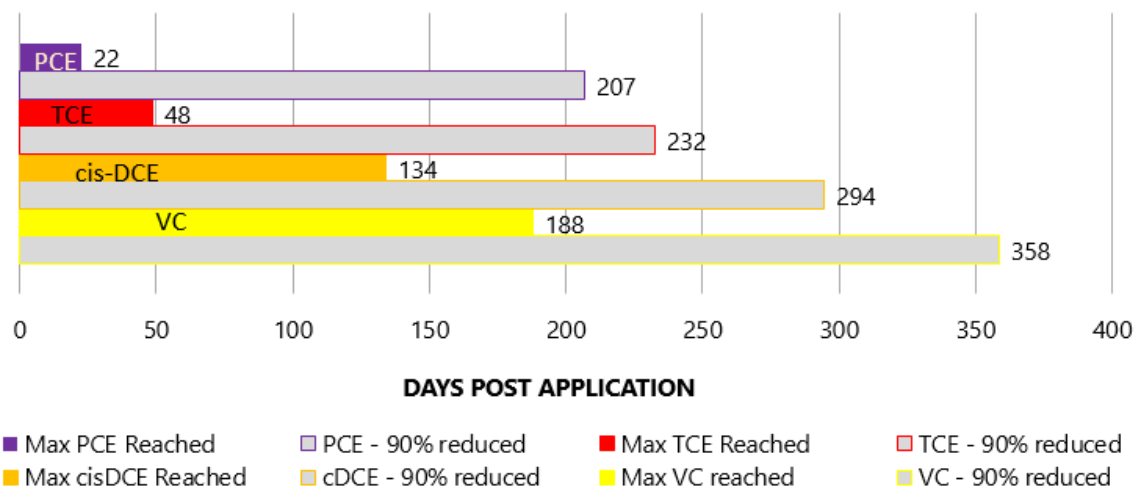


Table 2 summarizes the percentage of wells attaining the 90% reduction-from-peak benchmark for each contaminant as well as the average number of days for the monitoring period. In our experience, a 90% reduction (order of magnitude reduction) from the peak VC concentration signifies the remediation is mostly complete within a TTZ as VC is the final chloroethene species degraded before non-toxic end products are formed.

**TABLE 2. Percentage of wells attaining 90% reduction from maximum concentration for chlorinated ethenes (Average monitoring period of 605 days).**

Category	PCE	TCE	Cis-DCE	VC
Number of wells – compound observed	49	83	94	81
Number of wells – compound reduced 90%	45	74	71	58
Percent Attainment of 90% Reduction Metric	92%	89%	76%	72%
Average Monitoring Period (Days) for non-attaining wells	273(n=4)	521(n=9)	512(n=23)	493(n=23)

Another significant finding from this analysis was that, on average, it takes approximately 6 months to degrade each chlorinated ethene constituent once the peak concentration was reached, as shown in Table 3.

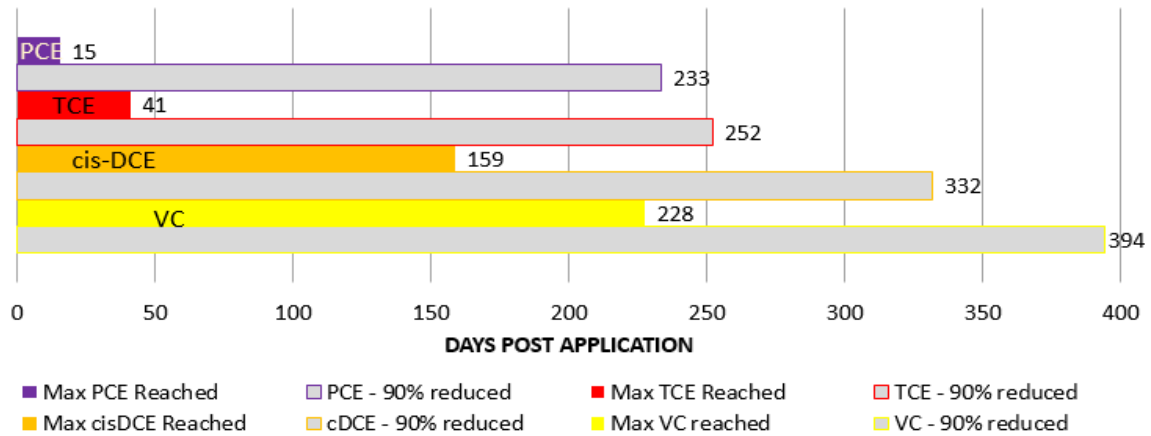
**TABLE 3. Time in days required to reach a 90% reduction in contaminant concentration after the maximum concentration has been reached in (n=100 wells).**

Chlorinated Ethene Compound	Days to Reach 90% Reduction from Maximum Concentration	Days to Reach Maximum Concentration	Difference
PCE	207	22	185 days
TCE	232	48	184 days
Cis-DCE	294	134	160 days
VC	358	188	170 days

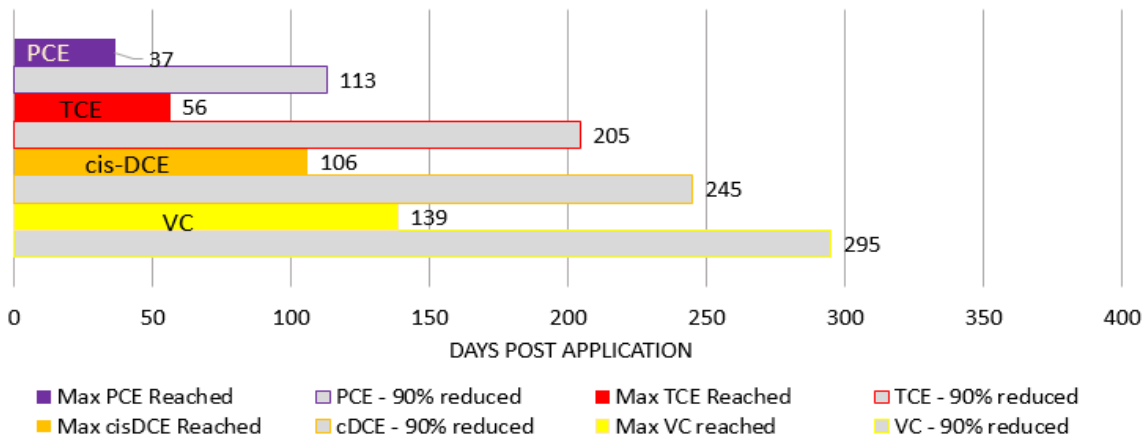
**Comparing Performance for DVI Treated Wells vs. Wells Not Treated With DVI**

The main purpose of this study was to assess the performance of wells where DVI was added to the electron donor mixture relative to wells where DVI was not added to the electron donor mixture. Below are figures showing the time analysis for wells without DVI (Figure 3) and with DVI (Figure 4). As shown, wells treated with both the electron donor and DVI required much less time to reach the 90% reduction metric for the four chlorinated ethene species.

**Figure 3. Average number of days when peak concentrations and 90% reductions from peak were attained for PCE, TCE, cis-DCE and VC, wells *without* DVI (n=54 wells).**



**Figure 4. Average number of days where peak concentrations and 90% reductions from peak were attained for PCE, TCE, cis-DCE and VC, wells *with* DVI addition (n=46 wells).**



The time required to attain 90% contaminant reduction from the maximum concentration was significantly improved when DVI was added to the electron donor mixture. Table 4 and Table 5 summarize the average and median values for this parameter, respectively.

**Table 4. Average number of days to attain 90% reduction after maximum concentration.**

Chlorinated Ethene Compound	No DVI (Days)	DVI Added (Days)	Difference (Days)
PCE	218	77	141
TCE	211	148	63
Cis-DCE	173	139	34
VC	167	156	11

**Table 5. Median number of days to attain 90% reduction after maximum concentration.**

Chlorinated Ethene Compound	No DVI (Days)	DVI Added (Days)	Difference (Days)
PCE	150	85	65
TCE	168	107	61
Cis-DCE	236	112	124
VC	193	158	35

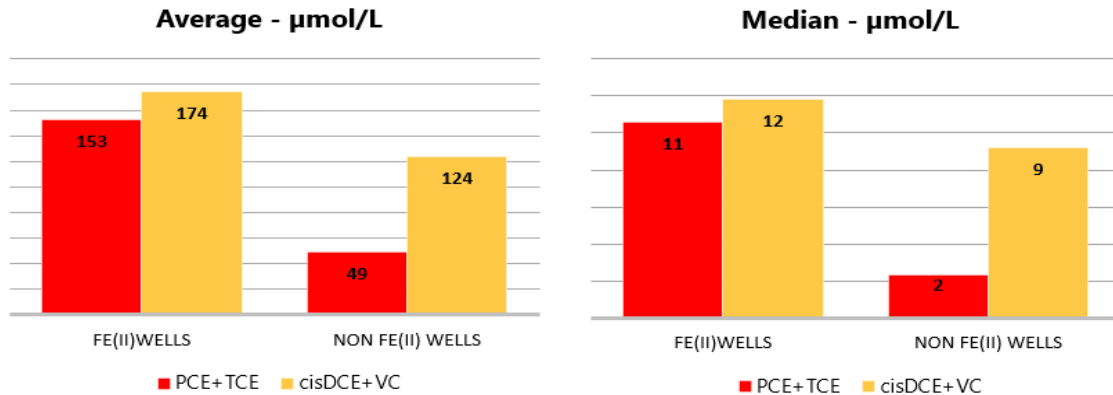
On average, the most significant improvement in time was observed for PCE, whereas for the median data set, cis-DCE was observed to have the biggest improvement in time relative to the other chlorinated ethenes. Additionally, the amount of time to achieve 90% reduction of vinyl chloride from peak concentration was reduced by 99 days on average (from 394 to 295 days); it was reduced by 39 days (312 to 273 days) based on the median concentrations.

Recall that the average starting concentrations are significantly higher than the median starting concentrations (Table 1) and that the reactivity rates between the contaminants and the applied remedial reagents applied might be expected to be enhanced for the average condition, especially in the early stages of remediation where parent products are typically more dominant. However, whether looking at the average or median condition, PCE has been observed to be reduced one order of magnitude in less than 90 days, all constituents show timeline improvements to meet the 90% reduction benchmark, and the overall time to achieve complete reduction of these contaminants is reduced when the DVI substrate was added to the electron donor mixture.

### **Comparing Daughter Product Formation for DVI Treated Wells vs. Wells Not Receiving DVI Treatment**

We also assessed the daughter product (cis-DCE and VC) formation relative to the parent (PCE and TCE) concentrations as shown in Figure 5. The chart depicts the peak expressions, in micromoles per liter, for daughter products relative to the peak parent concentrations (most often the starting concentrations). For both the median and average conditions, the daughter product formation was roughly equivalent to the parent compounds, on a molar basis, where DVI was used. For wells in treatment areas where DVI was not used, the daughter to parent ratios ranged from approximately 2.5:1 (average) to 4.5:1 (median). Here the use of the DVI substrate with the electron donor mixture clearly shows a reduction in daughter product formation relative to starting parent product concentrations.

**FIGURE 5. Maximum concentrations of chlorinated ethenes in micromoles per liter ( $\mu\text{mol/L}$ ).**



### **COST ANALYSIS**

A brief cost analysis was completed for a target treatment zone with dimensions of 10,000 square feet and 10 feet vertical treatment thickness (approximately 3,700 cubic yards). Based on 2018 costing which includes products, estimated tax and freight (15%), and application by an experienced contractor, the cost for injection of the remediation substrates including the electron donor, bioaugmentation and DVI substrates was \$25 per cubic yard. Subtracting the DVI, the resulting applied cost is \$22/cy. This results in a cost difference of \$3 per cubic yard where the high end DVI dose (40% of the electron donor mass) is utilized.

### **CONCLUSIONS**

In our assessment of the effects of adding a DVI substrate to electron donors to enhance the rates of reductive dechlorination we return to the questions introduced at the beginning of this study and provide the following answers.

Question 1 - Does the addition of DVI to electron donor mixtures allow the more rapid degradation of chlorinated ethenes?

Answer: Yes, a nearly 100-day time improvement was observed to achieve dechlorination through VC (based on 90% reduction of VC from peak concentrations, on average).

Question 2 - Are daughter product concentrations reduced?

Answer: Yes, daughter product concentrations were reduced significantly relative to parent starting concentrations. Daughter to parent ratios of 2.5:1 to 4.5:1 were reduced to approximately 1:1.

Question 3 - What is the relative cost difference?

Answer: A net difference of \$3 per cubic yard or less can be expected (product + application) in most cases.

Based on observing the differences between the average and median values, it appears that DVI addition may have more pronounced effects at improving remediation timeframes at higher concentrations. Although the data was not presented to support this conclusion, it has been observed that the relative concentration of sulfate in the treated wells may impact results. This study would be further enhanced by assessing the relative concentrations of sulfate at baseline and during the monitoring period for the wells. This analysis of sulfate effects is planned for completion in 2018.