Implementation of Enhanced Attenuation at the DOE Mound Site OU-1 Landfill: Accelerating Progress and Reducing Costs - 16270

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ABSTRACT

A field demonstration of enhanced attenuation (EA) was initiated in 2014 to expedite the remediation of industrial solvents in the groundwater impacted by the former landfill Operable Unit 1 (OU-1) at the US Department of Energy (DOE) Mound, Ohio, Site. EA uses active engineering solutions to alter the target site so that the contaminant plume will passively stabilize and shrink. For OU-1, the EA was implemented by targeted injection of an electron donor (vegetable oil) to create “structured geochemical zones.” Volatile organic compounds (VOCs) in the altered subsurface system encounter alternating anaerobic and aerobic environments along the plume flow path. The effect of these structured geochemical zones is effective and rapid degradation of parent compounds such as trichloroethene (TCE) and tetrachloroethene (PCE), and daughter compounds such as *cis*-1,2-dichloroethene and vinyl chloride. EA at Mound OU-1 provides a transition to natural attenuation and is an alternative to the baseline pump-and-treat (P&T) system.

Industrial solvents (primarily TCE) and other VOCs that originated from the former solid-waste landfill contaminated the groundwater in the Buried Valley Aquifer beneath the Mound site. A groundwater P&T system was initiated in 1996 to control the plume, and a soil vapor extraction system was installed and operated from 1997 to 2003 to remove the bulk of the VOC sources from the vadose zone. Physical removal of the landfill waste and contaminated soil was performed between 2006 and 2010. Approximately 76,100 cubic meters (99,500 cubic yards) of material were removed from the OU-1 landfill area. Operation of the groundwater P&T system continued throughout this period.

The principles and technical basis of the ongoing EA field demonstration were developed by the Interstate Technology and Regulatory Council. The goal of the EA implementation is to provide a bridge between active groundwater treatments and monitored natural attenuation. EA relies on understanding and manipulating the contaminant mass balance. Technologies are applied to sustainably reduce the contaminant loading from the source and/or increase the rate of natural attenuation processes within the plume.

In 2014, a core team that included DOE, the US Environmental Protection Agency (EPA), the Ohio EPA, and technical support organizations evaluated remedial options for OU-1. During the 2014 evaluation, the team projected a cleanup time frame for the baseline P&T system of 26 additional years and a cleanup time frame for the EA remedy of 13 years. On the basis of that evaluation, EPA approved the

implementation of the EA remedy that required the shutdown of the P&T system. The combination of technologies implemented for OU-1 EA included (a) neat vegetable oil in the vadose zone in the former landfill and (b) emulsified vegetable oil within the footprint of the groundwater plume. In the first part of the deployment, neat oil spreads laterally and forms a thin layer on the water table beneath residual soil sources to intercept and reduce future VOC loading and to reduce oxygen inputs to the local groundwater. In the second part of the deployment, emulsified oil forms active bioremediation anaerobic treatment zones within the plume footprint to degrade existing groundwater contaminants (via reductive dechlorination, cometabolism, or both) and stimulates long-term attenuation capacity in the downgradient aerobic plume (via cometabolism).

The results from the first year of the field demonstration indicate that the dissolved TCE and PCE plumes have decreased in size and mass. Statistical tests indicate that the VOC concentrations in the majority of the source-area wells are decreasing. The VOC concentrations throughout the plume are projected to be below the target maximum contaminant level of 2 to 5 µg/L within 5 to 10 years—sooner than the design projection of 13 years. The biogeochemistry and microbial community within the structured geochemical zones are consistent with the design and appear to be stable. At Mound OU-1, EA has accelerated progress toward the remedial action objectives and reduced costs. Ongoing monitoring will determine whether the EA remedy has transitioned the site into monitored natural attenuation status and whether the EA will continue to be effective, timely, and sustainable.

INTRODUCTION

At the US Department of Energy (DOE), Office of Legacy Management, Mound, Ohio, Site, chlorinated organic contaminants (cVOCs) originating from the former solid-waste landfill have impacted groundwater in Operable Unit 1 (OU-1). The baseline groundwater remedy was groundwater pump and treat (P&T). Since the source materials have been removed from the landfill, the Mound core team, which consists of DOE, US Environmental Protection Agency (US EPA), Ohio EPA, and other stakeholders, is assessing the feasibility of switching from the active P&T remedy to a passive attenuation-based remedy. Toward this end, an enhanced attenuation (EA) strategy based on the creation of structured geochemical zones was developed. This EA strategy addresses the residual areas of elevated cVOCs in soil and groundwater while minimizing the rebound of groundwater concentrations above regulatory targets (e.g., maximum contaminant levels [MCLs]) and avoiding plume expansion while the P&T system is turned off. The EA strategy has improved confidence and reduced risk on the OU-1 groundwater transition path to monitored natural attenuation (MNA).

To better evaluate the EA strategy, DOE is conducting a field demonstration to evaluate the use of edible oils to enhance the natural attenuation processes. The field demonstration is designed to determine whether structured geochemical zones can be established that expedite the attenuation of cVOCs in the OU-1 groundwater. The EA approach at OU-1 was designed based on “structured geochemical zones” and relies on groundwater flow through a succession of anaerobic and aerobic zones. The anaerobic zones stimulate relatively rapid degradation of the original solvent source compounds (e.g., cVOCs such as tetrachloroethene [PCE] and trichloroethene [TCE]). The surrounding aerobic areas encourage relatively rapid degradation of daughter products (such as dichloroethene [DCE] and vinyl chloride [VC]) as well as enhanced cometabolism of TCE resulting from the utilization of methane and other reduced hydrocarbons that are formed and released from the anaerobic zones.

PROCESS AND RESULTS

Operable Unit 1 Field Demonstration

The OU-1 groundwater field demonstration of EA was initiated in 2014 and will continue for a three-year period. For OU-1, the EA was implemented by targeted injection of an electron donor (vegetable oil) to create "structured geochemical zones." VOCs in the altered subsurface system encounter alternating anaerobic and aerobic environments along the plume flow path. The goal of these structured geochemical zones is the effective and rapid anaerobic degradation of parent compounds such as TCE and PCE and aerobic degradation daughter compounds such as *cis*-dichloroethene (cDCE) and VC. The principles and technical basis of EA were initially developed by Savannah River National Laboratory, and the regulatory guidance for EA was developed by the Interstate Technology and Regulatory Council. The goal of EA is to provide a bridge between active groundwater treatments and MNA. EA relies on understanding and manipulating the contaminant mass balance. Technologies are applied to sustainably reduce the contaminant loading from the source and/or increase the rate of natural attenuation processes within the plume. As described below, the OU-1 EA strategy includes actions that address both contaminant loading and natural attenuation rates.

An advantage of the structured geochemical zone concept compared to traditional bioremediation is that aerobic conditions are maintained in much of the aquifer so that negative impacts associated with creating reducing conditions over a large area are minimized. The EA strategy based on structured geochemical zones is consistent with the existing aquifer conditions in OU-1 where zones of reducing geochemistry are present in the areas of cVOC impact.

The combination of technologies implemented for OU-1 EA included the injection of emulsified vegetable oil within the footprint of the groundwater plume and the injection of neat soybean oil in the vadose zone beneath the former landfill. In the first part of the deployment, emulsified oil forms active bioremediation anaerobic treatment zones within the plume footprint to degrade existing groundwater contaminants (via reductive dechlorination, cometabolism, or both) and stimulates long-term attenuation capacity in the downgradient aerobic plume (via cometabolism smnf direct metabolism). In the second part of the deployment, neat (pure) soybean oil spreads laterally and forms a thin layer on the water table beneath residual soil sources to intercept and reduce future VOC loading and to reduce oxygen inputs to the local groundwater.

First-Year Data Evaluation

The injection of emulsified oil and blending water began on August 25, 2014, and was completed on September 22, 2014. Injection of neat soybean oil started on September 22, 2014, and was completed on December 7, 2014. Routine sampling was performed to assess the performance of the deployment strategy and for long-term attenuation as well as to assess the effectiveness of natural attenuation in terms of lines of evidence similar to those outlined in EPA's document *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tanks Sites* (OSWER 9200.4-17P).

First Line of Evidence: *Groundwater data demonstrate clear and meaningful trends of decreasing contaminant mass and/or concentration over time and the presence of degradation (daughter) products at appropriate monitoring points.*

The results from the first year of the field demonstration indicate that the dissolved TCE plume has decreased in size and mass (Figures 1 and 2). Statistical tests indicate the VOC concentrations in the majority of the source-area wells are decreasing. The VOC concentrations throughout the plume are projected to be below the target maximum contaminant level of 2 to 5 µg/L within 5 to 10 years—sooner than the design projection of 13 years.

Figures 3 and 4 depict the concentration of parent and daughter cVOCs in OU-1 monitoring wells located in the anaerobic treatment zones and downgradient of those areas. Data provide clear confirmation of reductive dechlorination in the anaerobic treatment zones. The lack of DCE (or vinyl chloride) in wells downgradient of the treatment zones is consistent with aerobic metabolism or cometabolism (Figures 5 and 6).

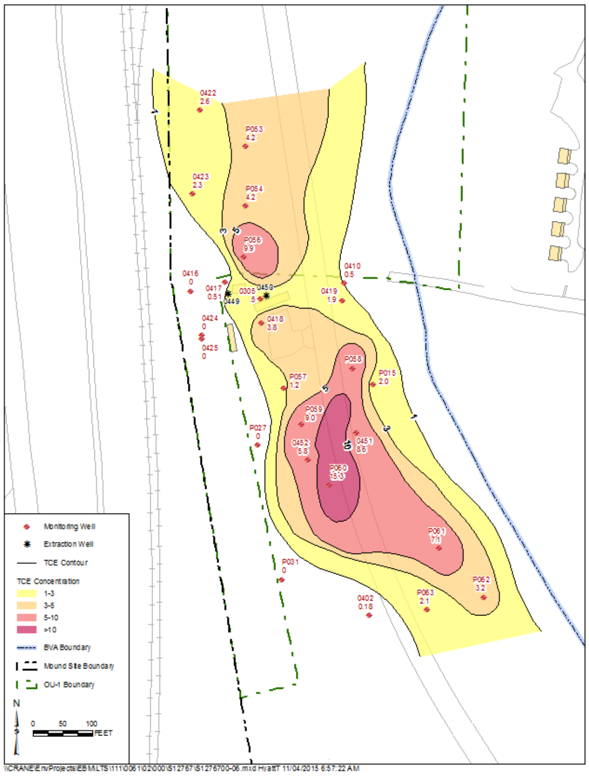

Figure 1. OU-1 TCE Plume Distribution in August 2014 (in µg/L concentration)

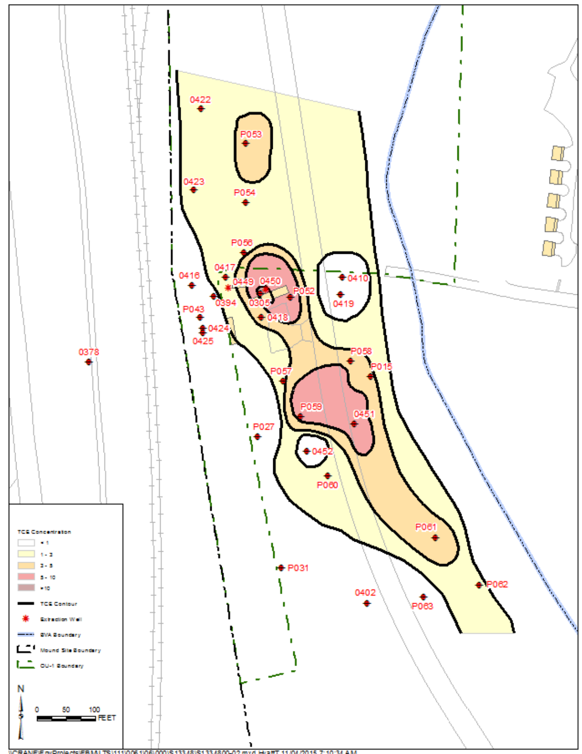

Figure 2. OU-1 TCE Plume Distribution in August 2015 (in µg/L concentration)

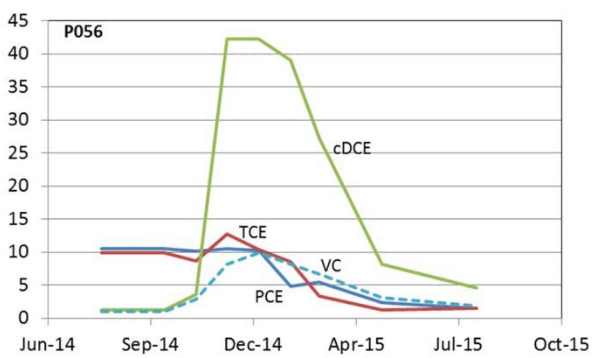

Figure 3. cVOC Concentrations in Treatment-Zone Monitoring Well P056 (in µg/L concentration)

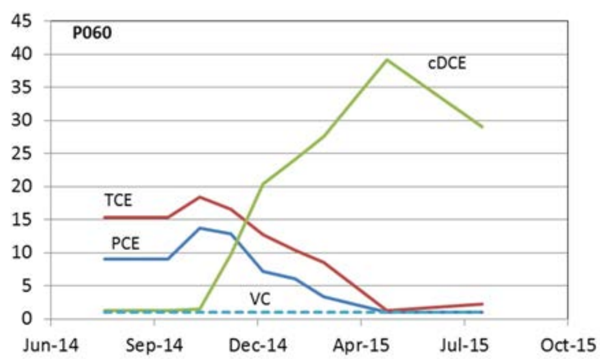

Figure 4. cVOC Concentrations in Treatment-Zone Monitoring Well P060 (in µg/L concentration)

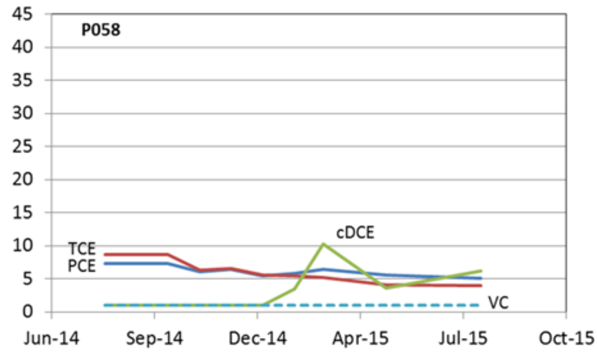

Figure 5. cVOC Concentrations in Intermediate Well P058 (in µg/L concentration)

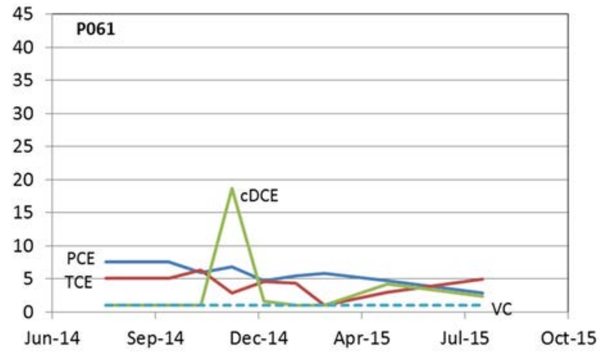

Figure 6. cVOC Concentrations in Downgradient Well P061 (in µg/L concentration)

The numbers of exceedances of regulatory limits (e.g., MCL or MCL guidelines) and how these change over time is an important line of evidence that documents progress toward specific end state goals. The following graphs provide additional detail, depicting the number of total exceedances of cVOC MCLs (Figure 7) and the total number of monitoring wells with one or more cVOC MCL exceedances (Figure 8) as a function of time. The trend evaluation covered the period from August 2014 through August 2015, which is considered the first year of the field demonstration. In Figure 7, multiple contaminant exceedances in a single well contribute to the totals for the sampling event, while in Figure 8, the total indicates the number of wells (i.e., locations) where one or more compounds is above the MCL. The exceedance trends provide an emergent metric that responds to all of the complex process and flow dynamics occurring in the field (e.g., contaminant degradation and ingrowth, partitioning, flushing, varying well locations relative to the source/plume/injection, increasing and decreasing concentrations, etc.).

An exponential (first-order) approximation provides a reasonable fit to the exceedance trends measured in the OU-1 monitoring wells for the period of the enhanced attenuation deployment. Assuming that the observed trends continue and using the exponential fit equations (projecting to a value of 0.01), the data suggest

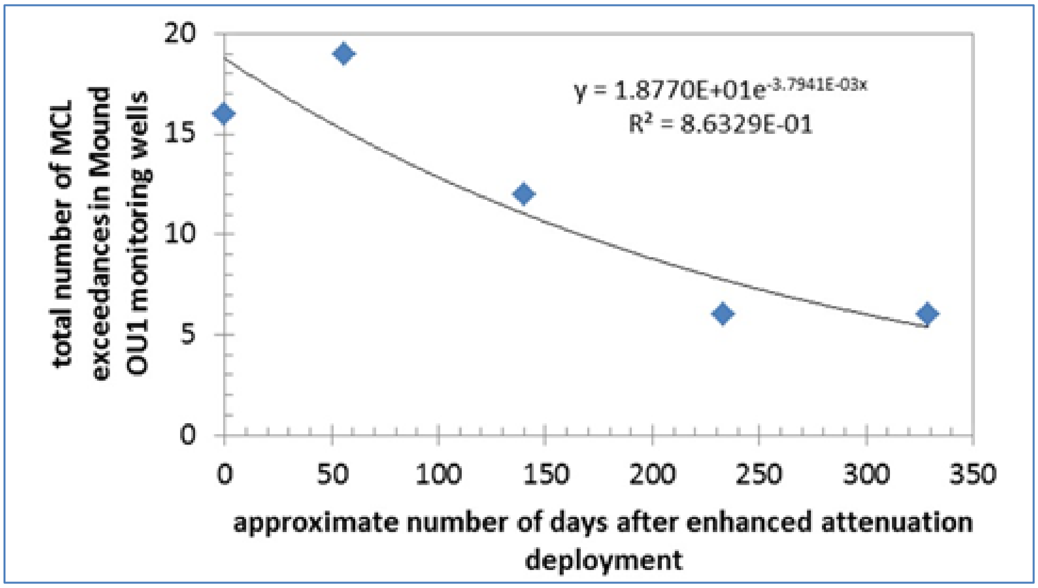

Figure 7. Total Number of MCL Exceedances for all cVOC Contaminants and Daughter Products in the Quarterly OU-1 Monitoring Well Sampling Results

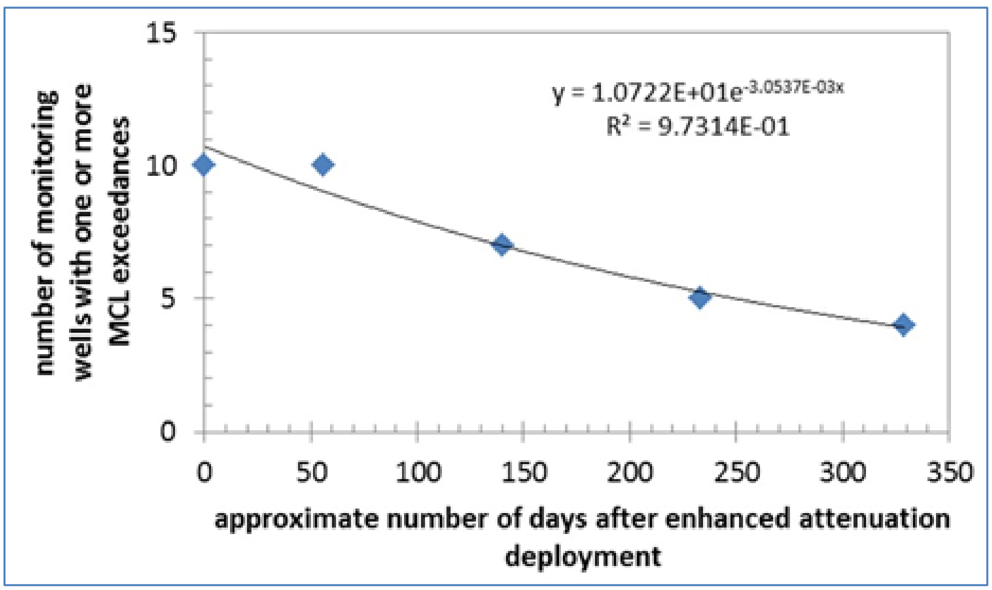

Figure 8. Total Number of Wells (locations) in Which One or More of the cVOC Contaminants or Daughter Products Exceeded MCL in the Quarterly OU-1 Monitoring Well Sampling Results

that OU-1 groundwater will reach MCL goals for all locations and constituents in approximately 7 years or less (circa 2020). This projected remediation time frame is generally consistent with meeting the Mound OU-1 core team design assumption of 13 years.

Concentrations and concentration trends in the downgradient sentinel wells are an important metric related to potential plume expansion. The concentrations and trends in these wells demonstrate that the cVOC plume is not expanding. The concentrations of both PCE and TCE in well P061, which is located between the cVOC plume and the downgradient wells, have decreased since the EA deployment; both constituents were above the MCL in the baseline sampling event and were below the MCL in the most recent sampling event. In the other distal downgradient sentinel wells, concentrations of all constituents have remained below MCL in all samples.

Second Line of Evidence: *Hydrologic and geochemical data that can be used to indirectly demonstrate the types of natural attenuation processes.*

Several monitoring parameters can be indicative of anaerobic biodegradation processes:

- Decreases in oxidation-reduction potential (ORP) and negative ORP indicate areas transitioning to anaerobic conditions.
- Decreases in dissolved oxygen (DO) indicate oxygen utilization from increases in microbial activity.
- Increases in metabolic byproducts (methane and alkalinity) indicate the initiation of fermentation and associated microbial activity.

ORP and DO data from monitoring wells support the interpretation that aquifer geochemistry is changing from oxidizing to reducing conditions and that depletion of oxygen is occurring within the treatment zones. Also, alkalinity data as well as increased methane concentrations in treatment-zone wells indicate areas where microbial activity has increased since injection of the edible oils. The chemistry of the aquifer at the downgradient wells continues to have higher ORP values and DO concentrations.

Third Line of Evidence: *Specific attenuation processes, such as microbial communities, demonstrate or quantify the occurrence of a particular natural attenuation process and ability to degrade cVOCs.*

To assess the biological response of the subsurface in representative areas of OU-1, quantitative polymerase chain reaction measurements of microbial community DNA isolated from groundwater samples were performed. Samples were collected prior to edible oil injection, and then the wells were resampled 3 and 6 months after the baseline samples. Six wells that represent different biogeochemical settings were sampled to provide information on changes within and downgradient of the reductive treatment zones, as well as provide insights on changes near the original source and in the distal portion of the plume.

All of the microbial counts have increased following the EA deployment: total bacteria, chlorinated-solvent-reducing bacteria, aerobic cometabolic bacteria, methanogens, and sulfate reducers. Reasonable target results for classes of related organisms to support the structured geochemical zones paradigm at low-concentration cVOC sites would generally be in the 10^3 to 10^5 per mL range (Figure 9); this range would be appropriate for both reductive dechlorination and aerobic (co)metabolism organisms/genes. This range would correspond to acceleration of reductive dechlorination of contaminants in the anaerobic zones while allowing the presence of the surrounding near-field aerobic zones for completing the degradation process to nontoxic end products.

The wells in the treatment zones have shown significant increases in chlorinated-solvent-reducing bacteria that are capable of degrading TCE and PCE. Side-gradient, intermediate, and downgradient wells have also shown increases in chlorinated-solvent-reducing bacteria counts.

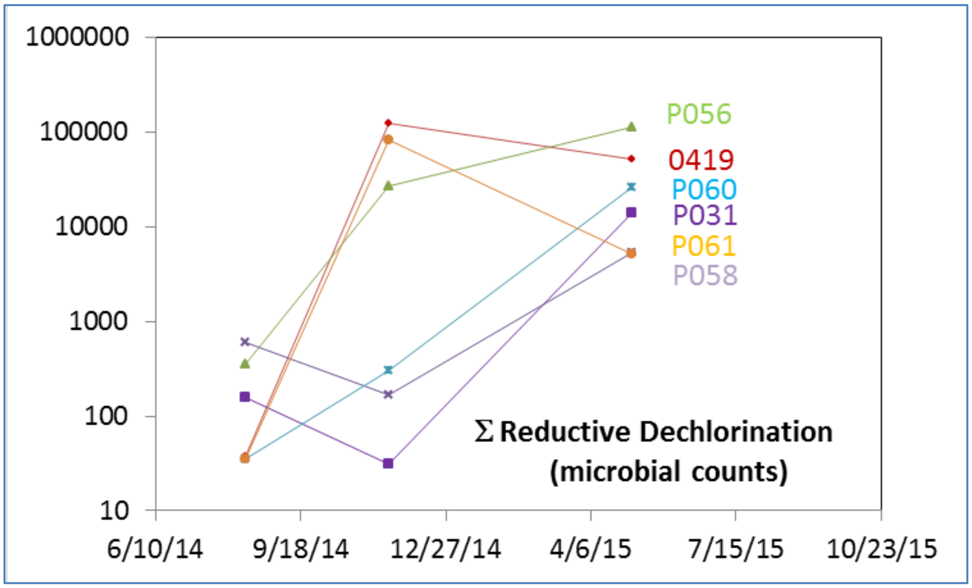

Figure 9. Sum of Reductive Dechlorinating Microbes Counts, per mL

COST

The results from the first year of the field demonstration indicate that the dissolved TCE and PCE plumes have decreased in size and mass. The VOC concentrations throughout the plume are projected to be below the target MCL of 2 to 5 µg/L within 5 to 10 years (calendar year [CY] 2019 to CY 2024)—somewhat faster than the original design projection of 13 years (CY 2027). Note that the estimated timeframe to reach target MCLs using the baseline P&T system was is 26 years (CY 2040) at a projected total cost of $7 million to $9 million. The projected total cost for the EA remedy was $1.7 million to $2.6 million based on the original 13 year EA design timeframe - a cost savings approximately $4 million to $7 million versus the baseline. The data from the first year of the field demonstration, and the shorter projected timeframe to reach MCLs suggest further cost reductions are possible (approximately $0.4 million to $2 million).

CONCLUSIONS

The hybrid structured geochemical zone approach supports reasonable progress toward remedial goals based on the complementary strengths of the processes that occur in the two redox conditions. Structured geochemical zones allow the microbial communities to work in sequence in environments to allow the overall degradation to be relatively rapid and robust (easing the requirements for specific microorganisms).

The results from the first year of the field demonstration support that the development of the structured geochemical zones is progressing as anticipated. Aquifer geochemistry is changing from an oxidizing to a reducing condition. The initiation of fermentation and associated microbial activity is indicated by increases in metabolic byproducts in groundwater samples. Microbial counts have increased (total bacteria, chlorinated-solvent-reducing bacteria, aerobic cometabolic bacteria, and methanogens). Chlorinated-solvent-reducing bacterial counts showed significant increases in treatment zones. Within these structured geochemical zones, the dissolved TCE plume has decreased in size, and statistical tests indicate the cVOC concentrations in the majority of the source-area wells are decreasing.

The cVOC concentrations throughout the plume are projected to be below the target maximum contaminant level of 2 to 5 µg/L within 5 to 10 years. This is sooner than the design projection of 13 years and significantly sooner than the projected cleanup time frame of 26 years for the baseline P&T system.