

OVERCOMING THE LIMITATIONS OF *IN SITU* BIOREMEDIATION IN LOW PERMEABILITY SOILS THROUGH HYDRAULIC SOIL FRACTURING

by

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ABSTRACT

Hydraulic Soil Fracturing is a process that is used to enhance the *in situ* remediation of contaminants present in low permeability soils (i.e. soils with a hydraulic conductivity of less than 10^{-6} m/s). Soil fracturing has been successfully applied since the early 1990's to accelerate site clean-ups using physical "mass transfer" remediation technologies such as soil vapour extraction and pump and treat.

The current trend in *in situ* remediation is moving away from physical mass transfer processes towards the use of bioremediation to remediate soil and groundwater contamination *in situ*. Motivating factors for the increasing use of *in situ* bioremediation include its non-intrusiveness, cost-effectiveness, and speedy conversion of contaminants to innocuous end products. The growing use of *in situ* bioremediation has also led to the realization that its effectiveness is severely limited in low permeability soils because of constraints for adequate delivery of electron acceptors, nutrients, etc. required for sustained microbial metabolism.

Recent applications of bioremediation have demonstrated how soil hydraulic fracturing can accelerate the degradation of contaminants *in situ* by overcoming the limitations of unfavourable geology. A pilot-scale field test of enhanced bioremediation was conducted at a U.S. EPA Superfund site near Louisville, Kentucky that combined the use of hydraulic soil fracturing and a natural polymeric organic bio-amendment called "chitin". The primary objectives of the field test were to determine if soil fracturing would enhance the geologic formation's permeability, and whether the simultaneous delivery of chitin would impact the aquifer's geochemistry in ways conducive to anaerobic reductive dechlorination (ARD) of dissolved chlorinated solvents. The distribution and impact of chitin- and sand-filled fractures to saturated, low permeability sediments was evaluated using hydrogeologic, geophysical, and geochemical parameters. The results indicated that, where distributed, chitin favourably impacted redox conditions and supported enhanced ARD of chlorinated solvents. This case study demonstrates how soil hydraulic fracturing and simultaneous injection of a bio-amendment, chitin, can be used to cost-effectively bioremediate solvents in a low permeability, variably saturated hydrogeologic system.

HYDRAULIC SOIL FRACTURING

Hydraulic Soil Fracturing (“HSF”) is an adaptation of conventional hydraulic fracturing, traditionally used in the oil & gas industry, to increase the effectiveness of remediation in contaminated, low permeability soils. It is a process whereby a sand-laden slurry is pumped into a formation (ie. soil or rock) at a rate and pressure high enough to overcome the in situ confining stress and the material strength of a formation resulting in the creation of a fracture or parting. The resulting fracture contains permeable sand which keeps the fracture “propped” open and serves as a permeable pathway for the flow of fluids toward the well.

Conventional Hydraulic Fracturing has been used in the petroleum industry since the late 1940’s to enhance the production of oil and gas from low yielding formations which would otherwise be uneconomical to produce. When a hydraulically fractured well is produced, the induced fractures provide permeable pathways so that fluids can flow to the well at a greater rate than would otherwise be possible. Presently, about 70% of all oil and gas wells drilled worldwide are hydraulically fractured to stimulate and enhance their production.

IN SITU REMEDIATION OF LOW PERMEABILITY SOILS

Much of North America is covered with fine-grained sediments of low inherent permeability. These fine-grained soils are generally not very permeable to either liquids or gases. Consequently, the effectiveness of conventional in situ remedial technologies at contaminated sites underlain by fine grained soils is extremely limited, and remediation is often long term and costly. Limitations to the in situ clean-up in fine-grained soils are generally manifested by low contaminant removal/treatment rates and small zones of influence at recovery wells.

Hydraulic Soil Fracturing, when coupled with the appropriate remedial technology(s), has been shown to enhance the effectiveness of clean-ups in low permeability soils (ie. those with a hydraulic conductivity of 10^{-6} m/s or less). The fracturing process creates a network of subhorizontal to subvertical fracture pathways in the contaminated soil mass. The permeable fractures created in this manner become the preferred migration pathways for the subsequent removal or in-place degradation of contaminants.

Frequently, the network of sand-filled fractures intersects natural fractures and permeable lenses in which contamination often resides. This serves to drain the contamination more effectively and generally results in an increased radius of influence and contaminant removal or treatment rate for the recovery well. Furthermore, as contaminant migration in fine-grained soils is controlled to a large degree by diffusion, the fracture network significantly lessens the time to remediate a site by reducing the length of the diffusion pathways.

Presently, the trend in remediation is moving away from physical mass transfer processes towards the use of bioremediation to remediate soil and groundwater contamination *in situ*. Advances in bioremediation technologies are making this approach more cost-effective. Bioremediation also has the advantages of being a relatively non-disruptive approach and can convert contaminants into innocuous end-products. However, the growing use of *in situ* bioremediation has also led to the realization that its effectiveness is severely limited in low permeability soils because of constraints for adequate delivery of electron acceptors, nutrients, and substrates required for sustained microbial metabolism. This realization has, until recently, precluded the widespread use of *in situ* bioremediation of contaminated soil or groundwater in low permeability sediments, as few sites have been successfully remediated in this manner (Walden, 1997).

FRACTURE-ENHANCED *IN SITU* BIOREMEDIATION

Remediation of contaminated sites having silty or clayey soils poses special technical challenges to site managers because such low permeability soils typically resist remediation with conventional technologies (American Petroleum Institute, 1995). Hydraulic Soil Fracturing and Bioremediation have both been identified as promising remedial techniques in low permeability soils (Walden, 1997). However, these two remedial technologies have until recently, never been applied in combination on a commercial scale, and very few sites exist that have undergone fracture-enhanced bioremediation.

There are four important factors that determine the efficacy of *in situ* fracture-enhanced bioremediation at contaminated sites, namely:

- Nature of the Contaminant
- Subsurface Geologic Factors
- Substrate Delivery Method, and,
- Subsurface Biochemical Processes.

The significance of each of these factors is summarized as follows:

Nature of Contaminant

The nature of the subsurface contaminant is important in determining whether it can be easily biodegraded. It also determines the type of biological metabolic process(es) that are likely to transform a specific contaminant to its end products (i.e. aerobic, anaerobic, cometabolic, etc.). The key limiting properties that may limit bioremediation are the contaminant's tendency to sorb to subsurface solids and to partition into a nonaqueous phase that travels separately from the groundwater (U.S. National Research Council, 1993). The nature of the contaminant will therefore influence the approach to effective bioremediation and the length of time to remediate a contaminated site.

Geologic Factors

Regardless of the *in situ* remedial technology used, its application will have limits when applied in the field to remediate a site. Those limits are related to basic geologic formations and properties (Nyer, 1996); site geology ultimately controls remediation. *In situ* remediation in low permeability soils is limited by diffusion-controlled movement of fluids which requires long remediation time frames and results in high life-cycle costs. Attempts at *in situ* bioremediation in low permeability soils has also led to the realization that its effectiveness is severely limited because of constraints for adequate delivery of electron acceptors, nutrients, etc. required for sustained microbial metabolism.

Substrate Delivery Method

Applications of *in situ* bioremediation documented in the literature often rely upon the introduction of fluids or solid phase bioamendments into the subsurface to either biostimulate or bioaugment microbial processes responsible for contaminant degradation. These fluids or bioamendments are often delivered or injected into boreholes or wells and rely on natural flushing to move the material through the aquifer to effect groundwater treatment (Nyer, 2003). However, the subsequent movement and distribution of these materials is more often than not poorly understood, as is their reactions with the surrounding contaminants and aquifer geochemistry. Low permeability sediments can also restrict the placement of treatment fluids and amendments to the near well bore, thus necessitating the placement of an impractically large number of wells to ensure full treatment coverage in a contaminant plume.

Subsurface Biochemical Processes

Microbial transformation of organic contaminants normally occurs because the organisms can use the contaminants for their own growth and reproduction. The exact form of this basic microbial metabolism is dependent on the type of organisms, contaminant, and geological and chemical conditions at the contaminated site. "Bioremediation" is the term generally associated with the attenuation of biodegradable contaminants through biochemical reactions.

There are two main categories for biological enhancement: aerobic and anaerobic. Contaminants such as petroleum hydrocarbons (e.g. gasoline) that use molecular oxygen as the primary electron acceptor are destroyed through *aerobic* respiration. Contaminants such as halogenated compounds (e.g. chlorinated solvents) that use inorganic chemicals other than molecular oxygen as the primary electron acceptor are destroyed by *anaerobic* respiration. The relative energy that bacteria can derive for the bioremediation of contaminants, and hence speed of contaminant degradation to innocuous end products, is a function of which electron acceptor is being used in the biochemical process. Since electron acceptors in *aerobic* biodegradation processes are associated with higher energy levels than in *anaerobic* processes, contaminants that degrade under aerobic conditions, such as gasoline, can be remediated faster than those that degrade anaerobically, such as chlorinated solvents.

**CASE STUDY:
FRACTURE-ENHANCED, *IN SITU* BIOREMEDIATION OF CHLORINATED
HYDROCARBONS, US EPA SUPERFUND SITE - KENTUCKY, USA**

Background

The United States National Science Foundation sponsored a pilot-scale field test of fracture-enhanced bioremediation at the former “Distler Brickyard” Superfund site near Louisville, Kentucky, from October 2001 to January 2002. The National Science Foundation retained North Wind Environmental Inc., an Idaho Falls, Idaho based environmental consulting firm, as the principal investigator into the application of innovative bioremediation techniques for remediating chlorinated aliphatic hydrocarbon (CAH) contaminants underlying the site. Frac Rite Environmental Ltd. was retained to provide fracture-enhancement services to enhance the effectiveness of bioremediation.

As a result of past waste-handling activities, groundwater at the Distler Brickyard site contains trichloroethene (TCE) and *cis*-1,2 dichloroethene (DCE) at concentrations reaching nearly 100 µg/L and 500 µg/L, respectively. Although some bioremediation of contaminants via anaerobic reductive dechlorination (ARD) was occurring naturally, the rate and extent of ARD reactions were limited by a lack of available electron donor and the low permeability of the formation. For this reason, a remediation technology that enhances natural ARD via electron donor addition was hypothesized to be a viable method for reducing CAH concentrations to acceptable levels.

Challenges

Remediation of CAHs at the Distler Site presented a number of challenges:

- 1) contamination is present in low permeability sediments,
- 2) the zone of contamination is variably saturated depending on seasonal changes in precipitation, and
- 3) available funding for remediation is limited.

In order to deal with these challenges, a low-cost, low-maintenance remedy that was effective under variably saturated conditions was required. The selected approach combined the use of soil hydraulic fracturing (HSF) with anaerobic bioremediation enhanced by the simultaneous injection of “chitin”, a solid, natural polymeric organic material consisting of shrimp and crab shells.

Operational and logistical challenges consisted of incorporating the required mass of chitin into the sand-laden fracture slurry without compromising the slurry and its ability to create discrete, permeable fractures in the contaminated soil mass.

Objectives

The primary objective of the field pilot was to determine if the fracture-enhanced application of chitin into soils containing chlorinated contaminants was a technically feasible approach for bioremediation on a commercial scale. The specific objectives were to determine whether a) chitin could be emplaced into a low permeability medium during soil hydraulic fracturing, b) soil hydraulic fracturing enhances the bulk permeability of the formation; and, c) chitin, once emplaced, produces concentrations of volatile fatty acids that impact the aquifer's geochemistry in ways conducive to anaerobic bioremediation.

Approach

The approach to the evaluation of fracture-enhanced bioremediation using chitin consisted of laboratory studies on chitin, baseline hydrogeologic and groundwater characterization, field fracturing and chitin emplacement, geophysical mapping of subsurface fractures, post-fracture hydrogeologic testing, and subsequent monthly groundwater monitoring and sampling. Chitin had been identified by North Wind Environmental Inc. and JRW Technologies Inc. as a relatively long-lived source of nitrogen and electron donor in the form of volatile fatty acids for anaerobic bioremediation. Laboratory studies conducted by the University of Illinois at Urbana/Champaign confirmed that chitin produces volatile fatty acids shown to be high quality electron donors for anaerobic reductive chlorination.

Bench scale testing conducted by Frac Rite Environmental Ltd. demonstrated that chitin could be incorporated into conventional, water-based fracture slurries at a ratio of chitin to frac sand of 1:4. Based on these results, a field pilot was designed to simultaneously fracture low permeability soils and deliver chitin into the source area containing chlorinated hydrocarbon contaminants (Figure 1). Geophysical mapping of the geometric configuration of each individual fracture was carried out using surface-mounted tiltmeters to correlate the distribution of chitin in the subsurface with groundwater sampling data from surrounding monitoring wells.

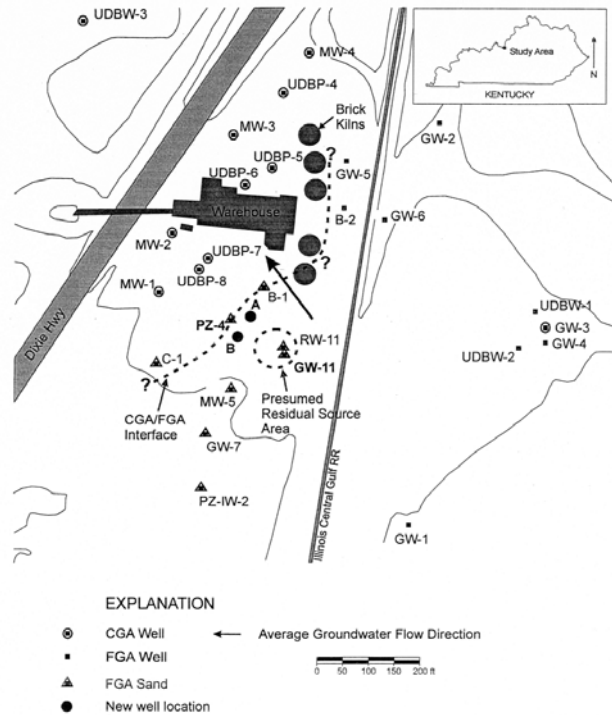


FIGURE 1 – Distler Site Plan

Field Pilot

Soil Hydraulic Fracturing was conducted at the Distler Brickyard in October, 2001. A single borehole was advanced within the contaminant source area near the bedrock surface. The subsurface stratigraphy consisted of approximately 12 metres of silty sand and silty clay overlying shale bedrock. The groundwater table was measured at approximately 9 metres below the ground surface.

Three fractures containing chitin and sand were initiated in a borehole at Fracture Well "B" (Figure 2) at depths of 7.6 m, 10.0 m, and 11.6 m in silty sand and silty clay soils. Fracture initiation and placement efficiency of the chitin/sand slurry was 80% in the silty sands and 100% in the silty clays. The total amount of chitin and sand injected by fracturing the subsoils at Fracture Well "B" was 150 kg and 700 kg, respectively. The borehole was subsequently completed as a monitoring well.

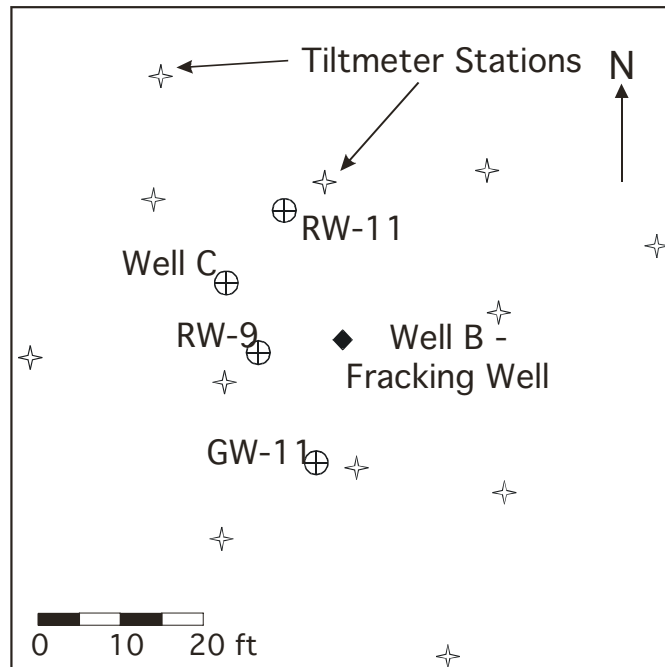


FIGURE 2 - Well locations in contaminant source area

Remote mapping of fractures was carried out using Eco-Scan Inc.'s proprietary tiltmeter geophysics to determine fracture geometry and orientation for each discrete fracture induced. Micro ground surface movements or "tilt signals" induced by subsurface fracturing were collected using an array of surface-mounted ES Model 700 biaxial tiltmeters and dataloggers. This method of fracture mapping was chosen due to its quick set-up in the field, past success on previous fracturing projects, high signal sensitivity, and rapid data acquisition capability.

Post-fracturing hydrogeologic testing was performed on Fracture Well B to determine whether fracturing enhanced the hydraulic conductivity of the surrounding soils. Changes

in hydraulic conductivity were evaluated using slug tests and by pump testing the fractured well. Hydraulic conductivity values were derived from the results of testing using the AQTESOLV hydrogeologic software. The hydrogeologic system was modeled as an unconfined aquifer using the Bouwer and Rice (1976) solution.

Groundwater sampling was conducted both prior to and monthly following the fracturing and chitin emplacement for a period of four months. The analytes consisted of electron donor parameters (chemical oxygen demand, and individual volatile fatty acids), reduction-oxidation parameters (nitrate, ferrous iron, sulphate, and methane), and anaerobic reductive dechlorination parameters (chloroethenes and ethane, chloroethanes and ethane).

Results

The results of post-fracture testing and monitoring over a four month period were analyzed to assess the performance of fracture-enhanced bioremediation of chlorinated solvents at the Distler site. The results are discussed in terms of the impact of chitin and fracture-enhancement to the Hydrogeologic System; the Geochemical Environment, and the Dechlorination of Contaminants.

Impact to the Hydrogeologic System

The results of the pre- and post-fracturing slug tests were compared to determine the effect of the fracturing on the hydraulic conductivity of the formation in the Well C area (Figure 2), approximately 4 m from Fracture Well B. The hydraulic conductivity values obtained from these slug tests were 1.2×10^{-5} cm/sec and 1.1×10^{-4} cm/sec for the pre- and post-fracturing slug tests, respectively. These results would appear to indicate that the fracturing process had increased the hydraulic conductivity of the formation by approximately an order of magnitude

A pumping test was performed to assess the relative connectivity of Fracture Well B to the surrounding monitoring wells based on the configuration of fractures produced (Table 1).

Table 1 - Fracture Characteristics from Tiltmeter Analysis

<i>Fracture No. and Depth</i>	<i>Fracture Fluid Volume (litres)</i>	<i>Fracture Dip Angle (degrees)</i>	<i>Fracture Azimuth (degrees)</i>	<i>Fracture Thickness (mm)</i>	<i>Effective Fracture Radius (m)</i>
FWB-1 (7.6m)	950	78	158	30	1.0
FWB-2 (10 m)	1040	22	106	23	4.2
FWB-3 (11.6 m)	1135	32	101	35	3.9

Each monitoring well responded almost immediately to pumping in Fracture Well B, suggesting that fractures hydraulically connected the group of monitoring wells in the vicinity of Fracture Well B.

Considering that the radius of influence of the fractures predicted from the tiltmeter modeling results described above, and the apparent connectivity of all four monitoring wells to Well B as indicated by the pumping test, it is likely that the fracturing process increased the hydraulic conductivity and connectivity in this area of the formation.

Impact to the Geochemical Environment

The impact of post-fracturing chitin placement was assessed by monitoring the presence of electron donors in groundwater, as measured by the concentrations of individual volatile fatty acids (VFAs); reduction-oxidation parameters; and, anaerobic reductive chlorination (ARD) parameters in monitoring wells RW-9 and Well C, respectively.

Figures 3(a) and 4(a) show that propionate was the dominant VFA observed in RW-9 and increased to a maximum concentration of around 600 mg/L. Isovalerate was also detected at RW-9 at concentrations as high as approximately 300 mg/L. These results are consistent with the laboratory column studies described above in which propionate is the dominant VFA and isovalerate the secondary VFA produced from fermentation of chitin. Concentrations of VFAs were not as well established at Well C. Concentrations of butyrate of approximately 25 mg/L were observed in November 2001, but all VFAs had dropped below detection by January 2002.

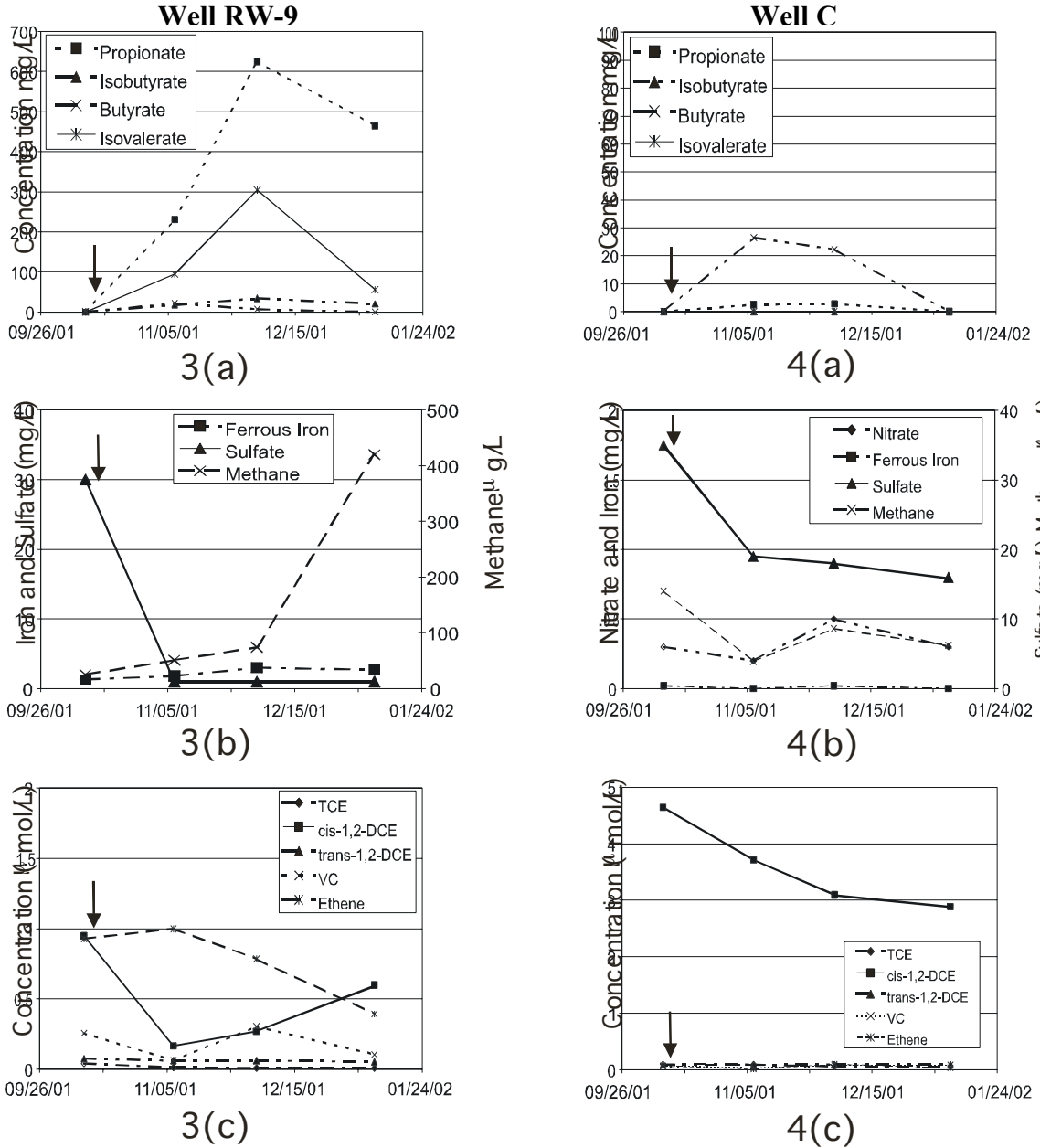
In order for complete ARD of chlorinated aliphatic hydrocarbons such as TCE to proceed to non-chlorinated products, the redox conditions must be very reducing (methanogenic). Redox conditions in the fracturing area were determined before and following the chitin emplacement by monitoring concentrations of nitrate, ferrous iron, sulfate, and methane.

As seen in Figure 3(b), prior to chitin emplacement ferrous iron was present in low but measurable concentrations (approximately 1.3 mg/L), sulfate concentrations were 30 mg/L, and methane was less than 40 μ g/L. These data indicate that iron-reducing conditions, not reducing enough for complete ARD of TCE, existed at RW-9 prior to chitin emplacement.

After chitin emplacement, ferrous iron concentrations increased to exceed the range of the analytical method, sulfate concentrations dropped to below detection, and methane increased to almost 450 μ g/L (Figure 3(a)). These trends indicate the onset of sulfate reduction and methanogenesis in the RW-9 area, suggesting that the presence of VFAs from chitin has resulted in the creation of a geochemical environment conducive to complete ARD of TCE.

The data indicate that conditions at Well C were mildly reducing (in the range of nitrate-reducing) prior to chitin emplacement. After chitin emplacement, sulfate decreased to about 16 mg/L; however, nitrate and methane remained consistent with pre-chitin values

(Figure 4(b)). The presence of sulfate and the absence of methane following chitin emplacement indicate that the redox conditions necessary for complete ARD of TCE were not created in the Well C area. This is not surprising given that significant concentrations of VFAs were not observed at this well.



FIGURES 3 and 4. Electron donor (a), redox parameters (b), and ARD parameters (c) in Well RW-9 (Figure 3) and Well C (Figure 4). The arrows () indicate the timing of chitin emplacement.

Impact on the Dechlorination of Contaminants

The effect of chitin emplacement on the ARD of TCE was assessed by monitoring the concentrations of TCE and degradation products cis-1,2-DCE, VC, and ethene in monitoring wells. Figure 3(c) presents the concentrations of chloroethenes in RW-9. Prior to chitin emplacement, cis-1,2-DCE was the dominant chloroethene, followed by significant concentrations of ethene and low levels of VC and TCE.

The presence of cis-1,2-DCE and ethene at significant concentrations and the absence of TCE indicate that ARD of TCE was already occurring to some extent at this location prior to chitin emplacement. After chitin emplacement, cis-1,2-DCE concentrations dropped and ethene became the dominant compound present, indicating enhanced ARD of cis-1,2-DCE. Concentrations of cis-1,2-DCE began to rebound in the last two monitoring rounds indicating that conditions were shifting back toward pre-chitin conditions.

In Well C, cis-1,2-DCE was the dominant chloroethene prior to chitin emplacement; the other chloroethenes were present at relatively low concentrations (< 15 µg/L) (Figure 4(c)). After chitin emplacement, concentrations of cis-1,2-DCE dropped; however, significant concentrations of less-chlorinated degradation products VC and ethene were not produced (Figure 4(c)). These data indicate that ARD of cis-1,2-DCE was not enhanced significantly in the vicinity of Well C by the chitin emplacement at Well B.

CONCLUSIONS

Hydrologic data, geochemical data, and ARD data were evaluated from a field pilot to describe the overall impact of the pilot-scale chitin emplacement on the hydrologic system, geochemical environment, and subsequent remediation potential of the chitin emplacement technology. The results of this pilot project indicated that:

- Soil hydraulic fracturing was successful in simultaneously distributing chitin into contaminated, low permeability soils and increasing the soil hydraulic conductivity by an order of magnitude;
- Chitin, where present, produced significant concentrations of propionate and other VFAs, was able to affect the redox conditions, and enhanced the anaerobic reductive dechlorination of TCE and cis-1,2-DCE contaminants;
- Chitin appears to be an effective slow release electron donor, useful even in variably saturated environments;
- *In situ* bioremediation of chlorinated aliphatic hydrocarbons using soil fracturing with chitin emplacement can be a viable remediation technology for low permeability systems.

Based on the success of this pilot project, the U.S. National Science Foundation authorized a full scale bioremediation of the site. Field work comprising 10 fracture wells and emplacement of 33 chitin fractures was completed in May, 2003. Groundwater monitoring is ongoing and will continue to the spring of 2004.

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