ESTCP FACT SHEET

# LONG-TERM PERFORMANCE MONITORING OF ZERO-VALENT IRON SITES

Environmental Security Technology Certification Program (ESTCP) Project #ER-201589-PR


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## INTRODUCTION

Zero valent iron (ZVI) has been used to treat chlorinated solvents in groundwater since the 1990s. When ZVI is added to an aquifer system, the iron begins to corrode, producing hydrogen and ferrous iron, depleting dissolved oxygen, and facilitating contaminant destruction through β-elimination and reductive dechlorination pathways. The focus of this project was to assess ZVI longevity at sites with mature remedies (>5 years since ZVI treatment) to determine if iron present at these sites was still reactive and was continuing to treat groundwater as intended. The investigative team also sought to understand the mechanisms through which the iron might be treating contaminants (i.e. through β-elimination or reductive dechlorination). The team also aimed to determine if mineral coatings had formed on the remaining iron and native materials which might either passivate the iron or reduce hydraulic conductivity, thereby hindering the efficacy of the treatment. The initial phase of the project consisted of a desk top review of existing data. The subsequent phase included more detailed field assessment at two sites (Allegany Ballistic Laboratory [ABL] Site 5 and St. Louis Ordnance Plant Operable Unit [OU] 1).

## DESK TOP REVIEW

Available data from nine sites where ZVI remedies were implemented between 2005 and 2013 were reviewed as part of the initial phase of this project. Sites reviewed included areas where barrier walls of ZVI were used to intercept a plume (permeable reactive barrier [PRB] sites), sites where ZVI was mixed with native soil or native soil and clay using large diameter augers (soil mixing sites), and sites were ZVI was directly injected into the ground (injection sites). The desk top study results are presented in **Table 1**. General conclusions are as follows:

- The greatest degree of volatile organic compound (VOC) treatment was achieved within ZVI soil mixing zones.
- Treatment was more effective with increasing ZVI dose (ZVI to soil ratio).
- Baseline oxidation reduction potential (ORP) was a factor in treatment effectiveness, with sites already under reducing conditions at the time of treatment performing slightly better than sites under oxidizing conditions.
- Evidence of degradation through the sequential reductive dechlorination pathway was found at all the injected ZVI treatment systems, downgradient of one PRB, and at two of the four soil mixing sites (example shown in **Figure 1**).

**Figure 1 – St. Julien's Creek Annex Site 21 MW15 Well Data with Evidence of Reductive Dechlorination**

*In this well, increases in daughter products were observed followed by subsequent decreases, supporting degradation, in part, through the reductive dechlorination pathway.*

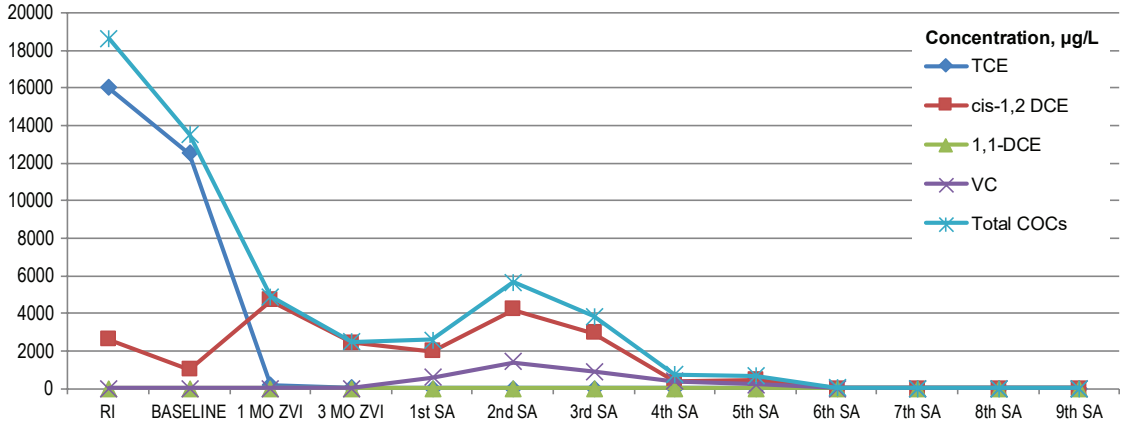




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**Table 1 – Desk Top Study Results**

| Site | Iron dose (ZVI: soil mass ratio percent) | Initial ORP (mV)[a] | Lowest ORP achieved during treatment (mV)[a] | Percent reduction/ increase in concentrations[a] | Generation of daughter products observed | If Yes, with or without subsequent reductions | If treatment effective, rebound based on recent results |
|---|---|---|---|---|---|---|---|
| **PRB Sites** | | | | | | | |
| Allegany Ballistics Lab (ABL) Site 5 | 40[b] | 128 | -212 | -70.7% | Yes (but may be due to migration) | Without | None |
| McGuire Air Force Base OT-16 | 0.5 | 19.92 | -501.4 | -33% | No | NA | Minimal |
| **Injection Sites** | | | | | | | |
| St. Julien's Creek Annex Site 21 | 0.8 | -2.8 to 128.5 | -418.1 | -96.3% | Yes | With | None |
| White Oak Site 13 | 0.2 (onsite)/ 0.5 (offsite) | -1 to 328 | -303 | -58.6% (onsite)/ -85.6% (offsite) | Yes | With | Minimal |
| Savannah Air National Guard Base Site 8 | 0.4 | -68 to -143 | -184.9 | -99.4% | Yes | With | None |
| **Soil Mixing Sites** | | | | | | | |
| Arnold Air Force Base Solid Waste Management Unit (SWMU) 16 | 0.2 | 79-151 | -205 | +397%[c] | Yes | Without | NA |
| St. Louis Ordnance Depot OU1 | 1 | 98.7-232 | -400 | -99.8% | Yes | With (source area) | None |
| Marine Corps Base Camp Lejeune Site 89 | 2 | -71 to -51 | -711 | -99.99% | No | NA | Minimal |
| Indian Head Site 17 | 1 | -54 to 123 | -308 | -99.98% | No | NA | None |

**Notes:**

a Treatment Area, or downgradient for the ABL PRB

b Based iron: sand ratio in PRB

c Maximum TCE concentration in the treatment area at SWMU 16 were reduced from 5,616 µg/L (April 2003) to 480 µg/L. However, concentrations of daughter products increased considerably, with the cis-1,2-DCE concentration rising from 64.02 µg/L to 15,500 µg/L and the VC concentration rising from 3.43 µg/L to 6,600 µg/L, resulting in an overall increase in total VOC concentrations. These data are indicative of possible movement of contaminants as well as an incomplete reductive dechlorination pathway rather than the β-elimination pathway.

mV = millivolts

NA = not applicable

ORP = oxidation/reduction potential

## FIELD STUDY METHOD SUMMARY

The PRB at ABL Site 5 and the soil mixing treatment at St. Louis Ordnance Plant OU1 were selected for further study in the field phase of the project. Field sample collection consisted of groundwater and iron samples from the ABL PRB site and the St. Louis Ordnance Plant soil mixing site. Profile samples of ZVI across the PRB at ABL were collected using diagonal direct push technology (DPT) drilling technology. ZVI samples from within and outside of the mixing zone at St. Louis Ordnance Plant OU1 were collected using vertically drilled DPT cores. Groundwater samples were collected from upgradient, cross-gradient, and downgradient of the ABL PRB for analysis of VOCs, total and dissolved metals, silica, strontium, sulfide, nitrate, nitrite, ammonia, total organic carbon (TOC), hardness, alkalinity, methane, ethane, ethene, acetylene, and the following anions: sulfide, chloride, phosphate, and fluoride. Additionally, one round of microbial samples was collected by pumping water through laboratory-provided biofilters and sending the filters for population analysis using next generation sequencing (NGS) and assessment of dechlorinating microbes using QuantArray-Chlor analysis.

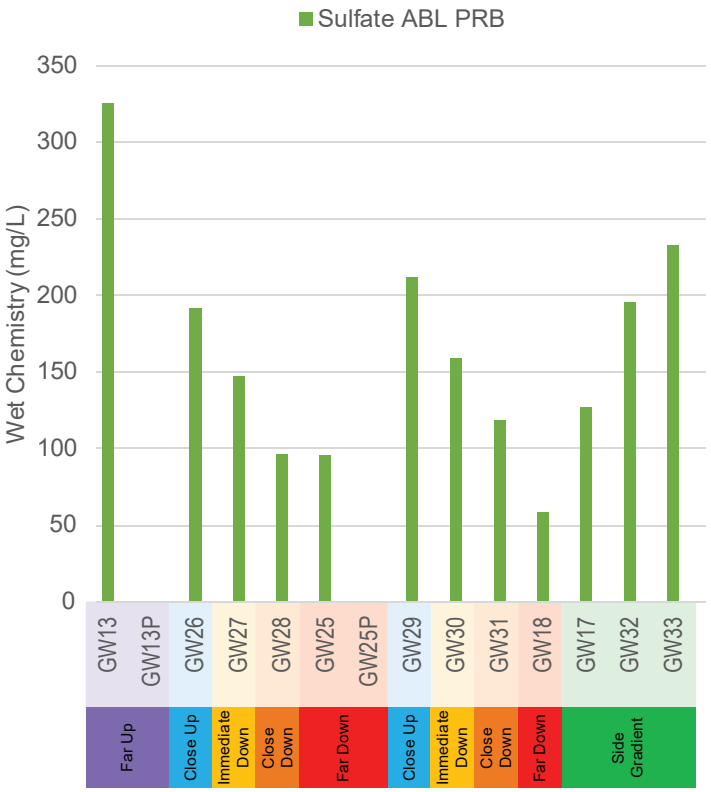
# GEOCHEMICAL RESULTS SUMMARY

## ABL Site 5 (PRB) Geochemical Findings

- Continued impacts from ZVI treatment were observed twelve years post-treatment.
- Increases in pH and decreases in ORP and DO were observed downgradient of the PRB, relative to upgradient
- TOC, alkalinity, hardness, and sulfate decreased across the two monitoring transects installed from upgradient to downgradient (see sulfate results graphed in **Figure 2**).
- Methane, ethane, and ethene concentrations increased across the transects.
- A "clean front" of non-detected VOC results was observed in one of the two transects sampled.
- Decreases of calcium, magnesium, and strontium were observed downgradient.
- Iron and silicon concentrations increased from upgradient to downgradient across the transects.

**Figure 2 – Sulfate Concentrations, ABL Site 5**

*Concentrations of sulfate decreased across both transects of the PRB at ABL.*

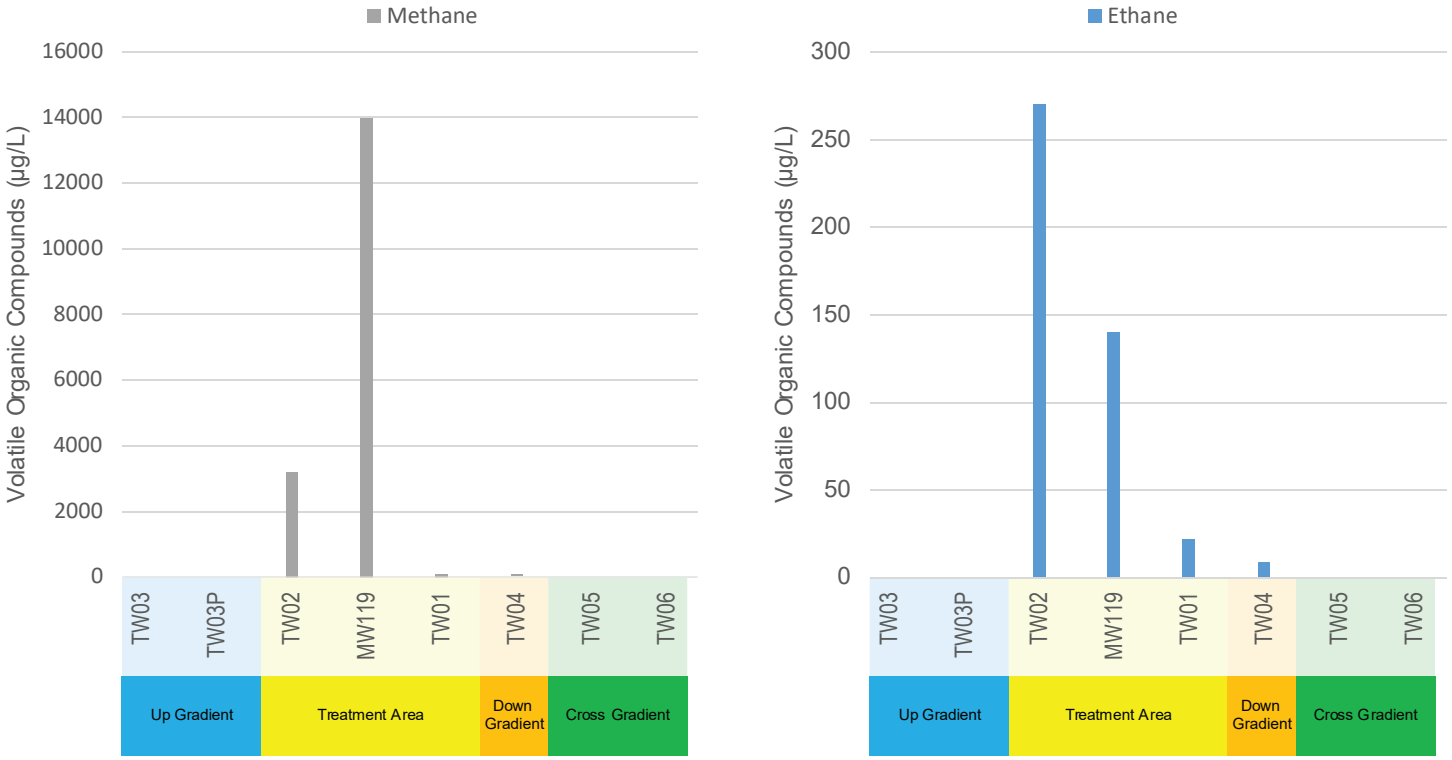



## St. Louis Ordnance Plant OU1 (ZVI Mixing Area) Geochemical Findings

- Continued impacts from ZVI were evident five years post-treatment.
- DO and ORP were considerably lower within the treatment area.
- pH was considerably higher within the treatment area.
- ORP levels were still within the optimal range for ZVI treatment (-<400 mV) in one treatment area sample.
- Sulfate concentrations were lower within the treatment area while chloride, methane, ethane, and ethene concentrations were higher (see methane and ethane results graphed in **Figure 3**).
- Concentrations of calcium, magnesium, manganese, barium, and strontium were highest in the upgradient portion of the mixing area.

**Figure 3 – Methane and Ethane Concentrations, St. Louis Ordnance Plant OU1**

*Concentrations of methane and ethane were higher within the ZVI mixing area relative to outside of the mixing area. High methane concentrations are generally indicative of oxygen-poor conditions expected in reactive ZVI treatment areas. High ethane may be the result of degradation of contaminants.*



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# MINERALOGICAL ASSESSMENT RESULTS

Various methods were used to assess the remaining mineral content of the iron particles collected from each of the field test sites. These analyses were completed to determine if the remaining iron was still ZVI, or whether it had weathered to less reactive mineral species. The investigative team also aimed to determine if mineral coatings had formed on the remaining iron particles that might prevent reactivity with contaminants at each site. This section presents the results of this testing.

## ABL Site 5 (PRB) Mineralogical Findings

- Electron micrographs and x-ray mapping showed a mottled appearance of remaining iron, indicative of corrosion (**Figure 4**).
- Coatings of calcium carbonate and iron oxides were observed on the iron particles, with the thickness of the coating decreasing inward from the upgradient ZVI/aquifer interface.
- Native quartz grains were cemented together by iron oxide and calcium carbonate, but none of the coatings of the quartz particles were significant enough to greatly influence hydraulic characteristics of the wall (**Figure 4**).
- X-ray Diffraction (XRD) indicated the presence of iron oxides (magnetite and hematite).
- Acid volatile sulfide (AVS) data were also consistent with presence of iron sulfide, which is thought to provide secondary reactivity to the PRB.
- Overall, mineralogical results indicate weathered ZVI with some passivation due to precipitation of coatings (e.g., calcium carbonate) and transformation of ZVI into less reactive minerals, although some secondary reactivity is likely.

## St. Louis Ordnance Plant OU1 (ZVI Mixing Area) Mineralogical Findings

- XRD, energy dispersive line scans, and x-ray absorption near edge structure (XANES) of a limited number of samples indicated no identifiable ZVI remaining in the few cores collected from the mixing area.
- Iron identified was primarily magnetite and goethite (**Figure 5**).
- Scanning electron microscopy (SEM) micrographs did not indicate the presence of precipitates on the transformed (to magnetite and goethite) iron particles.
- Particle size indicated remaining particles showed considerable reduction in size relative to the original ZVI product.
- Results indicate significant weathering of the ZVI.

# REACTIVITY ASSESSMENT RESULTS

OHSU assessed reactivity for the ABL Site 5 cores only and the findings are summarized below.

## St. Louis Ordnance Plant OU1 (ZVI Mixing Area) Reactivity Findings

- Magnetic and gravimetric analysis as well as acidification and hydrogen generation results for St. Louis Ordnance Plant OU1 indicated a small amount of remaining ZVI (less than 0.04 percent) in the three cores from two sample locations analyzed from the mixing area at the site (**Figure 6**).
- Total magnetic material observed in these samples was between 0.2 and 0.7 percent, consistent with the range of ZVI percentages measured in confirmation samples during the 2012 mixing.

**Figure 4 – SEM Image of a typical iron (Fe) grain from the ABL PRB**

*Left – This SEM image shows a thin oxide layer on the iron grain.*
*Right – This SEM image shows silicon dioxide ($SiO_2$) grains cemented together by an Fe-rich coating from the ZVI interface at ABL Site 5.*

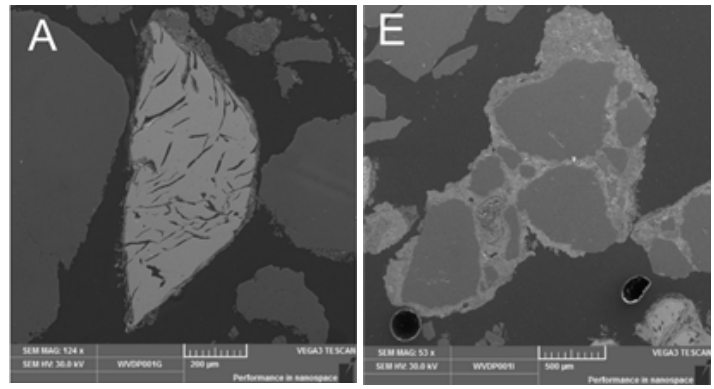



**Figure 5 – XANES Analysis of Five St. Louis Aquifer Samples**

*Normalized (edge jump = 1) X-ray absorption near edge structure (XANES) analysis of five aquifer samples and reference patterns for iron metal, magnetite, and goethite. The aquifer solids show no spectral component of ZVI. Linear combination fitting analysis indicates a mixture of magnetite and goethite-type spectra.*

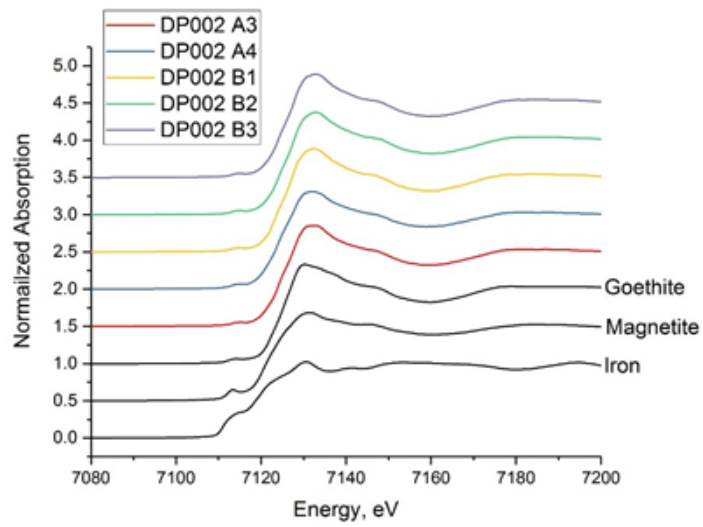
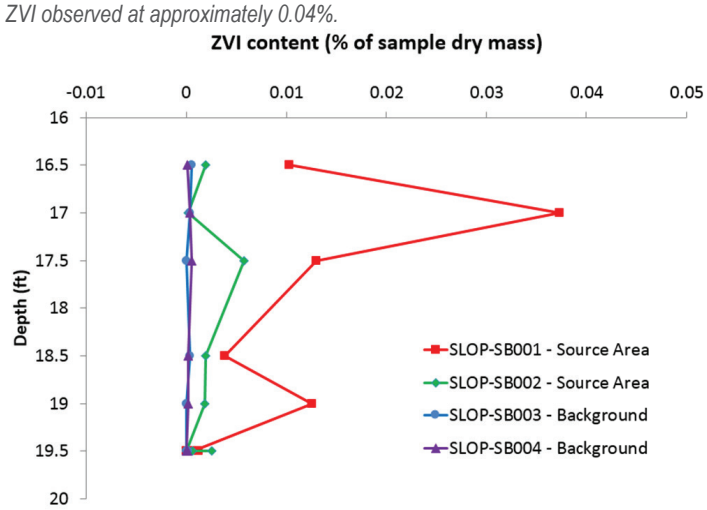



**Figure 6 – ZVI Content of St. Louis Samples (Percent of Sample Dry Mass) Based on Acidification and Hydrogen Generation Testing**

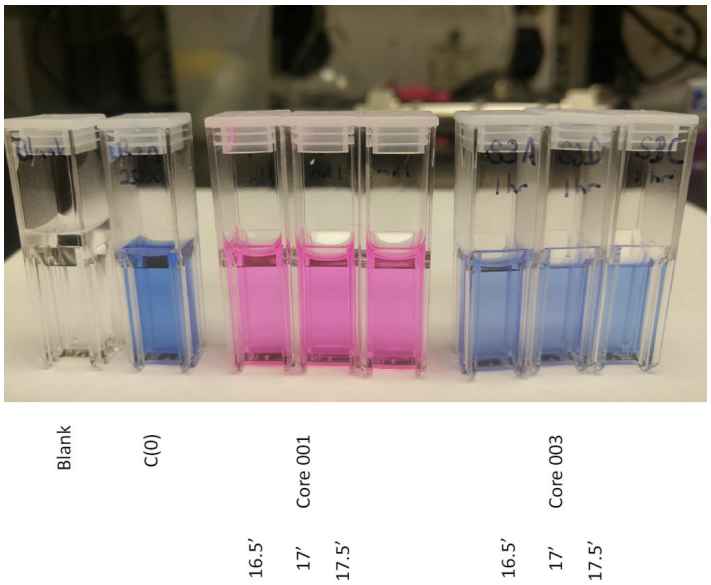
*St. Louis mixing area samples (SLOP-SB001 and SLOP-SB002) showed higher ZVI content than up- and downgradient samples, with maximum percentage of ZVI observed at approximately 0.04%.*



- Remaining iron observed in the mixing area cores was believed to primarily be in the form of magnetite.
- Resazurin testing indicated higher reduction potential for the treated source area core material relative to background, supporting that the magnetite is facilitating secondary reactivity in the treatment area (**Figure 7**).
- Because of the limited number of analyzed samples, it is unknown if more ZVI might be present in other areas of the mixing zone not sampled.

**Figure 7 – Resazurin Dye Testing in Mixing Area and Cross-gradient Cores, St. Louis Ordnance Plant**

*Photograph of 1-hour Mixing Area (DP001) Reaction with Resazurin (in Pink) in Comparison with Upgradient Reference Sample (DP003) Conversion to resorufin is evident in the mixing area sample, but not in the upgradient reference sample, indicating ongoing reduction capacity of the iron.*




# MICROBIAL ASSESSMENT RESULTS

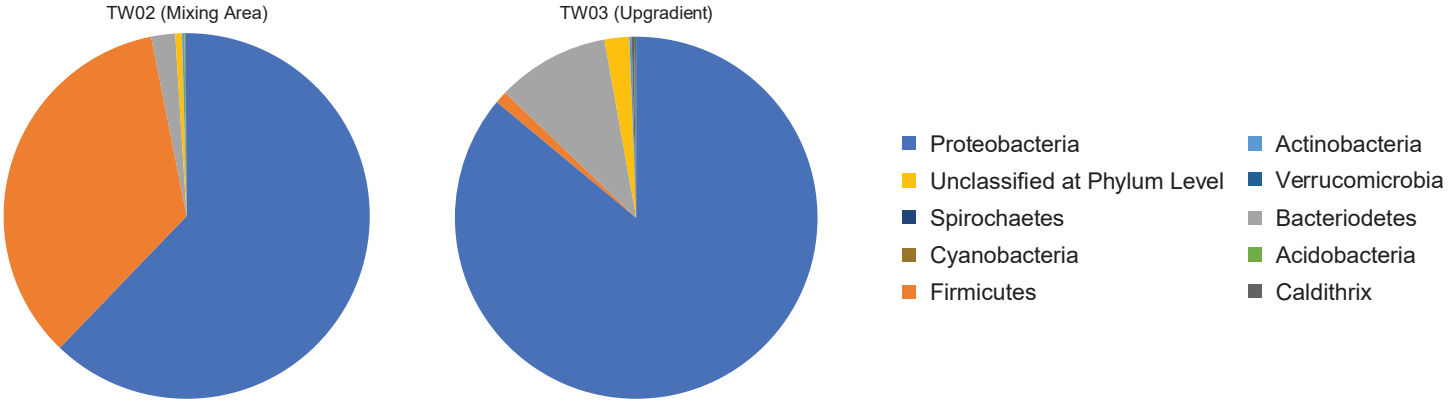
## ABL (PRB) Microbial Results

- Anaerobic dechlorinator populations were not improved downgradient of the wall.
- Genes involved in aerobic direct metabolism and cometabolism of VC were either not identified or were present in spatial patterns that did not support a significant impact of the PRB on microbes carrying these genes.
- Sulfate reducers and methanogens were detected consistently across the site, with no notable changes due to the presence of the PRB.
- NGS data indicate the presence of sulfur-oxidizing bacteria (*Sulfurimonas*) just downgradient of the wall, but not in other portions of the site, which may be a result of the release of reduced sulfur species in groundwater from the PRB.

## St. Louis (ZVI Mixing Area) Microbial Results

- Concentrations of reductive dechlorinators were one to three orders of magnitude higher within the mixing area and downgradient of the mixing area than they were cross-gradient or upgradient, indicating that the reducing conditions created by the ZVI may be facilitating reductive dechlorination.
- Genes involved in complete dechlorination of VC by *Dehalococcoides* were either not detected, or present at very low levels (<1 cell/mL).
- Genes associated with direct metabolism and/or cometabolism of VC were present throughout the site, indicating a complete dechlorination pathway may be present despite the absence of functional genes involved in reductive dechlorination of VC.
- NGS data also indicated significant changes in the microbial population with decreasing cell counts of the phylum *Proteobacteria* and genus *Pseudomonas* from the upgradient location moving downgradient into the treatment area in addition to increases in the phylum *Firmicutes* and the genera *Alkaliphilus*, *Sulfuricurvum*, and *Methylotenera*. *Fimicutes* are sometimes acetylenotrophic and may be an indicator of acetylene production through β-elimination of contaminants (**Figure 8**).

**Figure 8 – Example NGS Phyla Results, Within and Outside of the Mixing Area, St. Louis Ordnance Plant OU1**




# GROUNDWATER HYDROLOGY RESULTS

The two ZVI application sites studied did not indicate any discernible reduction in groundwater flow through the ZVI application area/barrier.

## CONCLUSIONS AND LESSONS LEARNED

Data collected during the desk top evaluation and field studies support the following conclusions:

- Based on mineralogical and reactivity testing at the two field test sites, ZVI shows some signs of corrosion and passivation years following treatment. However, based on geochemistry, continued treatment of contaminants was evident at most of the desk top review sites and both field sites five to twelve years after remedial actions were implemented. This treatment appears to occur through both primary and secondary reactivity.
- Destruction of contaminants through reductive dechlorination is common at ZVI sites and may augment abiotic processes as iron corrodes.
- Increases in *Firmicutes* may be an indicator of acetylene production at ZVI sites due to their acetylenotrophic behavior.
- Cementation of natural and iron particles is typically not significant enough to cause measurable reductions in hydraulic conductivity or divert groundwater flow.