

Implementing and Interpreting the Full Scale Zero Valent Iron and Anaerobic Reductive Dechlorination of Trichloroethene

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ABSTRACT: Enhanced reductive dechlorination and micro-scale zero valent iron injections were implemented to treat chlorinated volatile organic compounds at a former manufacturing facility in eastern Pennsylvania. These remedial approaches, commonly implemented as stand alone technologies, were combined to achieve synergistic reductions of trichloroethene and its reaction products. The assessment of remedial efficacy frequently becomes problematic with the mixed biotic and abiotic processes. The processes of valuing and validating field and laboratory data across a heterogeneous site such that an understanding of the efficacy of the implemented mixed technologies may occur presents interpretative challenges. The quarterly analytical evaluation of the targeted chloroethenes for the year after the injection event presents varied removal rates and trending, with inconsistent reductions in targeted compounds. The variance between the wells' data and their responses offer an insight into the influences on a remedial program. The interpretation of the appearance and disappearance of the parent and reaction compounds as they relate to field parameters and geochemical analysis, allows for a more complete understanding of the remedial processes across the site. By correlating all the available data on a well-by-well basis, a better and more thorough appreciation of the dynamic interactions between these synergistic technologies can be understood.

INTRODUCTION: A former manufacturing facility in Eastern Pennsylvania was identified as having historic releases of trichloroethene (TCE) that have impacted soil and groundwater at the site. Innovative Environmental Technologies, Inc (IET) has implemented two injection events at the site. The first series of injections occurred in 2005 as a limited scope injection program. The second, a more complete and comprehensive program, occurred in August 2007. Prior to the two IET injection events, the site's environmental consultant performed a pilot event consisting of approximately six injection points in which HRC was applied. Based on the geochemistry and the response to the HRC pilot, IET recommended a synergistic reductive program consistent with US Patent Number 7,129,388. The technology was applied via patented injection equipment (US Patent Number 7,044,152). The dosing of materials was based on both pore volume and targeted compound concentration. Zero valent iron (ZVI) and organic hydrogen donor masses were based on chlorinated volatile organic concentrations (CVOC) in the soils and groundwater whereas the vitamins, nutrients and yeast extract masses were based on impacted pore volume.

METHODS AND MATERIALS: The applied technology for the site integrated two compatible and synergistic approaches. One approach utilized ZVI and the second relied on biological transformations of the targeted compounds via reductive dechlorination. These technologies were chosen based on a review of the site's pre-injection conditions, including geochemical and biological parameters. The naturally reducing conditions and the production of daughter products (1,2-dichloroethene and vinyl chloride) indicated that

the best-suited applied technology would need to occur under anoxic conditions. The mechanisms employed by IET in the injection process utilized compressed gas followed by the remedial liquid introduction. A summary of the IET injections is presented below in Table 1.

TABLE 1: Summary of Remedial Materials used during the Injection Events

2005 Injections										
	H2O - gallons	HRC - Lbs	HRC-X -Lbs	B12-grams	B2-grams	Iron-lbs	Nutrient - Lbs	Propionate - Lbs	Yeast- Lbs	Sulfite-Lbs
Injections	4,840.00	660.00	660.00	1,760.00	16,500.00	748.00	110.00	165.00	220.00	220.00
Infiltration	3,600.00			500.00	5,000.00	100.00	200.00	400.00	200.00	200.00
2005 Total	8,440.00	660.00	660.00	2,260.00	21,500.00	848.00	310.00	565.00	420.00	420.00
2007 Injections										
A	1,350.00	405.00	405.00	270.90	3,009.60	990.00	180.00	270.00	180.00	58.00
B	3,225.00	1,290.00	1,290.00	776.58	8,630.10	2,365.00	860.00	1,290.00	860.00	258.00
C	900.00	240.00	240.00	144.48	1,605.60	660.00	240.00	360.00	240.00	72.00
Infiltration Gallery										
	1,800.00	300.00				100.00	100.00	500.00	100.00	120.00
2007 Total	5,475.00	1,935.00	1,935.00	1,191.96	13,245.30	4,015.00	1,280.00	1,920.00	1,280.00	388.00
Total - 2005 & 2007	13,915.00	2,595.00	2,595.00	3,451.96	34,745.30	4,863.00	1,590.00	2,485.00	1,700.00	808.00

Nearly 2,600 lbs (1179.34kg) of HRC-X has been applied since 2005 at the site and of this amount, nearly 2,000 lbs (907.18kg) were applied in 2007. When not influenced by dissolved oxygen, HRC-X has an expected longevity of two to three years. In order to minimize dissolved oxygen affect, an oxygen scavenger, sodium sulfite, was added. A map of the monitoring wells is shown below in Figure 1 and a map of the injection program is seen in Figure 2.

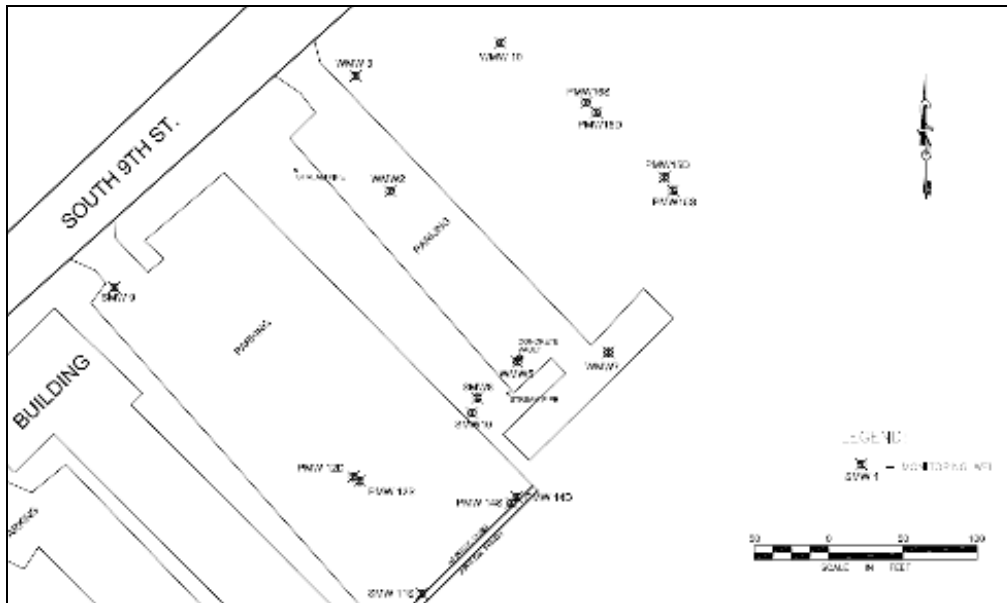


FIGURE 1: Location of the Monitoring Wells on the Site

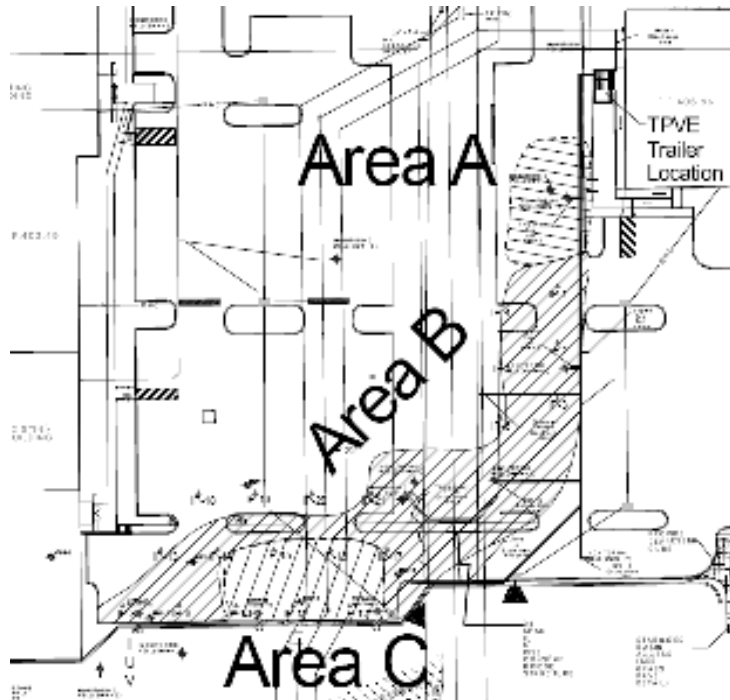


FIGURE 2: Location of the Remedial Activities on the Site

RESULTS AND DISCUSSION: The applied materials have demonstrated effective and long-term viability in the areas of the site where reductive conditions have been maintained due to the asphalt cover at and up-gradient from the wells. Monitoring wells WMW-2S, SMW-11s and PMW-14S represent these areas. These three wells have seen dramatic reductions in CVOC concentration.

WMW-2S. Before the injection events, the concentrations of CVOCs in July 2007 at this well were 2,400 µg/L of TCE, 120 µg/L cis-1,2-DCE, and 3.2 µg/L vinyl chloride. During the May 2008 sampling event, these concentrations were greatly reduced for TCE and cis-1,2-DCE to 1.3 µg/L TCE, below the standard of 5 µg/L, and 8.4 µg/L cis-1,2-DCE, below the standard of 70 µg/L. Vinyl chloride concentrations had increased from 3.2 µg/L to 11.3 µg/L. This increase is due to the increase in the reductive dechlorination rate which produces vinyl chloride as a reaction product. These trends are seen in Figure 3.

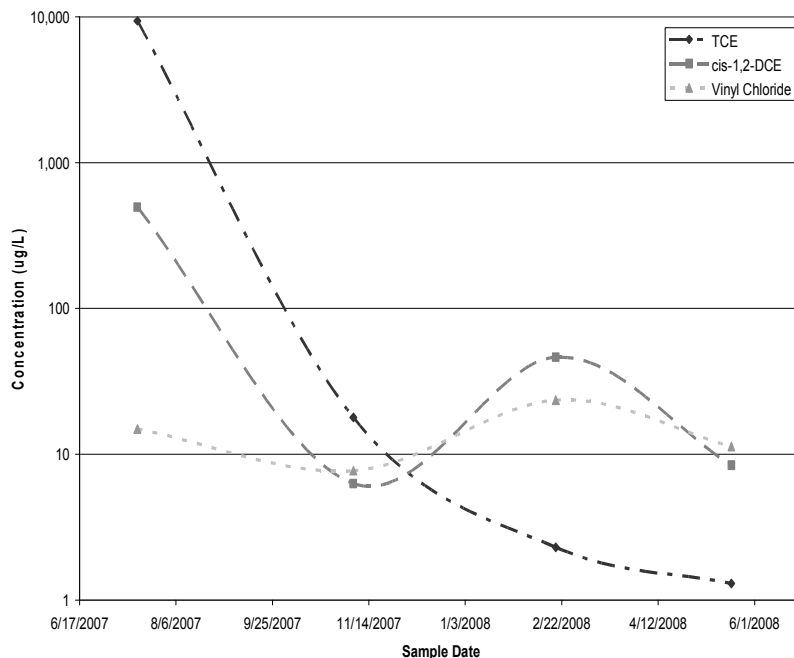


FIGURE 3: WMW-2S CVOC Concentrations

SMW-11S. One year from the injection event at the site, in SMW-11S all contaminants were below the PADEP standards except vinyl chloride, as seen in Figure 4. In July 2007, before the injection event in August 2007, the concentrations of CVOCs in SMW-11S were elevated with the TCE concentration at 1,560 µg/L, PCE concentration at 21.7 µg/L, cis-1,2-DCE concentration at 118 µg/L, and vinyl chloride concentration at 15.7 µg/L. In one year, TCE and PCE concentrations were below the laboratory detection limit and cis-1,2-DCE was below the PADEP standard. Only vinyl chloride was present above the PADEP standard a year after the last injection event.

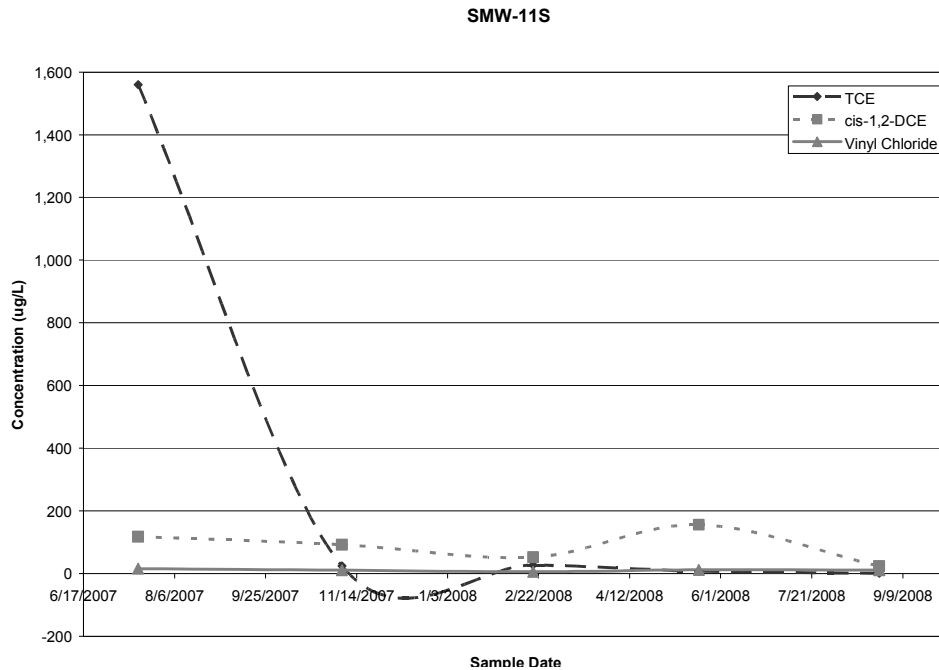


FIGURE 4: SMW-11S CVOC Concentrations

PMW-14S. One year from the injection event at the site in Eastern PA, all contaminants of concern were below the PADEP standards. In July 2007, before the injection event in August 2007, the concentrations of CVOCs in PMW-14S were elevated with the TCE concentration at 182 µg/L, cis-1,2-DCE concentration at 85.2 µg/L, and vinyl chloride concentration at 12.5 µg/L. The concentrations decreased significantly one year after the second injection event. TCE concentrations are now below the laboratory detection limit. Cis-1,2-DCE and vinyl chloride concentrations are below the PADEP standard of 70 µg/L and 2 µg/L, with a concentration of 2.4 µg/L and 1.2 µg/L, respectively, as seen in Figure 5.

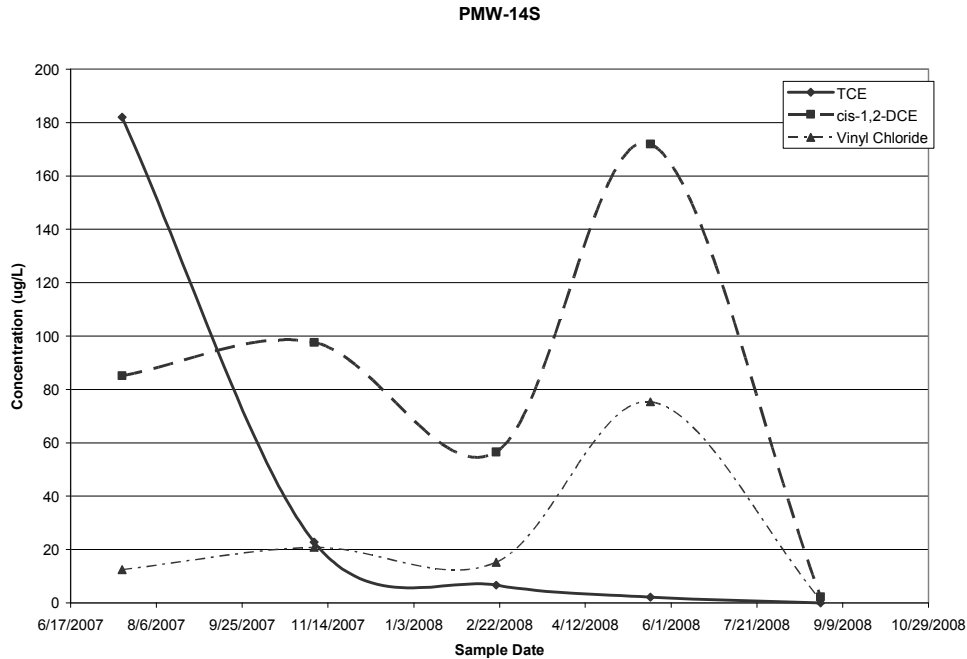


FIGURE 5: PMW-14S CVOC Concentrations

In these wells where reductive conditions have been maintained, remediation has been almost complete with decreases of 99% of total CVOC concentrations. In areas where surface infiltration and the adjacent stream have contributed dissolved oxygen and as a result, turned the environment oxidizing, the reductive process was maintained only as long as the iron and the organic compounds were in sufficient supply. In particular, monitoring wells WMW-5S and SMW-8S represent this process. It may be seen that the sampling event subsequent to the injections still maintained reducing conditions (reflected by the reduction of targeted compounds and the production of daughter products). However, once the process described above consumed the iron and organic hydrogen donors, the desired processes were stalled.

WMW-5S. Due to its proximity to the stream and the influence of dissolved oxygen, there was a decrease in the reductive dechlorination process around WMW-5S, occurring several months after the August 2007 injection event. The time lag during which CVOC removal occurred corresponds to that time in which reducing conditions were maintained. The loss of reducing conditions occurred only after the ZVI surfaces were fully oxidized and organic hydrogen donors were consumed by aerobic heterotrophs. The concentrations of CVOCs directly preceding the injection event in July 2007 were 1,490 µg/L TCE, 62.4 µg/L cis-1,2-DCE, 1.1 µg/L vinyl chloride, and 16.2 µg/L PCE. A year after the injection event, in August 2008, the CVOC concentrations were as follows; 1,290 µg/L TCE, 102 µg/L cis-1,2-DCE, 7.5 µg/L vinyl chloride, and 15.3 µg/L PCE. While these results might appear to show that this monitoring well has not improved, that is not quite the case. The reductive dechlorination at this monitoring well has stalled and is not proceeding at the same rate as it did after the injection event and is most likely experiencing a rebound from the plume surrounding this well. As can be seen from the following data, reductive dechlorination did occur at this monitoring well during the first

seven months after the injection event. Starting in February 2008, monitoring well WMW-5S lost the reducing conditions established by-way of the amendments added and has rebounded due to up-gradient CVOC sources and the oxidative environment it is currently exhibiting.

TABLE 2: CVOC Concentrations at WMW-5S

WMW-5S					
Sampling Date	7/17/2007	11/5/2007	2/19/2008	5/20/2008	8/28/2008
PCE	16.2	ND	6.7	17.6	15.3
TCE	1,490	245	944	1,600	1,290
cis-1,2-DCE	62.4	47	ND	48.7	102
Vinyl chloride	1.1	12.9	6.6	2.5	7.5

SMW-8S. As is seen in 5S, due to its proximity to the stream in the middle of the site, SMW-8S has also begun to lose reductive conditions several months following the August 2007 injection event. The concentrations of CVOCs directly preceding the injection event in July 2007 were 294 µg/L TCE, 10.9 µg/L cis-1,2-DCE, non-detectable vinyl chloride, and 6.6 µg/L PCE. A year after the injection event, in August 2008, the CVOC concentrations were as follows; 197 µg/L TCE, 11.3 µg/L cis-1,2-DCE, 1.4 µg/L vinyl chloride, and 7.5 µg/L PCE. The results at SMW-8S also appear to have stalled or not worked, but there was a decrease in TCE concentrations for over seven months and cis-1,2-DCE and vinyl chloride concentrations increased during these seven months also, which indicates that reductive dechlorination was definitely occurring at this monitoring well. The reductive dechlorination at this monitoring well has stalled and is not proceeding at the same rate as it did after the injection event and is most likely experiencing a rebound from the plume surrounding this well. As can be seen from the following data, reductive dechlorination did occur at this monitoring well during the first seven months after the injection event. Since May 2008, monitoring well SMW-8S has rebounded due to the oxidative environment it is currently exhibiting.

TABLE 3: CVOC Concentrations at SMW-8S

SMW-8S					
Sampling Date	7/17/2007	11/5/2007	2/19/2008	5/20/2008	8/27/2008
PCE	6.6	2	2.8	6	7.5
TCE	294	110	108	257	197
cis-1,2-DCE	10.9	165	35.4	30.3	11.3
Vinyl Chloride	ND 1.0	33.9	7.2	2.5	1.4

PMW-12S. In areas where oxygen is infiltrating the monitored area from up-gradient points not sufficiently dosed with iron and reducing compounds, a slowing of the remedial processes was expected and observed for the May 2008 sampling event. In PMW-12S, reductive dechlorination has continued, however as of the August 2008 sampling event, all CVOC concentrations are below PADEP standards. PMW-12S began with TCE concentrations of 46.4 µg/L in July 2007. The concentration of TCE in PMW-12S a year after the injection event is now 3.1 µg/L, which is below the PADEP standard of 5.0 µg/L. Vinyl chloride concentrations are currently below laboratory detection limits and cis-1,2-DCE concentrations are at 3.0 µg/L, well below the PADEP standard of 70 µg/L.

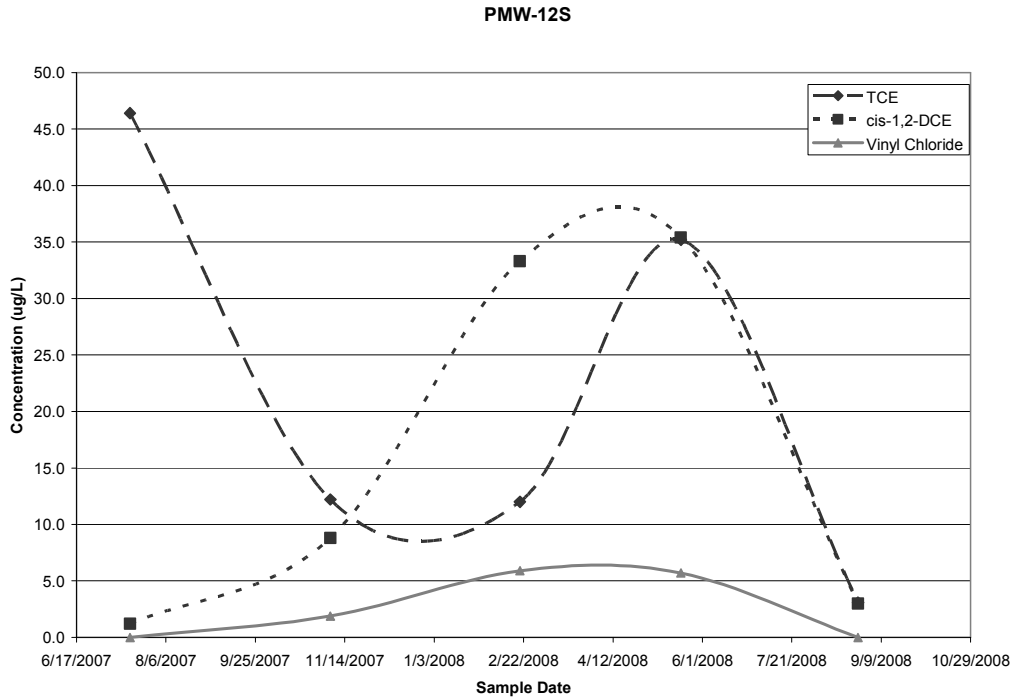


FIGURE 6: PMW-12S CVOC Concentrations

CONCLUSIONS: The efficacy of the applied technology has been shown across the site. In those areas that are heavily affected by surface water infiltration reductive processes have been lost. The decreases seen in these wells over the past six months are most probably due to the remedial effectiveness up gradient from these sampling points.

In the year after the injection event of August 2007, all but two of the monitoring wells in the area of the injections have seen remarkable improvement. The shallow wells affected by the remedial events are at or near clean-up standards set by the PADEP. As noted in the Table 4 below, the percentage of TCE reduction in the last year at the affected monitoring wells has been near complete.

TABLE 4: TCE Reductions in the Year Following the Injection Events

Monitoring Well	% TCE Reduction
WMW-2S	99.9%
SMW-11S	100%
PMW-14S	100%
MWM-5S*	13.4%
SMW-8S*	33.0%
PMW-12S	93.3%

* Wells immediately impacted by surface water via the adjacent stream.