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Field-scale demonstration of induced biogeochemical reductive dechlorination at Dover Air Force Base, Dover, Delaware

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Abstract

Biogeochemical reductive dechlorination (BiRD) is a new remediation approach for chlorinated aliphatic hydrocarbons (CAHs). The approach stimulates common sulfate-reducing soil bacteria, facilitating the geochemical conversion of native iron minerals into iron sulfides. Iron sulfides have the ability to chemically reduce many common CAH compounds including PCE, TCE, DCE, similar to zero valent iron (Fe^0). Results of a field test at Dover Air Force Base, Dover, Delaware, are given in this paper. BiRD was stimulated by direct injection of Epson salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and sodium (L) lactate ($\text{NaC}_3\text{H}_5\text{O}_3$) in five injection wells. Sediment was sampled before and 8 months after injection. Significant iron sulfide minerals developed in the sandy aquifer matrix. From ground water analyses, treatment began a few weeks after injection with up to 95% reduction in PCE, TCE, and cDCE in less than 1 year. More complete CAH treatment is likely at a larger scale than this demonstration.

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Keywords: Biogeochemical reductive dechlorination; TCE; FeS; Reduced minerals

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1. Introduction

The bioremediation of chlorinated aliphatic hydrocarbons (CAHs), including perchloroethylene (PCE), trichloroethylene (TCE), trichloroethane (TCA), has generally focused on direct microbially facilitated oxidation/reduction reactions (Bouwer, 1994; Wiedemeier et al., 1998). Both natural and enhanced bioremediation of CAH compounds normally requires the presence of labile organics and special chlororespiring bacteria, which facilitate the oxidation of the organic through the complimentary reductive dechlorination of the targeted CAH. The bioremediation of CAH compounds is typically stepwise with highly chlorinated compounds (e.g., PCE or TCE) biotransformed to intermediate, less chlorinated, daughter products (e.g., DCE or VC). Active CAH bioremediation is often recognized by the generation of these daughter products. In some instances, if these are not further biodegraded, they can persist in the environment.

Biogeochemical reductive dechlorination (BiRD) is a new approach to CAH treatment (Kennedy, 2005). Under certain natural or stimulated conditions, native sulfate-reducing soil bacteria have the ability to significantly modify the mineralogical composition of their environment, inducing the rapid authigenic formation of mineral iron sulfides. FeS minerals are strongly reduced and facilitate the autoreduction of CAH compounds similar to exposure to elemental iron. Synthetic FeS has been documented to dechlorinate a wide range of chlorinated compounds including PCE, TCE, PCA, CT, PCA, and others (Butler and Hayes, 1998, 1999, 2000; Gander et al., 2002). Lee and Batchelor (2002) also found good dechlorination rates for PCE, cDCE, and VC by reaction with pyrite (FeS₂).

FeS forms in many natural subsurface environments and has also been documented to occur in sediment contaminated with labile organics, including landfill leachate and fuel hydrocarbons (Howarth and Jorgensen, 1984; Morse et al., 1987; Kennedy et al., 1998a,b; Kennedy et al., in press). By stimulation, high concentrations of FeS and FeS₂ have been developed in just a few weeks under controlled conditions simulating natural aquifers in typical sediment (Kennedy and Everett, 2001). BiRD can be stimulated through the addition of sulfate and a labile organic in the presence of natural or supplemented Fe (typically mineral).

There are several theoretical advantages to BiRD. Sulfate bacteria are ubiquitous and sulfate reduction is simple and rapid to stimulate. The formation of iron sulfide minerals during sulfate reduction is almost instantaneous. Reaction half-lives for dechlorination by iron sulfides range from only hours to weeks. CAH treatment via BiRD results in the generation of comparatively little daughter products. BiRD is also inexpensive, requiring only the addition of sulfate salts, manufactured for agricultural purposes, and any of a number of organic materials, such as lactate or plant mulch.

The demonstration project presented here is the first to stimulate the formation of FeS under field conditions for the purpose of CAH remediation. The project was located in a chlorinated solvent plume at Dover Air Force Base, Dover, Delaware (DAFB). DAFB is a National Test Site, and multiple treatment technologies have been evaluated there. The BiRD treatment area is located 160 ft cross-hydraulic gradient to a bioremediation test site performed as a separate effort (Lee, 2002) so that CAH treatment response could be compared. Both field tests were conducted as part of the Air Force Center for Environmental Excellence (Brooks City-Base, San Antonio, Texas) Enhanced In Situ Bioremediation (EISB) Initiative.

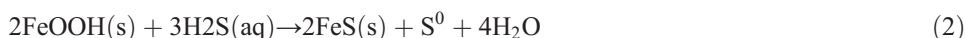
2. BiRD background

BiRD can be divided into three parts: (1) biological sulfate reduction, (2) geochemical mineral formation, and (3) dechlorination. To facilitate the biological phase, a soluble labile organic (e.g.,

lactate) is added to the aquifer with sufficient SO_4^{2-} to facilitate the desired end treatment parameters. These amendments are added to stimulate sulfate-reducing bacteria (SRBs). SRBs are ubiquitous in most subsurface environments so bioaugmentation is normally not required. Oxidation of the organic by SRBs initially produces hydrogen sulfide (H_2S) according to the reaction:



In the geochemical phase, iron sulfide minerals develop in response to geochemical perturbations induced in the preceding biological step. Most sediment contains high concentrations of available Fe^{3+} oxide/hydroxide minerals. Surveys of multiple sites contaminated with fuel oils and/or chlorinated solvents show mineral Fe normally ranging from 1000 to 20,000 mg/kg (Kennedy et al., 1998a,b, 2003, 2004a, 2006). Assuming normal soil densities, a large mass of mineral Fe ranging from 1.6 to 32 kg/m³ normally exists which could be available for geochemical conversion to FeS minerals. Native iron minerals provide a strong chemical sink for H_2S , forming iron sulfide minerals as, for example, with Fe(III) as goethite:



Alternatively, H_2S reaction with Fe(II) as iron hydroxide can be expressed as:



Sulfide reactions with Fe are almost instantaneous. Iron sulfides form as microfine minerals of high surface area. Preexisting iron minerals are converted to iron sulfides so matrix permeability is not affected significantly. With time some FeS may be converted to FeS_2 as:



Microcosm studies were conducted by Kennedy and Everett (2001) to observe the development of mineral iron sulfides in native sandy sediments. Sand was amended with a mixture of fatty acids, for carbon, and sulfate. Organic and sulfate consumption and mineral iron sulfide precipitation was monitored. Concentrations of over 150 and 20 mg/kg of S as FeS and FeS_2 , respectively, developed in just 12 weeks.

The reductive dechlorination step occurs spontaneously and may be expressed, for TCE as:



From laboratory studies with pure minerals, acetylene is the primary end product of CAH dechlorination (Butler and Hayes, 1998, 1999, 2000; Gander et al., 2002; Lee and Batchelor, 2002). However, acetylene may not be useful as an indicator of abiotic dechlorination in live systems as it is labile and certainly transient. The pseudo half-life for reactive CAH compounds can be measured in days to weeks. Many partial oxidation products for Fe and S may be possible.

In contrast to microbial reductive dechlorination, CAH treatment via BiRD is difficult to observe in the field because few, if any, partially dechlorinated daughter products are formed. However, it has been suggested that iron sulfide minerals could be more important than microorganisms under some conditions (e.g., sulfate reducing conditions) in affecting the fate of chlorinated ethylenes (Lee and Batchelor, 2002). Fe and S mineralogical investigations of sites where sulfate reduction is dominant suggest this may be the case (Kennedy et al., 2004b). Finally, the reactions in Eqs. (1)–(5) are straightforward to induce, facilitating BiRD by engineering design.

3. Methods and experimental design

3.1. BiRD field site

The study site at DAFB is known as Target Area 1. Contaminants originated from surface impoundments that received hazardous waste from 1963 to 1984. The plume is approximately 183 m wide and 1158 m long. A monitoring well network was established during the characterization phase, and ground water, monitored for many years, consistently shows significantly elevated concentrations of chlorinated compounds.

As shown in Fig. 1, the BiRD treatment array consisted of five injection wells (ESI1–ESI5) and six monitoring wells (ESM1–ESM6). The injectors were positioned 3 m apart and perpendicular to the prevailing ground water flow direction. Monitoring wells ESM1 through ESM5 were aligned perpendicular to the central injection at distances of 0, 0.9, 2.1, 3.6, and 5.6 m and intended to be down-flow gradient with respect to the prevailing ground water flow direction. ESM6 is located 7.9 m west northwest of the injection system, up-flow gradient relative to the prevailing ground water flow direction.

The injectate was prepared in batches in two 1900 l tanks using ground water pumped from a nearby recovery well (Fig. 1)), approximately 21 m from INJ3 and within the contaminant plume. Monitoring well sampling before and after injection was made specifically to demonstrate the affects of injection water on the system. Those analyses show that concentrations fluctuated near the injectors for a few days then returned to near original concentration. A total of 450 kg Epson salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and 318 kg of 60% sodium (L) lactate ($\text{NaC}_3\text{H}_5\text{O}_3$) was injected. Each well received 10,000 l of amended ground water/injectate. The resulting concentrations of SO_4^{2+} and lactate in the injectate were 3500 and 3000 mg/l, respectively. Sulfate and lactate were mixed in a ratio of approximately 1:1.25 according to the following stoichiometry:



It is desirable to fully consume all added sulfate during the biological phase. Therefore, slightly more than the stoichiometric amount of organic was added.

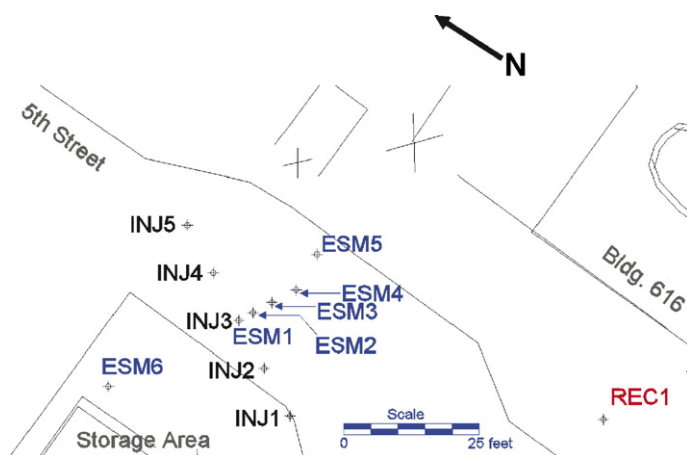


Fig. 1. BiRD injection and monitoring array.

The number and location of injection wells used at a BiRD remediation will depend on site conditions and the goals of treatment. In this case, as the goal was only to demonstrate that BiRD can be engineered, not to treat the entire plume, a short line of injection wells was located within the plume. To allow comparison with the bioremediation test, BiRD injection wells were located at cross-hydraulic gradient. A 3 m separation between wells was deemed to be close enough to allow the zones of influence of the injection wells to overlap, given the volume of injectate introduced to each well. The concentration of SO_4^{2+} and lactate resulting about each injection well should not produce sulfide in excess of the local supply of iron, but should produce enough iron sulfide mineral to destroy any contaminant entering the zone for a sufficiently long time. In the case presented here, the concentrations were more than sufficient, considering the relatively short duration of the test.

The potentiometric surface for the study site is rather flat with ground water flow generally towards the east northeast. Based on water level data collected during the field demonstration, there was a ground water flow reversal during the last third of the test, which influenced observations as described below. The ground water flow reversal is documented in Fig. 2, which is used to present the change in ground water elevation difference between monitoring wells ESM1 and ESM6. The change in flow direction that occurred during the demonstration made data interpretation more complex, but not impossible.

3.2. Sediment analyses

At the BiRD field site, sediment was sampled two times for Fe and S mineral constituents, once before the injection (August 2003) and 8 months after the injection (April 2004). Borings were located at or adjacent to the monitoring wells and were full-hole cored from surface to total depth (0 to 12.2 m). Sediment samples were acquired in intervals between 0.6 and 1.8 m. Cores were inspected and the lithology described. Sediment sampling and analyses methods were used as per Kennedy et al. (2000). Briefly, sediment were acquired anoxically and preserved under N_2 headspace. Total Fe and Fe^{2+} are measured using Hach Methods 8146 and 8147, respectively, adopted from Standard Methods for Water and Wastewater (Eaton et al., 1995). Sulfide is

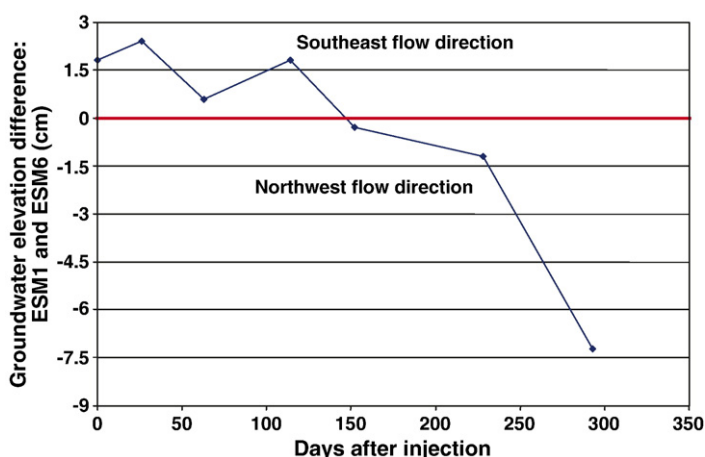


Fig. 2. Ground water flow gradient between ESM6 and ESM1 with respect to time. A positive gradient indicates flow from ESM6 towards ESM1 (the injector) while negative indices indicate the reversal in ground water flow.

measured using Hach Method 8131, which is EPA approved. Mineral sulfides are volatilized from sediment using a sequential extraction process. Initially, the sediment sample is subjected to 6 N HCl for 72 h to extract monosulfides, e.g., FeS. The same sediment is subjected to 1 N Cr^{2+} and 12 N HCl for an additional 72 h to extract sulfides from FeS_2 and S^0 . For both extractions, sulfides are trapped in a zinc acetate solution and analyzed using Hach Method 8131. The 6 N acid solution from the first extraction is analyzed for Fe(II) and Fe Total to measure bulk Fe in the sediment. Bulk iron is the total amount of Fe(II) and Fe(III) found on sediment particles. Bulk Fe (III) is determined by subtracting Fe(II) from Fe Total. Some forms of iron, e.g., magnetite, are resistant to extraction by 6 N HCl. If the presence of resistant iron minerals is suspected, and a complete iron extraction required, a stronger extractant can be used, e.g., 12 N HCl. Sediment analyses were performed at Rowan University, Glassboro, NJ.

3.3. Aqueous sampling

Water from monitoring wells was sampled before and immediately after injection, then periodically (approximately each month). Water samples were collected from all monitoring wells for laboratory analyses of PCE, TCE, cDCE, and VC using gas chromatography (EPA Method 8021), and total organic carbon (TOC) and SO_4^{2-} using a TOC analyzer (EPA Method 415) and ion chromatograph (EPA Method 300), respectively. Chlorinated compound analyses were performed by the Dover National Test Site Research Laboratory, Dover AFB, Dover, DE. TOC and Sulfate analyses were performed at Rowan University, Glassboro, NJ.

3.4. Microcosm methods

Sediment samples from the BiRD field site were obtained for microcosm testing 8 months after the injection treatment. Samples were acquired next to ESM1 from a depth of 11.6 to 12.2 m in a sand layer which had visible darkening (an indication of FeS minerals). Upon retrieval, the core was immediately placed into a field portable anaerobic glove bag which had been quadruple purged with ultrapure N_2 gas. Approximately 10 g sediment was placed into serum tubes filling them to approximately 3/4 the bottle volume. Each bottle was sealed with a rubber stopper secured with an aluminum seal. The bottles were then removed from the glove bag, triple vacuum purged, and refilled with N_2 gas in the field. Half the bottles were sterilized by irradiation to kill any chlororespiring bacteria which may have been present. Irradiation was selected as the sterilization technique as it does not adversely affect FeS mineral reactivity as, perhaps, autoclaving or chemical bactericides. Each bottle was then filled with 2500 $\mu\text{g/l}$ TCE in deoxygenated deionized water. Water in the microcosm had <0.1 mg/l organic carbon, removing any carbon source and further inhibiting bioremediation from occurring. Sample bottles from both the killed and live systems were sacrificed in duplicate and periodically analyzed for TCE, cDCE, and VC using gas chromatography.

3.5. Bioremediation field cell

The bioremediation treatment cell was a separate effort and is reported here as a standard for comparison with BiRD Field Cell (Lee, 2002). Bioremediation was stimulated using edible vegetable oil (VegOil) as an organic substrate. The treatment cell is located approximately 49 m south of the BiRD test site and is laterally positioned with respect to ground water flow. Similar injection and monitoring arrays were used for both the bioremediation and BiRD test sites. The

bioremediation treatment array consisted of four injectors on 1.5 m spacing and a series of ground water monitoring wells ranging from 0.6 to 4.3 m down-flow gradient. A total of 830 l of soybean oil, 83 l of lecithin (an emulsifier), and 30,300 gal of ground water were injected.

4. Results

In this section results from the BiRD field site are presented first. This is followed by results from the microcosm test on sediment from the BiRD field site. Finally, results from the BiRD field site are compared with results from the nearby bioremediation study.

4.1. Lithology

Sediment lithology, and by extension its hydraulic characteristics, affected the distribution and migration of injectate and subsequent treatment. The mineral concentration profiles that follow are superimposed onto a lithology cross-section. The sedimentary sequence includes fine silts grading to sands with underlying gravel to approximately 12.2 m. That sand sequence rests on a low conductivity clay confining layer. As shown below, injectate moved preferentially through conductive sand and gravel layers underlain by clay.

Prior to injection, sediment was orange or yellow brown in color at the level where wells were screened. This color indicated abundant iron oxide mineral coating on grains of quartz sand or gravel. Post injection, there was a distinct change in sediment color which became medium to dark gray, indicating the presence of black colored mineral iron sulfides. This was confirmed by laboratory analysis.

4.2. Mineral iron

Figs. 3–5 show results from sediment analyses along the line of the monitoring wells. Fig. 3 shows a concentration profile of total mineral iron (Fe(II) + Fe(III)) through the monitoring wells, as measured before the injection. Variations in total iron are the result of historical events at the site, from the deposition of sediment to the sampling event. The results indicate that Fe was naturally leached from sediment above approximately 3.4 m (gleying) resulting in lower concentrations (250 and 2000 mg/kg, respectively). Below the leached boundary, iron concentrations are higher, ranging from 2000 to 21,000 mg/kg. Concentrations of iron were adequate for FeS development. Sulfate reduction is not normally a prominent microbial respiration pathway at this site as ground water has less than 25 mg/l sulfate. Prior to injection the sediment had no measurable concentrations of mineral FeS or FeS₂.

Post injection FeS and FeS₂ concentrations are shown through the monitoring well profile in Figs. 4 and 5, respectively. FeS concentrations increased significantly after injection in all borings, attaining a maximum of 112 mg/kg at ESM2. FeS₂ distribution mirrors that of FeS in profile but extends slightly higher in the sediment section with slightly higher concentrations (maximum = 174 mg/kg at ESM2). The distribution of iron sulfide minerals follows local flow pathways that dictated injectate distribution and conformed to conductive sand/gravel layers immediately above clay layers. As with any treatment technology relying on injection, it was not possible to generate iron sulfide minerals throughout the entire injection interval, as defined by the injection well screens. Because the plume has been present for a year, contaminants have penetrated beyond local flow pathways. Therefore, contact between the generated iron sulfide minerals and with entire plume is not possible. However, as the majority of the contaminants

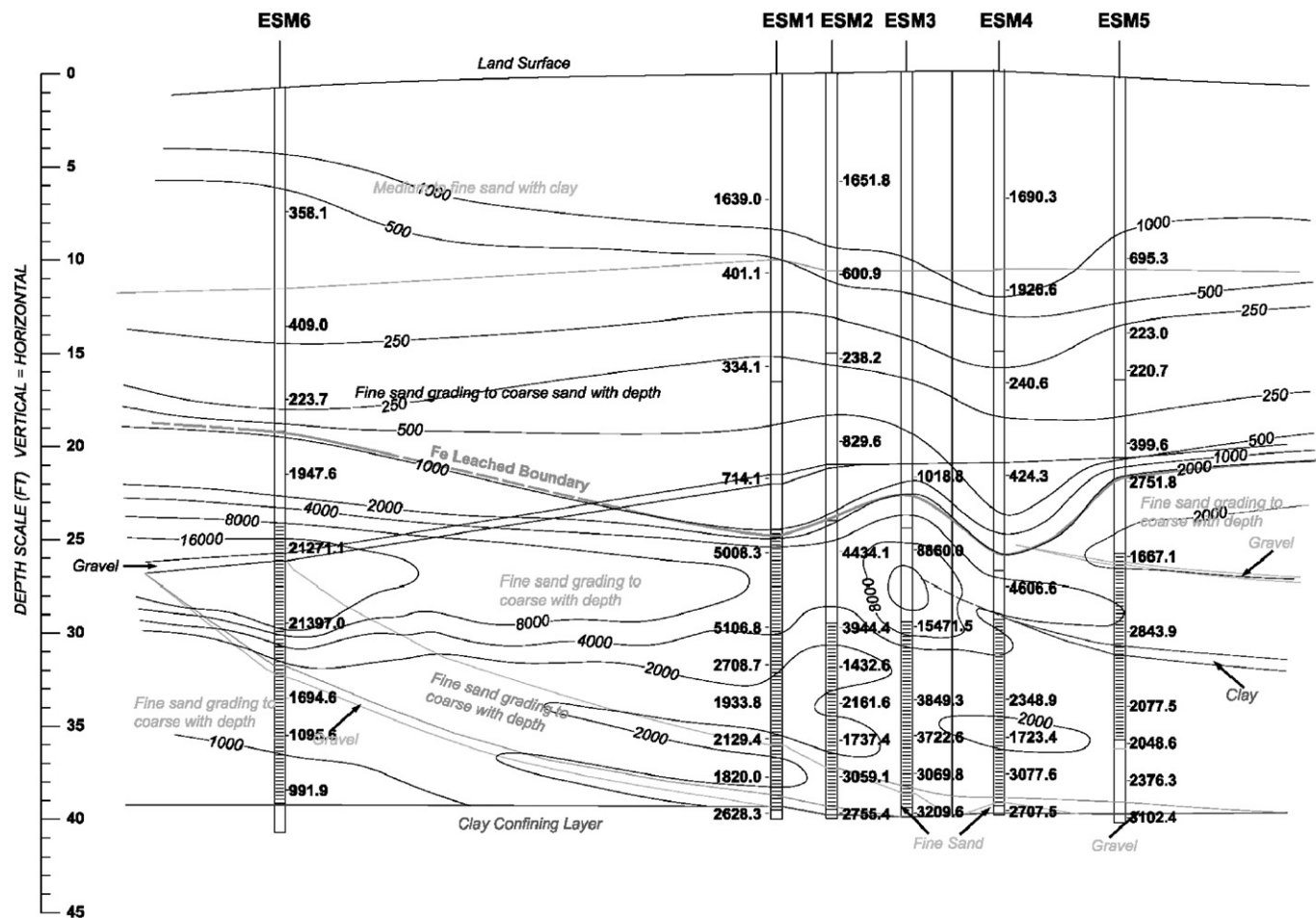


Fig. 3. Total iron, mg/kg (sediment collected before injection).

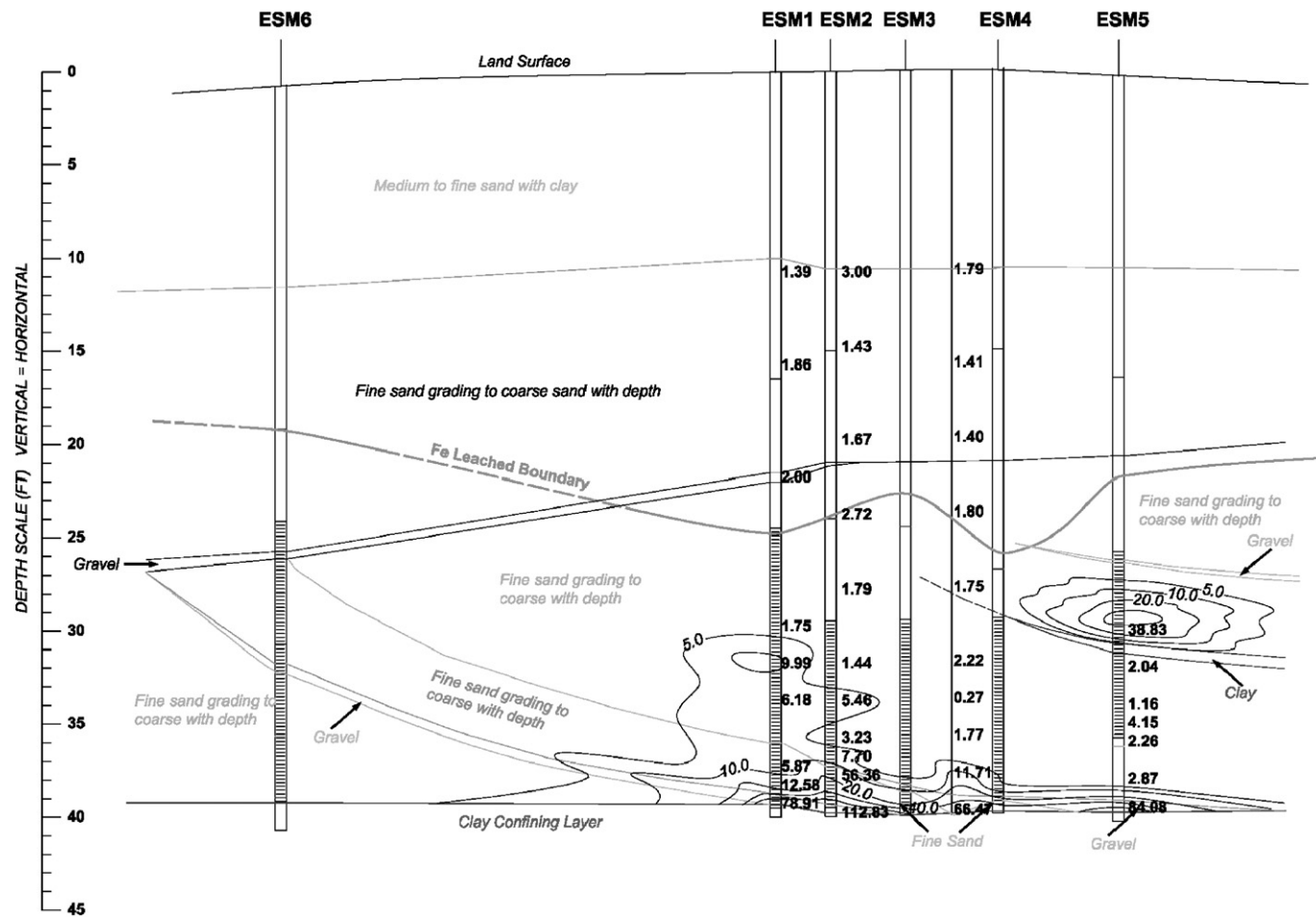
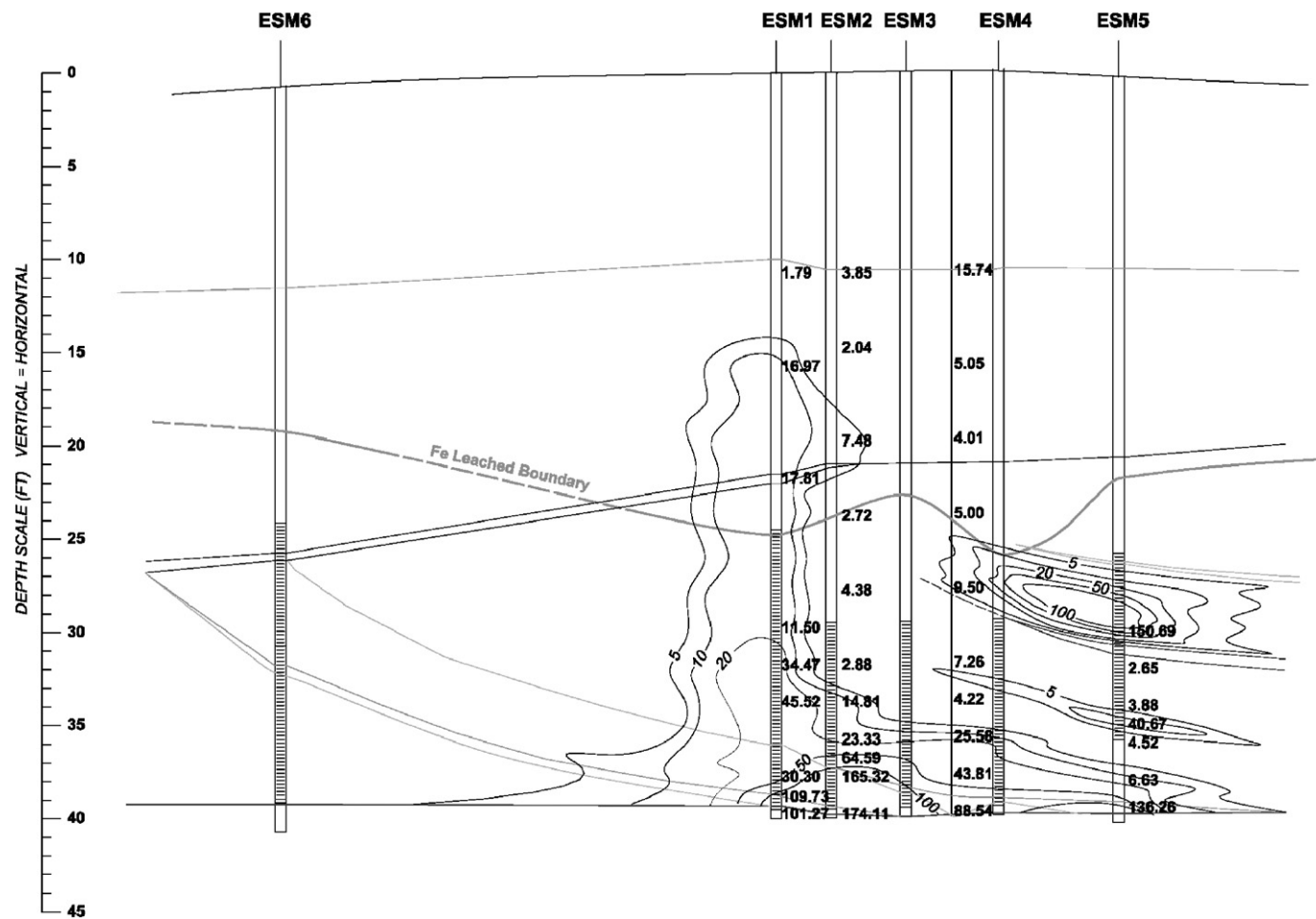


Fig. 4. FeS, mg/kg (sediment collected 9 months after injection).

Fig. 5. FeS_2 , mg/kg (sediment collected 9 months after injection).

move through these local flow pathways, a large portion of the contaminants can be treated; thus, the treatment can be effective.

Most FeS was found about 12.2 m below the ground surface, near the base of the sand and top of the lower clay confining layer. However, FeS was found much higher at ESM5, at about 9.1 m, in an isolated conductive sand channel bound by an underlying clay lens. This channel sand is evidently oblique to the monitoring well array, essentially connecting ESM5 to the injectors. Evidently, injectate was preferentially conducted to ESM5 via this upper channel sand layer resulting in more FeS development and faster treatment at this well compared to monitoring wells that were closer to the injectors but less hydraulically connected.

4.3. Aqueous observations

Concentrations with respect to time for ESM1 to ESM6 are shown in Figs. 6–11. Post injection, concentrations of both SO_4^{2-} and TOC declined rapidly near the injectors (ESM1 and ESM2) due to biological consumption and advection. Small transient quantities of injectate were observed over time in the intermediate monitoring wells. Little SO_4^{2-} or TOC was observed at ESM5.

Contaminated ground water from the site was used for the injectate so CAH concentrations were little perturbed by actual injection. CAH removal began to occur rapidly after injection, especially in the most up-gradient observation points (ESM1 and ESM2) and in the most down-gradient monitoring point, ESM5. Treatment for the intermediate observation points (ESM3 and ESM4) was slightly delayed. Treatment response was influenced by hydraulic heterogeneities in the aquifer media. All wells ultimately responded favorably with marked decreases in both TCE and DCE. VC was not generated. Concentrations of PCE for the observations wells are plotted separately (Fig. 12). Most of the monitoring wells showed decreases in PCE, averaging approximately 120 $\mu\text{g/l}$ before injection and 20 $\mu\text{g/l}$ during the final monitoring event.

ESM6 was designed to monitor up-gradient background conditions. CAH concentrations were generally stable at ESM6 during the early part of the demonstration, when ground water flow was towards the east and CAH was decreasing in ESM1 to ESM5. However, when the ground water flow direction reversed, both TCE and DCE concentrations decreased rapidly at ESM6 as well. Small quantities of sulfate were also observed late in the test for this well further indicating the reversal in ground water flow direction.

The largest decline in CAH concentrations were observed in ESM5 which is logical as the treatment time through the reaction front increases with distance down-flow gradient. At this point, TCE was reduced to 6% of its original concentration and DCE was treated to 3% of its original concentration. Maximum treatment was achieved 228 days after injection. At the end of the test, CAH concentrations increased slightly at ESM5 due to the ground water flow reversal.

4.4. Microcosm results

Sediment used for microcosm construction was determined to have 59 mg/kg FeS and 134 mg/kg FeS_2 and was characteristically dark gray in color when obtained. Concentrations of TCE with respect to time for the live and killed microcosms are shown in Fig. 13. TCE was removed from both the live and killed systems at the same rate demonstrating that abiotic processes dominate treatment. Overall, TCE was treated to approximately 17% of its original concentration during 76 days with an apparent half-life of approximately 30 days. DCE was mostly not detectable; however, transient concentrations up to 0.17 mg/l were occasionally observed. VC was not generated.

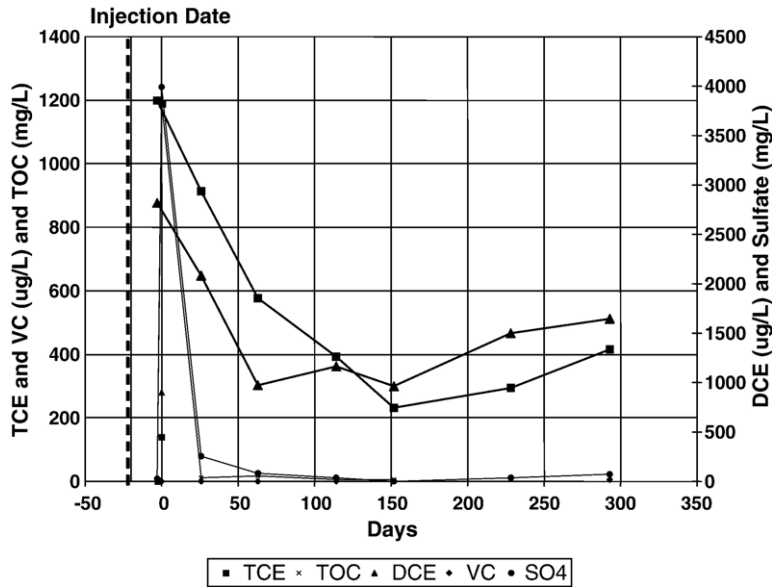


Fig. 6. ESM1 aqueous CAH and injectate concentrations with respect to time.

4.5. Comparison with VegOil bioremediation

Comparisons were made between the VegOil bioremediation and BiRD test cells at DAFB for the most up-gradient and down-gradient observation points for both systems. VegOil bioremediation resulted in significant decreases in TCE; however, there were also equivalent

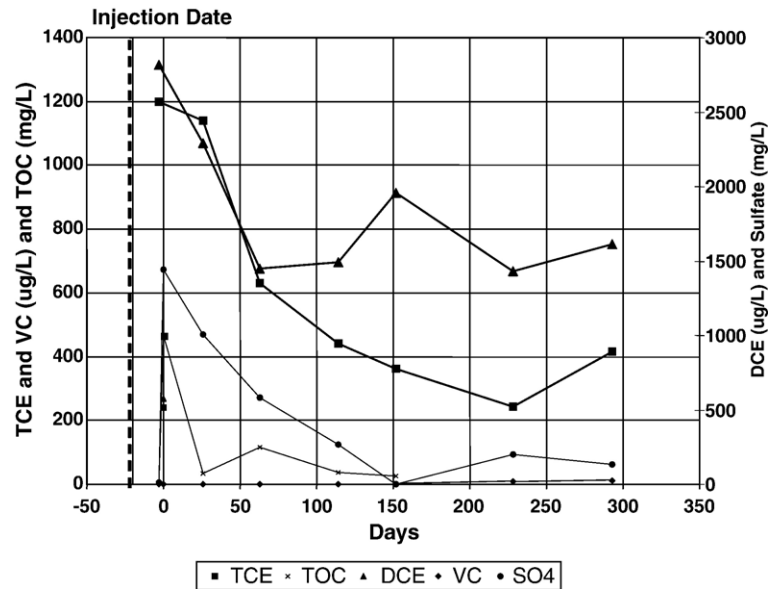


Fig. 7. ESM2 aqueous CAH and injectate concentrations with respect to time.

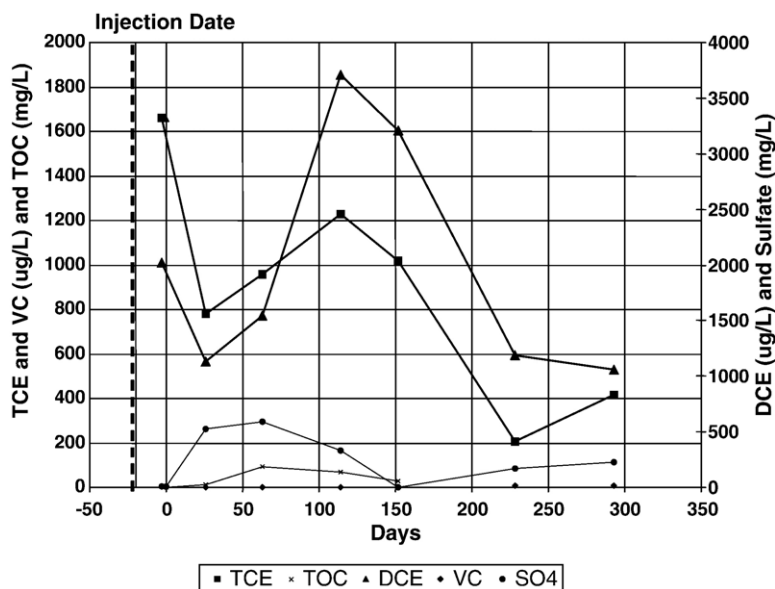


Fig. 8. ESM3 aqueous CAH and injectate concentrations with respect to time.

increases in daughter products, principally cDCE and to a lesser extent VC. Initial concentrations of TCE and cDCE for ESM1 and ESM5 (BiRD) and comparably positioned wells in the VegOil bioremediation test cell were normalized to 1.0 to permit direct comparison (Figs. 14 and 15). As shown, both BiRD and VegOil bioremediation resulted in TCE reduction; however, significant

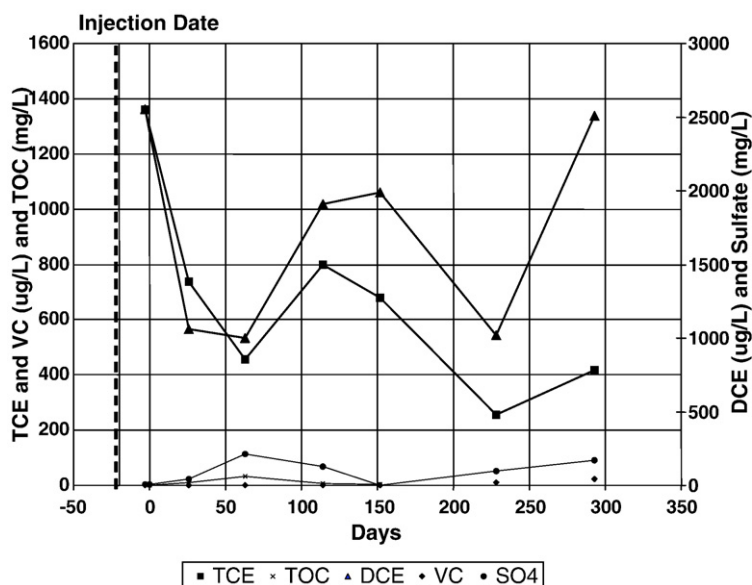


Fig. 9. ESM4 aqueous CAH and injectate concentrations with respect to time.

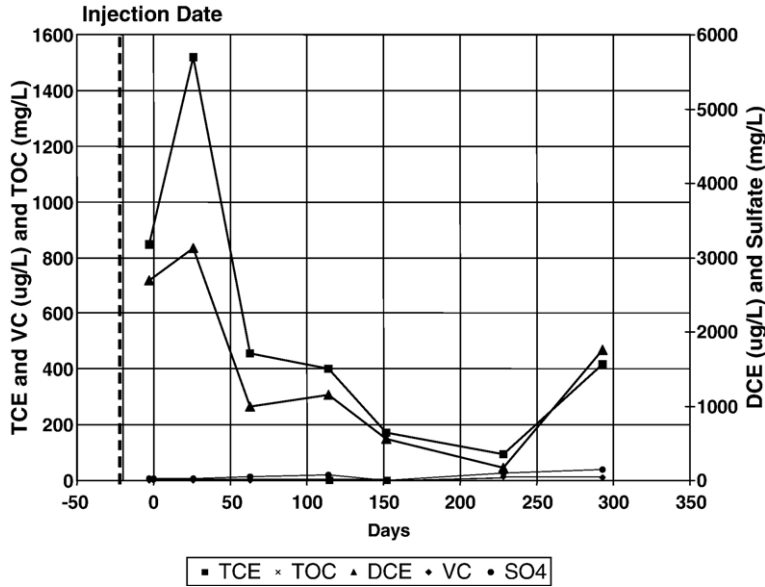


Fig. 10. ESM5 aqueous CAH and injectate concentrations with respect to time.

differences between the remediation plots were observed with respect to cDCE. For the bioremediation plot, cDCE experienced a two-fold increase but for the BiRD plot DCE was not produced and pre-existing cDCE was reduced up to 97%. However, more monitoring should be conducted to determine the longevity of both remediation methods.

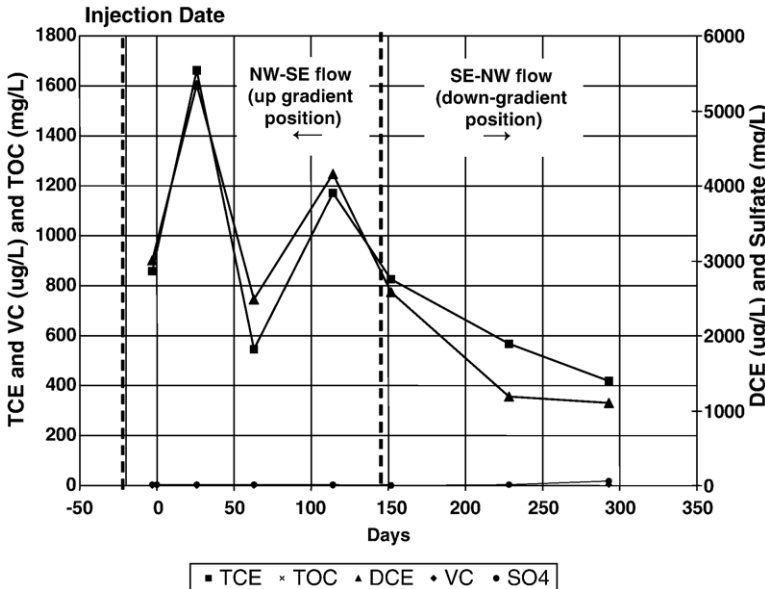


Fig. 11. ESM6 aqueous CAH and injectate concentrations with respect to time.

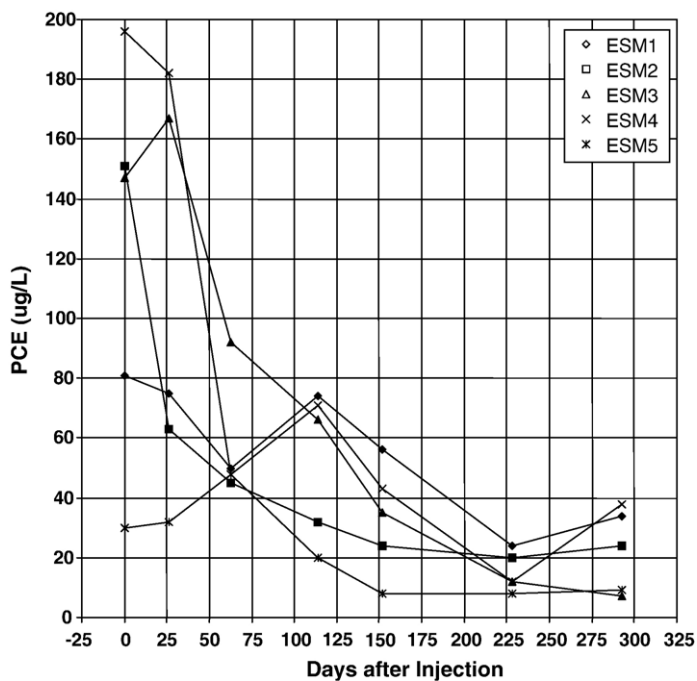


Fig. 12. PCE concentrations for monitoring wells ESM1 and ESM5.

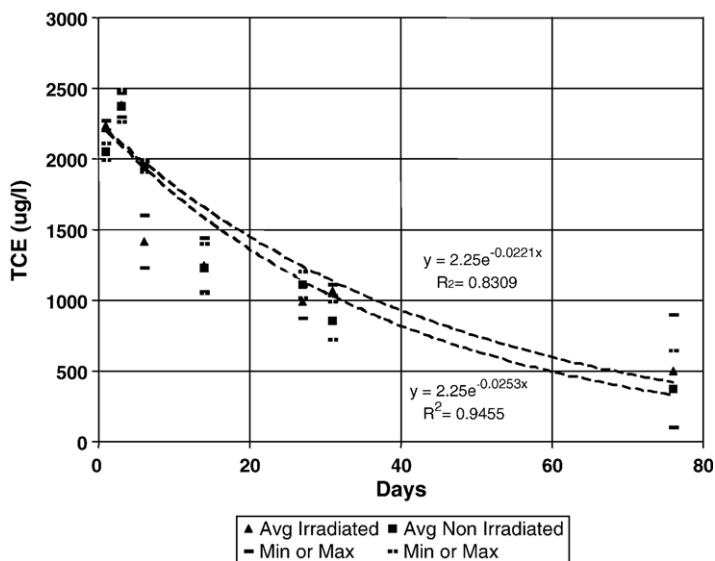


Fig. 13. TCE concentrations for the live and killed microcosms. Dashes are maximum and minimum values. Triangles and squares are average of three values.

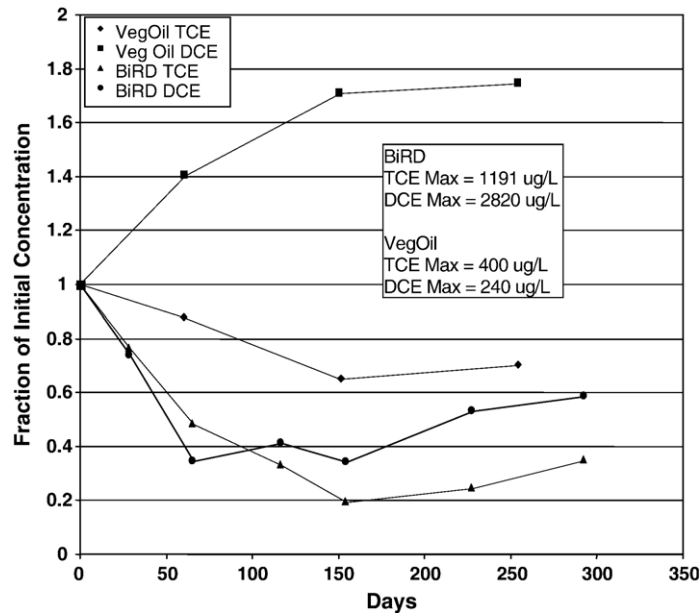


Fig. 14. TCE and DCE concentrations for the BiRD and bioremediation sites for monitoring points closest to injection. Initial values normalized to 1.0.

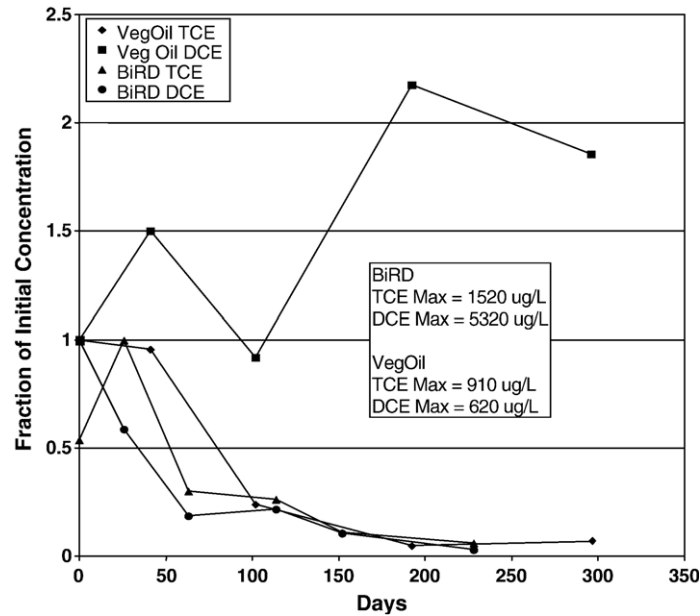


Fig. 15. Comparison of TCE and DCE concentrations for BiRD and bioremediation sites for most down-gradient monitoring points. Initial values normalized to 1.0.

5. Conclusions

Biogeochemical Reductive Dechlorination (BiRD) was successfully tested at the Target Area 1 site at DAFB. DAFB was a good test site as the ground water had very low naturally occurring concentrations of SO_4^{2-} and bioremediation had been tested nearby. Therefore, as BiRD would not have occurred naturally at the DAFB site, a direct comparison between biostimulation and BiRD could be made.

The native sediment contained, as is typical, adequate quantities of native iron for mineral iron sulfide formation. Biogeochemical stimulation required the addition of both organic and sulfate which resulted in the generation of significant quantities of FeS and FeS_2 via biogeochemical processes. This demonstrates that the in-situ formation of iron sulfides can be stimulated by design. The treatment was simple to apply and, compared to the VegOil bioremediation plot, required only the addition of a soluble organic (sodium (L) lactate) and a common sulfate salt (magnesium sulfate, also known as Epsom salt) which is used as a cattle feed additive and soil amendment.

CAH treatment response was observed within a few weeks of injection indicating a very short lag period. PCE, TCE, and DCE concentrations were all reduced and VC was not generated. The generated iron sulfides apparently formed a flow-through reactive treatment zone. Therefore, maximum treatment generally occurred at the most down-gradient observation point (ESM5) where the original concentrations of TCE (1520 $\mu\text{g/l}$) and DCE (5320 $\mu\text{g/l}$) were reduced by 95% or more. The microcosm tests performed using FeS bearing sediment from the site demonstrated that abiotic processes were responsible for TCE treatment. The observed TCE half-life was approximately 30 days which is acceptably rapid. It should be noted that although encouraging results were observed, the test was quite limited both in aerial extent and in the quantity of injectate added. More conclusive results may have been achieved by monitoring the site for a longer period of time or by developing a larger treatment area with higher concentrations or volume of injectate. TCE was also treated in the bioremediation test plot but equivalent concentrations of persistent cDCE, with lesser amount of VC, daughter products were generated.

It is likely that iron sulfides reduce CAH at many sites where sulfate and organics occur naturally or as a result of human impact; however, BiRD has been overlooked because (a) investigators were not looking for it and (b) no distinct daughter products are generated. This demonstration project indicates that BiRD can be stimulated in aquifers that lack necessary organic and/or sulfate. These may be added by injection in soluble form, the method employed in the project described in this paper, or by placement in permeable reactive trench as solids. Future research should explore the use of permeable reactive trenches.

There are several theoretical advantages related to stimulating BiRD for the purpose of destroying contaminants. Sulfate-reducing bacteria are ubiquitous in the subsurface and are easy to stimulate. The necessary amendments for BiRD are readily available and inexpensive. The problems associated with subsurface mixing are diminished as highly soluble injectates are used, and native sediment is essentially transformed into a permeable reactive zone. Finally, CAH treatment via BiRD may be more complete with few daughter products. BiRD may be a viable and economic alternative method for chlorinated solvent remediation combining the beneficial attributes of bioremediation and chemical treatment. Further demonstrations are needed, of longer duration and treating larger aquifer volumes.

It is unlikely that BiRD could be used to completely remove a contaminant source. Thus, other technologies should be used to remove the source. BiRD can be used to disconnect a source from its plume, by creating a treatment zone in the up-gradient portion of the plume. Of course, this

would only be needed if the source cannot be removed. BiRD can also be used to stop down-gradient movement of plume, by creating a treatment zone in the down-gradient portion of the plume. Finally, BiRD can be used to treat any portion of a plume, by locating injection wells appropriately. However, long-term maintenance of any treatment zone will require periodic reinjection if the outer layer of iron sulfide minerals, the layer most in contact with contaminants, become oxidized over time. Reinjection will convert the oxidized outer layer once again to iron sulfide minerals.

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