REGENESIS

Technology-Based Solutions for the Environment

Treatment Solution for Back Diffusion - Tank Study

PlumeStop Technical Bulletin 6.1

Contents:

1. Abstract

PlumeStop® Liquid Activated Carbon™ demonstrated enhanced treatment of matrix back diffusion relative to an ERD treatment in a 10-month long, controlled laboratory tank experiment conducted at Colorado State University. The tanks treated with PlumeStop removed between 90 and 99.9% of the total VOCs from the water throughout the treatment period, correlating to 60+ pore volumes of treatment. Further, the tank that received a combined PlumeStop + ERD treatment resulted in 1 to 2 orders of magnitude increases in the Dehalococcoides and functional gene populations compared to the ERD treatment alone.

2. Background

A. Back diffusion

When left unchecked, a source of groundwater pollution will produce a plume of dissolved or phase-separated pollutant molecules that moves through the groundwater system or aquifer. In aquifers composed of heterogeneous materials (e.g. sand and clay layers), the pollutant tends to flow primarily through zones of higher permeability (e.g. sands). As the zones of higher permeability transport elevated pollutant concentrations, a diffusion gradient is established that drives the pollutant into adjacent zones of lower permeability (e.g. clays). Over time, this can result in adjacent lower permeability zones storing significant masses of dissolved pollutants.

Thus, while historical remediation approaches remove contaminant concentrations from the more permeable zones, zones of lower permeability are less treated. This sets up a reversal in the contaminant diffusion gradient that is referred to as "back diffusion", in which dissolved contaminant concentrations stored in the lower permeability zones diffuse back into the areas of higher permeability where contaminants have been removed. Back diffusion has been shown to occur over very long periods of time, causing persistent low levels of contaminants to impact groundwater wells long after attempts at aquifer remediation.

In a 2013 report from the National Research Council (NRC), it was estimated that over $200 billion will be spent on cleanup at 300,000 contaminated sites in the U.S. through the year 2033.[1] Some of the key

[1] National Research Council. 2013. Alternatives for Managing the Nation's Complex Contaminated Groundwater Sites. Washington, DC: The National Academies Press. doi:https://doi.org/10.17226/14668.

reasons for protracted timeframes and increased costs on these site cleanups are: “difficulties in characterizing the nature and extent of the problem in highly heterogeneous subsurface environments, as well as use of remedial technologies that have not been capable of achieving restoration in many of these geologic settings.” In addition, the document identifies back diffusion (also known as matrix back diffusion) as one of the prominent processes that limit our ability to clean up groundwater at complex sites. The NRC report also states that “there are no proven remedial techniques to preferentially target and accelerate the removal of contaminants from localized sites that are desorption/diffusion limited.” In light of this report, there is clearly a need for techniques that address groundwater contamination associated with matrix back diffusion and thus allow faster and lower-cost cleanup of contaminated sites.

B. SERDP Funded Tank Study

The experiment described in the present study closely follows a procedure used within a SERDP funded project, Management of Contaminants Stored in Low Permeability Zones, that was led by Professor Tom Sale of Colorado State University.[2] In that study, tanks with alternating layers of high and low conductivity soils (see Figure 1) were used to simulate the storage and subsequent release of TCE from low permeability zones and to test the sustained treatment effectiveness of various remedial strategies. The treatment conditions in the SERDP study included:

1. Control tank: Clean water flushing only
2. Enhanced flushing: Clean water flushing at 5x the rate of the control
3. Chemical oxidation: Permanganate
4. Bioremediation/bioaugmentation: Sodium lactate and KB1 culture
5. Bioremediation + “flux clog:” Sodium lactate, KB1 culture, xanthan gum
6. Biogeochemical: Sodium lactate, sulfate, sulfate reducing bacteria

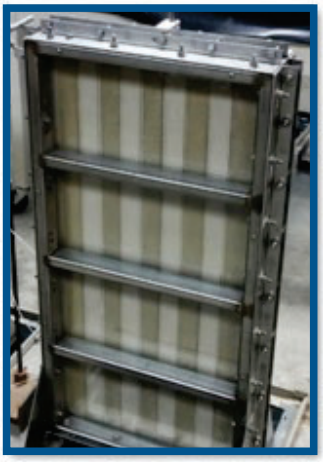

FIGURE 1

Tank set-up with nine alternating layers of low and high permeable soils.

A timeline of events during the study is summarized in Figure 2. Each treatment was applied to the respective tanks for approximately 9 pore volumes (PVs) before returning to a water-only flush. Throughout the study, effluent samples were collected for VOC analysis.

[2] T. Sale, B.L. Parker, C.J. Newell, J.F. Devlin. 2013. State of the Science Review: Management of Contaminants Stored in Low Permeability Zones. Strategic Environmental Research and Development Program (SERDP) Project ER-1740.

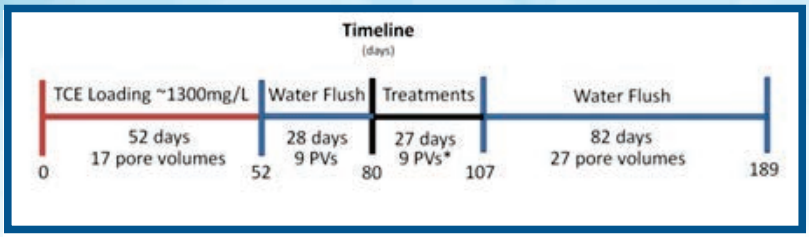

FIGURE 2

Timeline of events in the SERDP Project.1

A summary of the study's results revealed that chemical oxidation and the three varieties of biological treatments all demonstrated enhanced treatment compared to the tanks that were only flushed. However, in all cases, the concentrations eventually rebounded to some extent. The tank that received permanganate was the fastest to rebound upon completion of the treatment, whereas the biologically treated tanks showed sustained treatment for approximately 20 PVs before concentrations rebounded to similar levels as the control.

Given the expected persistence of back diffusion on the order of years to decades, long lasting treatment options that better match the timeframe of back diffusion are needed.

3. Test Procedure

This experiment was performed in the laboratory of Tom Sale at Colorado State University (Fort Collins, CO) and was managed by Kevin Saller, Ph.D. (CDM Smith, former student in the Sale lab) and REGENESIS. The test set-up closely followed the procedure used by Kevin Saller and Tom Sale in the SERDP-funded project described above, with some changes made to better represent the conditions in which PlumeStop is commonly used.

Four stainless steel tanks with glass panes (0.5m x 1.0m x 2.54 cm) were packed on their side with nine alternating layers of silt and sand, each approximately 5 cm wide (Figure 1). The silt represented the lower permeable soil and was from F.E. Warren AFB, WY (k = 1 x 10-4 cm/sec, foc = 0.3%). The sand layer was a mixture of 80% medium sand and 20% sandy loam (Laguna Beach, CA) with a conductivity approximately two orders of magnitude more permeable than the silt. The tanks flowed upward with a flow rate of ~0.33 pore volumes/day.

Tank #	Description of Treatment Condition
1	TCE control: Water flushing only, no amendments
2	PlumeStop Treatment: The only amendment applied was PlumeStop® Liquid Activated Carbon™
3	ERD Treatment: The tank was treated with an electron donor (sodium lactate) and was bioaugmented with a culture of *Dehalococcoides* (DHC, BDI® Plus)
4	PlumeStop + ERD Treatment: The tank was treated with PlumeStop and an electron donor (sodium lactate) and was bioaugmented with a culture of DHC (BDI® Plus)

TABLE 1

Treatment conditions tested in this experiment.

The first phase of the experiment involved flushing the tanks with TCE-saturated water (~1,300 mg/L) for 35 days to forward diffuse TCE into the low k zones. This phase was followed by flushing clean, anaerobic water through the tanks for the duration of the experiment, with the only exceptions being during the application of amendments. A description of the treatment conditions tested in this experiment is provided in Table 1. At Day 103, PlumeStop was introduced into Tank 2 for a total of approximately 1.5 pore volumes. At the same time, sodium lactate and BDI Plus were co-mixed with PlumeStop and applied

to Tank 4, and a mixture of sodium lactate and BDI Plus were also applied to Tank 3. Due to a lack of response to the ERD treatment, a second ERD treatment was applied to Tanks 3 and 4 at Day 129. A final treatment of only sodium lactate was applied at Day 229. A timeline of these events is summarized in Figure 3.

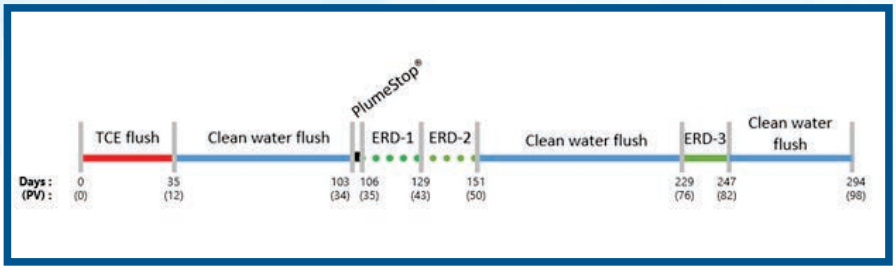

FIGURE 3

Timeline of injection events in this study. ERD-1 and ERD-2 consisted of a sodium lactate and Bio-Dechlor Inoculum® Plus mixed solution. Only sodium lactate was applied during ERD-3. Total timeframe of study was 9.8 months.

Throughout the experiment, effluent samples were collected for VOC analysis. Upon completion of the experiment, water and soil samples were sent to Microbial Insights Inc. for qPCR analysis.[3] In total, the experiment ran for nearly 10 months, with 6.5 months of monitoring after the remedial applications. Note that the goal of this study was to establish the relative efficiencies of the remedial technologies tested rather than to demonstrate the ability to meet groundwater standards within the residence time of the tank. Given that TCE was back diffusing along the entire flow path of the tank and thus creating a spectrum of residence times, the ability to show complete degradation within the scope of this set-up is limited.

4. Results & Discussion

The ability of PlumeStop to distribute in these dual-porosity tanks was documented throughout the study, and images are provided in Figure 4. During the first pore volume of the application, PlumeStop can be seen to transport preferentially through the high k zones. Over time, noticeable penetration into the low k zones was observed in both tanks that received a PlumeStop treatment; however, it was not known if the PlumeStop distributed completely through the entire thickness of the low k zone or if it was localized to the surface as a result of a side-wall transport effect. To determine the extent of distribution, the tanks were dismantled upon completion of the experiment, and cross section samples confirmed that the penetration was complete (see Figure 5).

For reference, a comparison between PlumeStop and permanganate1 distribution into the low k zone of these tanks is depicted in Figure 6.

FIGURE 4

PlumeStop distribution in Tank 4, PlumeStop + ERD Treatment, at 0.5 PV (left) and 18 PV (right) after PlumeStop was applied.

[3] Microbial Insights, Inc. Knoxville, TN: CENSUS (qPCR) Analysis.

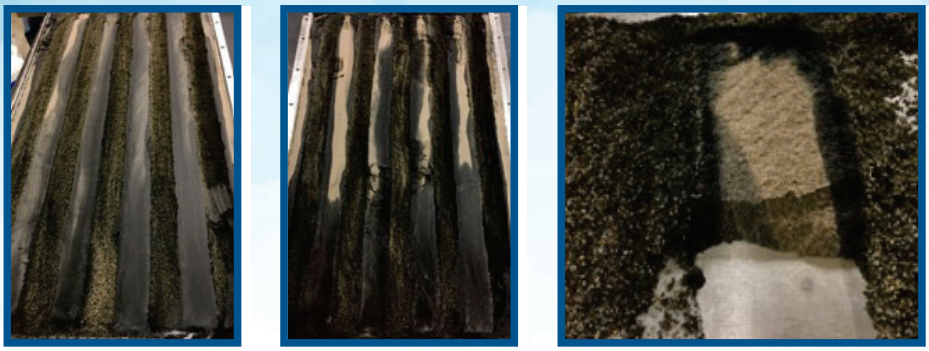

FIGURE 5

Picture of tanks at the end of the experiment with the front panel removed. Tank 2: PlumeStop Treatmeant (top left), Tank 2: PlumeStop + ERD Treatment (top right), cross section of Tank 4 (bottom).

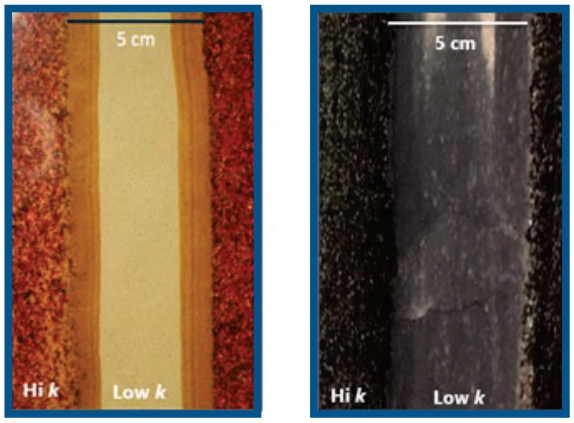

FIGURE 6

Low k soil distribution comparision between permanaganate1 (left) and PlumeStop (right).

B. Effluent results

Throughout the study, effluent samples were collected and analyzed for VOC concentrations. Results from each of the tanks are illustrated graphically in Figure 7. Initial observations indicate that the tanks treated with PlumeStop experienced immediate drops in effluent concentrations upon application of PlumeStop, and substantially lower total VOC effluent concentrations were maintained throughout the experiment compared to the ERD treatment alone.

Treatment 1:

Control tank. Effluent data from the entire experiment is shown for Tank 1 in Figure 7. In the initial stage of the study in which a saturated TCE solution was introduced into the tanks for ~12 PVs to load the low k zones, the effluent concentration of TCE was approximately equivalent to the influent concentration (1,300 mg/L or 10,000 mM). Once the influent was switched to clean water, back diffusion was induced, and the effluent TCE concentration decreased by three orders of magnitude (OoM) over the next 20 PVs to 15-30 mM (2-4 mg/L). At the ~34 PV mark, the amendments were applied to the other tanks. Over the duration of the experiment, which was equivalent to an additional 65 PVs of flushing, the TCE concentration eluting from the control tank dropped by another OoM to 0.8 mM or 0.1 mg/L TCE at the end of the study. In summary, the concentration of TCE in the control tank effluent decreased by 4 OoM from 1,300 mg/L to 0.1 mg/L throughout the study with 85 PVs of flushing.

Treatment 2:

PlumeStop only. The only remedial treatment applied to this tank was ~1.5 PV of PlumeStop starting at the 34 PV mark of the experiment. The effluent results show a dramatic drop in the TCE effluent concentration relative to the control of ~3 OoM for 20 PVs, followed by just over a 1 OoM decrease in concentration that was sustained for the duration of the experiment (45 PVs). Although this tank was not bioaugmented, cDCE was detected starting 20 PVs after PlumeStop was injected. The observation of this

degradation product is attributed to the non-sterilized silt from a contaminated site, and the ability of the stabilizing polymer in PlumeStop to act as an electron donor. Overall, the PlumeStop treatment in this tank reduced VOC concentrations between 1.5 and 3 OoM for the entirety of the treatment period (64 PVs).

Treatment 3:

ERD only. Tank 3 received amendments to support ERD at three points during the study. The first application of sodium lactate (1,000 mg/L) and BDI Plus (total of 100 mL of 109 cells DHC/mL) occurred at the 34 PV mark for a total of 9 PVs. No significant reduction in TCE was observed after this application, so an identical amendment solution was re-applied at the 43 PV mark for 7.3 PVs before switching back to an anaerobic water flush. At this time, an 80% drop in TCE relative to the control tank was observed along with a stoichiometric increase in cDCE and trace VC that persisted for 10 PVs, followed by a period of ~20 PVs with an overall 40-50% TCE decrease. After the final lactate treatment, the TCE concentration decreased again to 80-90% of the control tank with a corresponding increase in cDCE. Throughout the entire study, the total mass balance could be accounted for in TCE, cDCE, and VC, indicating that while there was conversion of the species, the contaminants back diffusing from the low k zones were not contained.

Treatment 4:

PlumeStop + ERD treatment. Tank 4 received the same PlumeStop treatment as described for Tank 2 and the same ERD treatments as described for Tank 3. An immediate 1-3 OoM drop in the TCE concentration was observed during the first 5 PVs following the initial application, followed by partial rebound of concentrations until the second ERD application, at which point a relatively consistent 0.8 to 1 OoM reduction was observed through the final lactate application and to the end of the study. Between the second and third ERD treatments, cDCE and VC were measured at concentrations one and two OoM lower than the TCE, respectively. After the final lactate treatment, approximately equimolar concentrations of TCE and cDCE were measured, and the VC concentration was one OoM lower.

The PlumeStop + ERD treatment consistently reduced the total VOCs by 1 OoM throughout the experiment. The presence of the daughter products support the concept that biodegradation was occurring in conjunction with sorption. It is not clear why this tank had a higher baseline concentration than what was observed in Tank 2, although heterogeneities between the tanks and subsequent differences in the PlumeStop distribution is suspected to be the cause.

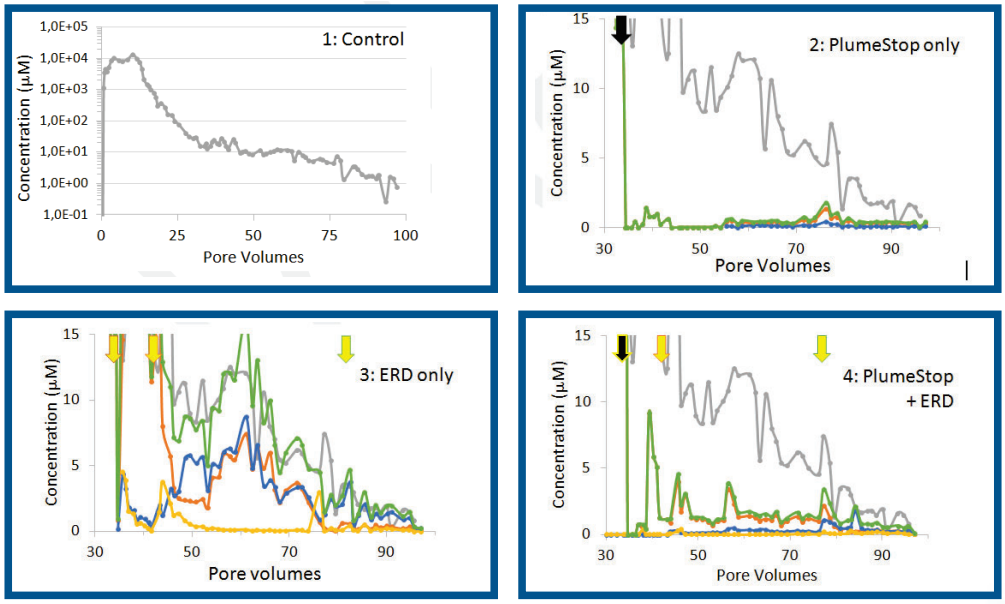

FIGURE 7

Effluent VOC data from each tank graphed as micromolar concentrations. Tank 1: TCE control showing data from the entirety of the experiment plotted on a log scale. Data from Tanks 2-4 show data

only over the time frame of the experiment in which amendments were applied. The control tank data is included as a grey line on these plots for reference. Key: TCE control tank, grey; TCE, orange; cDCE, blue; VC, yellow; Mass balance = TCE + cDCE + VC, green. The black arrow indicates a application of PlumeStop, black arrow with yellow outline indicates a PlumeStop, lactate, and BDI Plus application, yellow arrows with orange outline represent lactate + BDI Plus applications, and yellow arrows with green outline represent a lactate only application.

C. Microbial Results

Upon completion of the experiment, water and soil samples were collected from each tank for qPCR CENSUS analysis to quantify Dehalococcoides (DHC) populations and DHC functional genes, including TCE reductase (TCE) and vinyl chloride reductases (VCR and BVC). Soil samples were collected from the mid-section of the tank at the interface of the high and low k soils. Results from the aqueous phase qPCR analyses are given in Figure 8, and the soil results are given in Figure 9.

In the two tanks that were not bioaugmented (1: Control, 2: PlumeStop only), microbial populations in both the water and soil were below the reporting limits for DHC and the functional genes. In contrast, in the tanks that were bioaugmented (2: ERD only, 4: PlumeStop + ERD), detectable DHC, TCE, and VCR populations were observed. BVC was not detected in any sample from any of the four tanks.

Across all of the phases analyzed, the PlumeStop + ERD treatment resulted in enhanced microbial populations of at least 1-2 OoM when compared to the ERD treatment alone. In the water phase, the microbial populations in the presence of PlumeStop were consistently about 1 OoM higher and reached a concentration of 1 x 104 cells/mL, which is the level deemed to provide “generally useful” reductive dechlorination rates.[4] The soil data indicated over 2 OoM increases in the microbial populations in the presence of PlumeStop. The measured populations for the ERD only treatment correspond well with the results from the SERDP project, in which similar DHC levels were detected at the sand-silt interface in the tank that received lactate and KB1.1as observed along with a stoichiometric increase in cDCE and Plumelyspected to be the cause.

Of note in the qPCR soil dataset is the distribution of the microbial populations in the two soil zones between the two bioaugmented tanks; in the ERD only treatment, detectable populations were found only in the low k soil, whereas the PlumeStop + ERD tank had detectable populations in both zones. This can be attributed to the presence of PlumeStop in the high k zone, which provides a surface for the contaminants diffusing out of the low k zone to be contained on, effectively increasing their residence time in the treatment zone of the tank. This in turn allows microbes to respire and colonize the PlumeStop surface and surrounding high K matrix In contrast, in the ERD only treatment, once contaminants diffuse out of the low k zone, they are quickly transported out of the tank, resulting in a very short residence time.

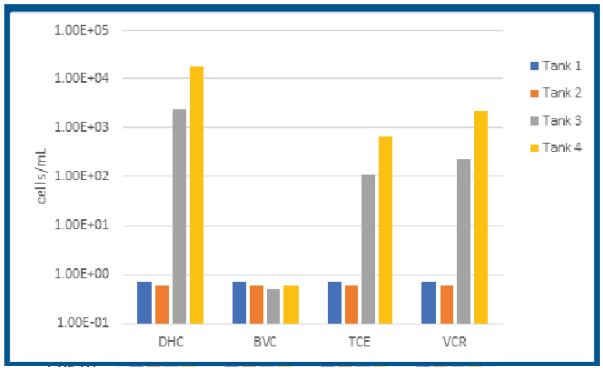

FIGURE 8

qPCR results from the aqueous phase analysis. Key:
1:Control, blue;
2: PlumeStop only, orange;
3: ERD only, grey;
4: PlumeStop + ERD, yellow.

[4] X. Lu, J.T. Wilson, D.H. Kampbell. 2006. Relationship between Dehalococcoides DNA in ground water and rates of reductive dichlorination at field scale. Water Research 40(16), 3131-3140.

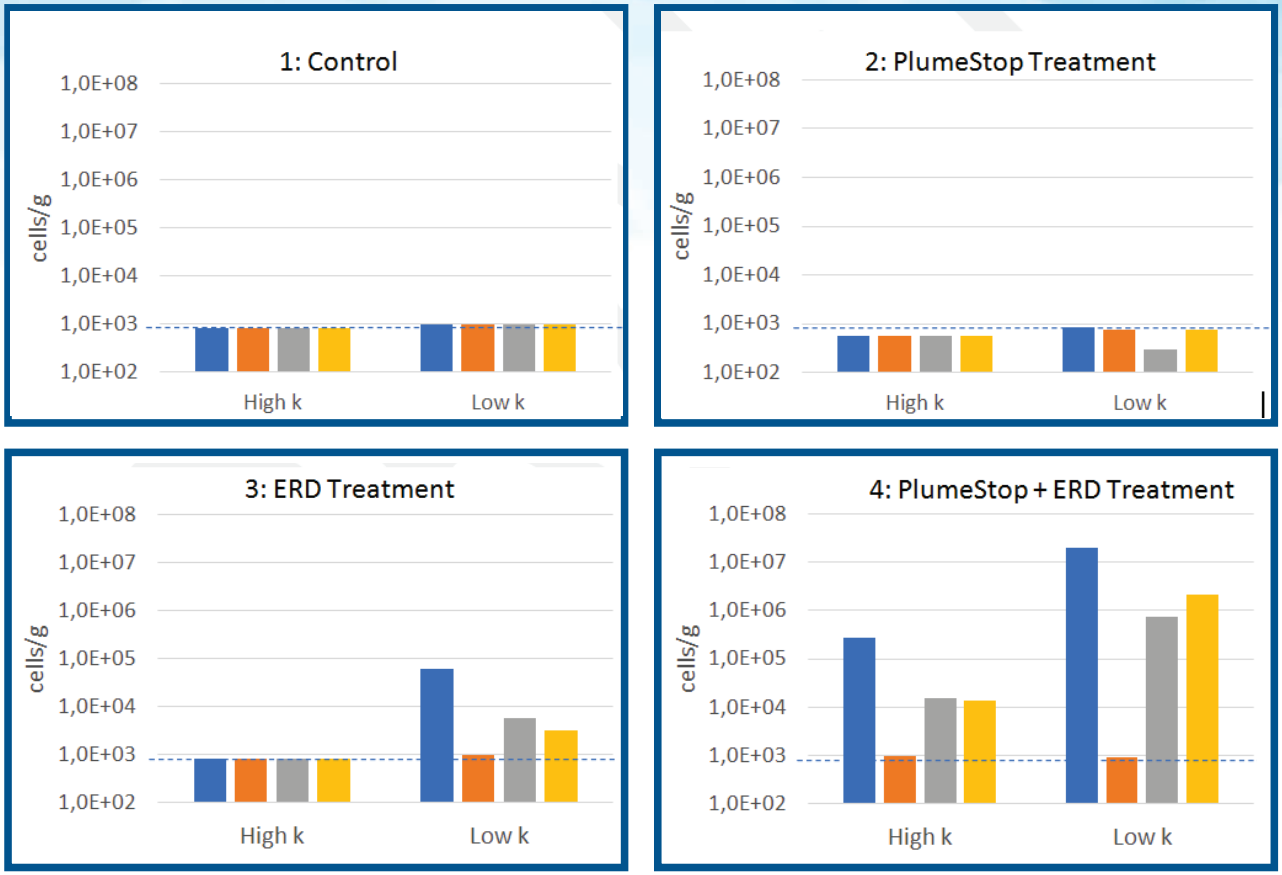

FIGURE 9 qPCR results from the high k and low k soil analyses. Key: DHC, blue; BVC, orange; TCE, grey; VCR, yellow. Dotted line represent the reporting limit for the qPCR analysis.

Conclusions

Results from this 10 month long, dual porosity tank study demonstrated the ability of PlumeStop to provide an immediate and sustained treatment for contaminants back diffusing out of low permeable soil zones. Compared to ERD treatment, the PlumeStop contained the contaminants and showed longer and more consistent treatment. The effluent VOC data demonstrated between 90 and 99.9% removal of the total VOCs from the groundwater in the tanks treated with PlumeStop throughout the treatment period, correlating to 60+ pore volumes of treatment. In contrast, the ERD treated tank showed conversion of the parent contaminant to daughter products, however there was no containment of the contaminants as there was essentially 0% removal of the net contaminants from groundwater. Furthermore, the tank that received a combined PlumeStop + ERD treatment resulted in 1 to 2 orders of magnitude increases in the Dehalococcoides and functional gene populations. Finally, the distributivity of PlumeStop was further demonstrated in this tank study, as the PlumeStop not only transported through the higher k soils, but also penetrated the lower k soils more than what had been observed previously with even a soluble agent like permanganate.

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(949) 366-8000
www.regenesis.com

1011 Calle Sombra
San Clemente, CA 92673