Ground Water Monitoring&Remediation

Behavior of a Chlorinated Ethene Plume following Source-Area Treatment with Fenton's Reagent

by Francis H. Chapelle, Paul M. Bradley, and Clifton C. Casey

Abstract

Monitoring data collected over a 6-year period show that a plume of chlorinated ethene–contaminated ground water has contracted significantly following treatment of the contaminant source area using in situ oxidation. Prior to treatment (1998), concentrations of perchloroethene (PCE) exceeded 4500 μg/L in a contaminant source area associated with a municipal landfill in Kings Bay, Georgia. The plume emanating from this source area was characterized by vinyl chloride (VC) concentrations exceeding 800 μg/L. In situ oxidation using Fenton's reagent lowered PCE concentrations in the source area below 100 μg/L, and PCE concentrations have not rebounded above this level since treatment. In the 6 years following treatment, VC concentrations in the plume have decreased significantly. These concentration declines can be attributed to the movement of Fenton's reagent–treated water downgradient through the system, the cessation of a previously installed pump-and-treat system, and the significant natural attenuation capacity of this anoxic aquifer. While in situ oxidation briefly decreased the abundance and activity of microorganisms in the source area, this activity rebounded in <6 months. Nevertheless, the shift from sulfate-reducing to Fe(III)-reducing conditions induced by Fenton's treatment may have decreased the efficiency of reductive dechlorination in the injection zone. The results of this study indicate that source-area removal actions, particularly when applied to ground water systems that have significant natural attenuation capacity, can be effective in decreasing the areal extent and contaminant concentrations of chlorinated ethene plumes.

Introduction

The effectiveness of removing residual, dense non–aqueous phase liquids (DNAPLs) from contaminant source areas of chlorinated ethene–contaminated aquifers is a controversial issue in remediation technology. The regulatory community has consistently maintained that the removal of contaminant mass from source areas is a preferred remedial approach (U.S. EPA 1999; Interstate Technology and Regulatory Council 2001). On the other hand, direct observation of DNAPLs in aquifer sediments (Parker and Cherry 1999) and theoretical considerations of DNAPL behavior (Freeze and McWhorter 1997; Sale and McWhorter 2001) suggest that source-removal actions need to remove a high percentage of DNAPL mass (90% to 99%) in order to significantly lower contaminant concentrations in plumes (Cherry et al. 1992). Thus, the usefulness of source-area treatment technologies for remediating contaminated ground water systems is presently a matter of debate (Jackson 2001). Such questions are best addressed by observing how aquifers respond to source-area treatment technologies and documenting plume behavior over time with long-term monitoring. The purpose of this paper is to report the observed behavior of a chlorinated ethene contaminant plume following source-area treatment using Fenton's reagent in a shallow coastal plain aquifer near Kings Bay, Georgia.

Materials and Methods

Geology, Hydrology, and Site History

The study site is an abandoned landfill known as the Old Camden Road Landfill located at the Naval Submarine Base Kings Bay, Georgia. A map of the site showing the location of the contaminant source area and the locations of monitoring wells is shown in Figure 1. This site is underlain by marginal marine sediments of barrier island and back-barrier lagoon origin. The most permeable sands underlying the site are present between depths of 10 and 13 m below land surface and record the sedimentation of a prograding barrier island. This permeable zone is underlain and overlain by finer-grained sands and clays of back-barrier lagoon origin characterized by lower hydraulic conductivity. Aquifer tests at this site indicate that the hydraulic conductivity of the sands ranges from 0.6 to 3 m/d. The lithology of these sands suggests that the permeable aquifer is characterized by higher hydraulic conductivities ($K \sim 3$ m/d) relative to overlying and underlying sediments.

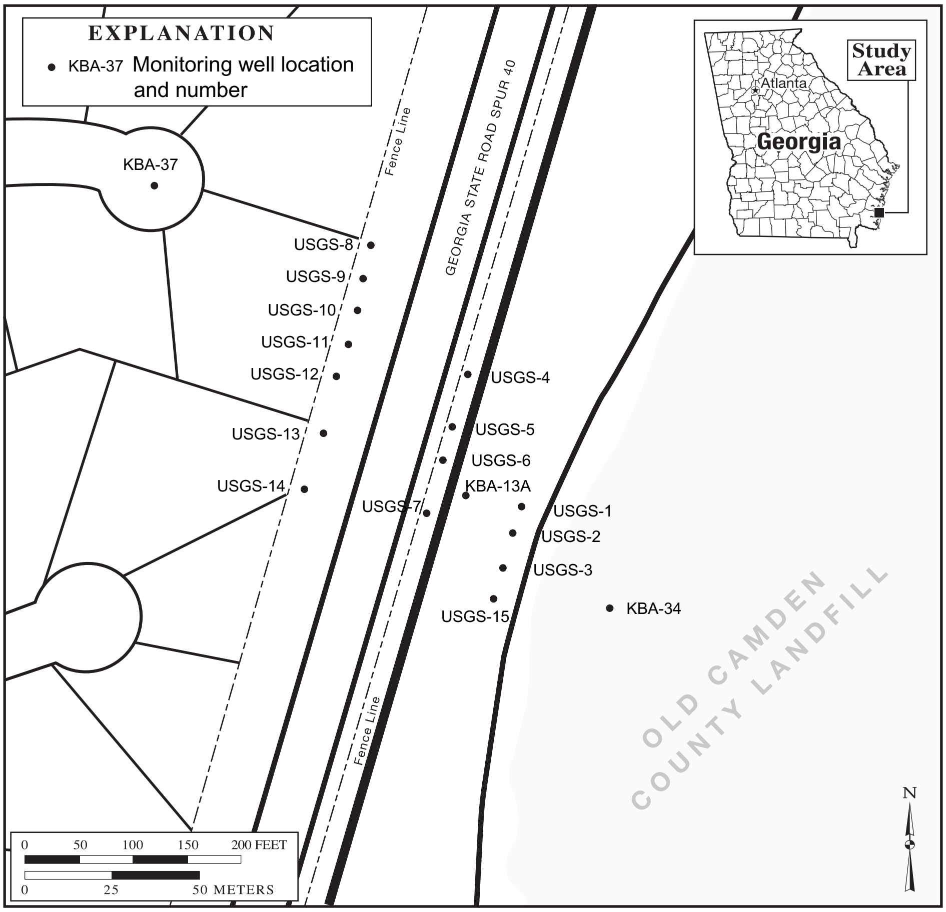

Figure 1. Map showing study site and locations of monitoring wells.

Because of its relatively high hydraulic conductivity, the aquifer is a preferential pathway for horizontal ground water flow and contaminant transport in this system. Overlying the aquifer at depths of ~3 to 5 m below land surface is a layer of organic-rich sands. This organic-rich layer has an important effect of removing dissolved oxygen (D.O.) from recharging water, producing uniformly anoxic conditions in the permeable zone.

The Old Camden Road Landfill was used to dispose of municipal waste between 1974 and 1981. Trenches were excavated to a depth of between 2 and 3 m, filled with waste, and covered with fill. At some time during waste-disposal operations, perchloroethene (PCE) was released at the landfill. Two discrete PCE sources were previously identified by direct-push sampling of ground water and aquifer sediments (ABB Environmental Services 1997; Chapelle and Bradley 1998). These sources are highly localized, suggesting that contamination resulted from at least two events. A plume of chlorinated ethene–contaminated ground water emanated from these sources and flowed toward a housing subdivision located to the west of the landfill. Prior to 1998, the relatively high organic carbon content of aquifer sediments led to a distribution of redox processes that favored rapid natural attenuation of chlorinated ethenes. Specifically, sulfate-reducing conditions conducive to reductive dechlorination predominated near the landfill, driving rapid transformation of PCE and trichloroethene (TCE) to *cis*-dichloroethene (*cis*-DCE) and vinyl chloride (VC). As ground water flowed downgradient toward the fence line of facility, however, Fe(III) reduction became the predominant redox process, facilitating the oxidation of VC to carbon dioxide. The rapid biodegradation of chlorinated ethenes facilitated by these sequential reducing-oxidizing redox zones produced a substantial natural attenuation capacity for chlorinated ethenes at this site (Chapelle and Bradley 1998). Nevertheless, natural attenuation was not by itself sufficient to prevent contaminant transport to the nearby subdivision, suggesting that source-zone treatment was required to reach remediation goals.

In situ chemical oxidation using Fenton's reagent was used to treat the contaminant source area in four separate campaigns that occurred between December 1998 and November 2001. All the campaigns were focused on roughly the same area within the landfill, with later applications addressing areas of contaminant rebound observed in performance monitoring wells. Approximately 48,000 gallons of a 50% hydrogen peroxide (H_2O_2) solution with a similar volume of ferrous sulfate catalyst was ultimately injected into the aquifer. The principal injection zone was between 10 and 16 m below land surface, corresponding roughly to the most permeable part of the aquifer. Following Fenton's injection, ~25,000 gallons of emulsified vegetable oil consisting of 35% oil with lecithin and 65% water with a sodium bromide tracer was injected in the former source area. The purpose of the vegetable oil was to provide a source of organic matter that would persist for the foreseeable future, providing a substrate for continued reductive dechlorination.

Water Chemistry Sampling

Ground water samples were collected quarterly between August 1998 and August 2004 from a network of monitoring wells (Figure 1) installed to delineate the areal extent of the plume. During sampling, each well was purged with a peristaltic pump until stable measurements of water temperature, conductivity, and pH were obtained. Samples for analysis of chlorinated ethenes (EPA method 8260) were collected in 40-mL glass vials, preserved with HCl, and capped with Teflon®-lined septa for transport to the laboratory. Dissolved hydrogen (H_2) was measured using the gas-stripping procedure described in Chapelle et al. (1997) and reported in units of nanomoles per liter (nM). Concentrations of dissolved Fe(II) (Hach Co., Loveland, Colorado), sulfide (Hach Co.), and oxygen (Chemetrics Inc., Calverton, Virginia) were measured in the field using colorimetric methods. Sulfate concentrations were measured using anion exchange chromatography with conductivity detection (Dionex Inc., Salt Lake City, Utah). Samples for the analysis of methane were collected by filtering 2 mL of ground water (0.2-µm filters) into sealed 20-mL serum vials. In the laboratory, methane in the headspace of the vial was measured using gas chromatography with thermal conductivity detection. The amount of methane in ground water was then calculated from the headspace methane concentration using the Henry's law partition coefficient between the gaseous and dissolved phases. Determination of predominant terminal electron–accepting processes was based on consumption of electron acceptors such as D.O. and sulfate; production of final products such as ferrous iron, sulfide, and methane; and concentrations of the intermediate product, hydrogen (Chapelle et al. 1997).

Results and Discussion

Ground Water Monitoring Data

Concentrations of total chlorinated ethenes in and near the contaminant source area prior to initiation of Fenton's reagent treatment were relatively high in 1998, exceeding 4500 µg/L. Near the source area, PCE, TCE, and *cis*-DCE were the predominant contaminants present. As ground water flowed downgradient, however, concentrations of VC, the principal contaminant of concern at the site, increased significantly. Concentrations of VC in ground

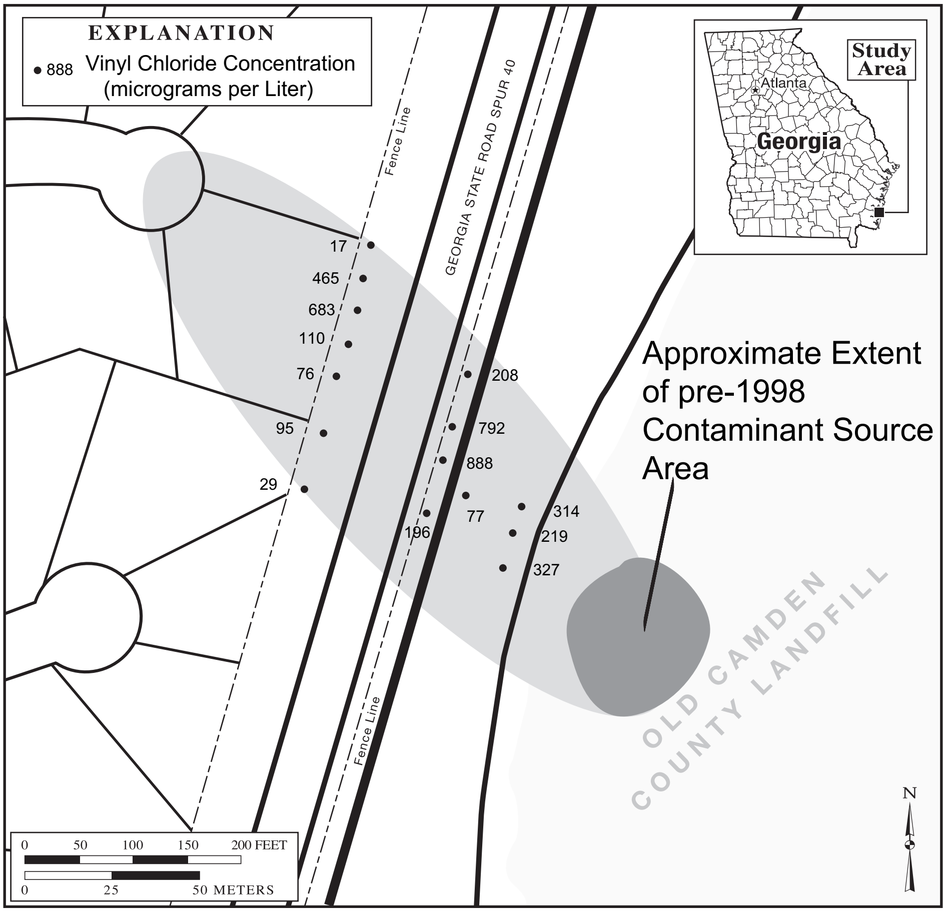

Figure 2. Concentrations of VC in ground water, August 1998.

water measured in August 1998, prior to initiation of the in situ oxidation campaigns, are shown in Figure 2. The highest VC concentrations were measured in ground water produced from wells USGS-5 (792 µg/L) and USGS-6 (888 µg/L). In addition, relatively high concentrations of VC were also found at the downgradient line of observation wells, with VC concentrations of 456 and 683 µg/L measured in water produced from wells USGS-9 and USGS-10, respectively. Because of these high concentrations of VC, a known carcinogen, the U.S. Navy instituted an aggressive source-area remediation strategy using Fenton's reagent for in situ oxidation. As part of this remedial action, a quarterly monitoring program was instituted to document the plume's response to source-area treatment over time.

The distribution of VC concentrations in the contaminant plume in August 2004, 5.5 years after initiation of the Fenton's reagent treatment, is shown in Figure 3. These data show that the areal extent and concentrations of the VC plume have decreased significantly following the Fenton's treatment. The highest observed VC concentrations in August 2004 were measured in ground water produced from well USGS-4 (106 µg/L). In most of the plume, observed concentrations of VC have decreased by a factor of 10 or more. In August 1998, all 14 of the original USGS monitoring wells produced water containing measurable concentrations of VC. In August 2004, 9 of these 14 wells produced water with VC concentrations below the reporting limit of 1 µg/L.

A closer inspection of water chemistry data collected at selected wells shows how contaminant concentrations have changed over time at different points within the plume (Figures 4 through 9). At well USGS-3, which is directly adjacent to where Fenton's reagent was injected (Figure 3), concentrations of sulfate (a tracer of the ferrous sulfate catalyst used in Fenton's reagent) increased rapidly from 1999 to late 2000. In the same period of time, concentrations of VC decreased sharply and have been below detectable levels (<2 µg/L) since June 1999 (Figure 4). Similarly, concentrations of TCE and *cis*-DCE also decreased rapidly and have remained below detectable levels since 2001. In contrast, there has been a rebound in PCE concentrations from below detectable levels in 1999 to ~30 µg/L in 2004. There are at least four possible factors that may contribute to observed rebound of PCE concentrations at USGS-3. These include (1) accelerated downgradient transport of PCE due to the pressure of Fenton's injection; (2) mobilization of PCE sorbed onto aquifer sediments due to Fenton's reagent; (3) less efficient Fenton's oxidation of PCE than other chlorinated ethenes; or (4) a change in the efficiency of reductive dechlorination near the former source area due to Fenton's treatment. It is not clear, however, which of these factors or combination of factors has affected PCE concentrations at this site.

A different pattern was observed at well KBA-13A, located ~20 m downgradient of the treatment zone (Figure 1). It took ~16 months before high-sulfate water

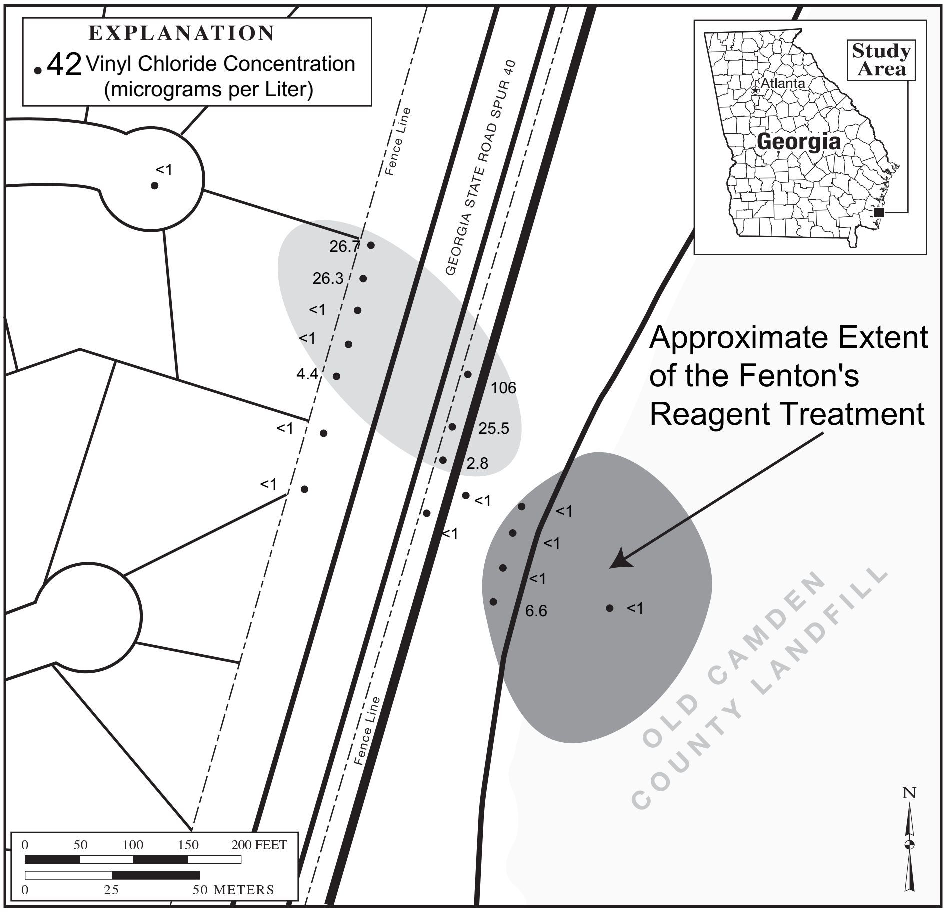

Figure 3. Concentrations of VC in ground water, January 2004.

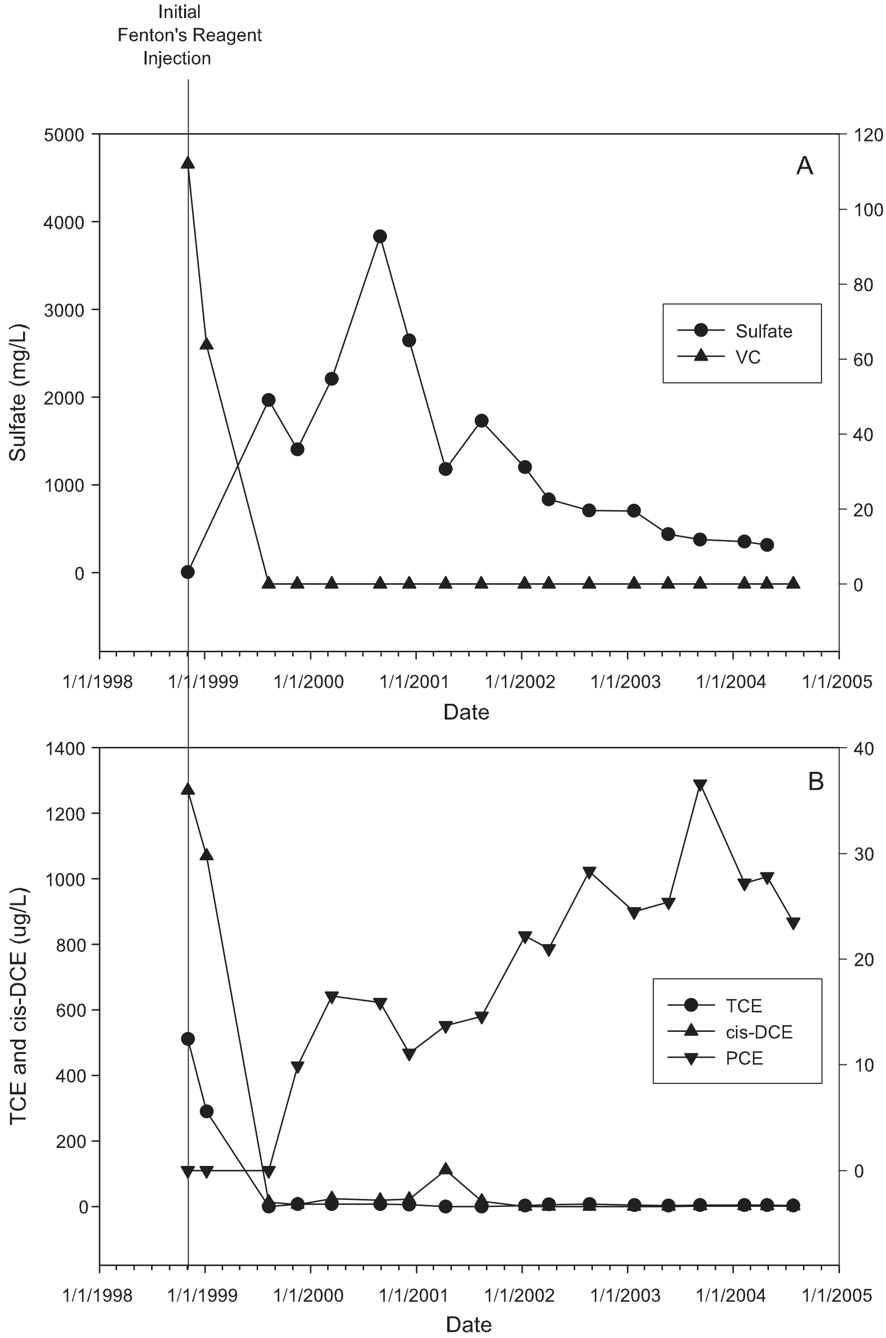

Figure 4. Concentration changes of sulfate and chlorinated ethenes at well USGS-3 between 1998 and 2004.

indicative of Fenton's treatment arrived at well KBA-13A (Figure 5). Concentrations of VC were observed to decline prior to the arrival of the high sulfate–treated water and declined below detectable levels a year after treated water arrived at KBA-13A. Concentrations of TCE and *cis*-DCE also declined after the arrival of treated water. Concentrations of *cis*-DCE exceeded 400 µg/L prior to the arrival of the high sulfate–treated water and decreased below measurable levels by 2004. PCE concentrations have been undetectable or low at well KBA-13A, reflecting reductive dechlorination as ground water moved downgradient of the source area in this anoxic aquifer.

Treated water did not arrive at well USGS-5, located ~30 m downgradient of the treatment zone (Figure 1), until 3 years following the initial Fenton's injection. At well USGS-5 (Figure 6), the pattern of sulfate concentration increases and VC concentration decreases was similar to the pattern observed at KBA-13A. Interestingly, however, concentrations of *cis*-DCE increased as sulfate concentrations increased. This distinctive "spike" of *cis*-DCE coinciding with the highest sulfate concentrations was also observed at well KBA-13A (Figure 5) and suggests that the Fenton's reagent treatment may have mobilized contaminants from the source area. Sulfate concentrations have not increased at well USGS-4 (Figure 6), indicating that the Fenton's-treated ground water is passing to the south of that well. In the absence of the arrival of Fenton's-treated ground water, concentrations of *cis*-DCE have increased

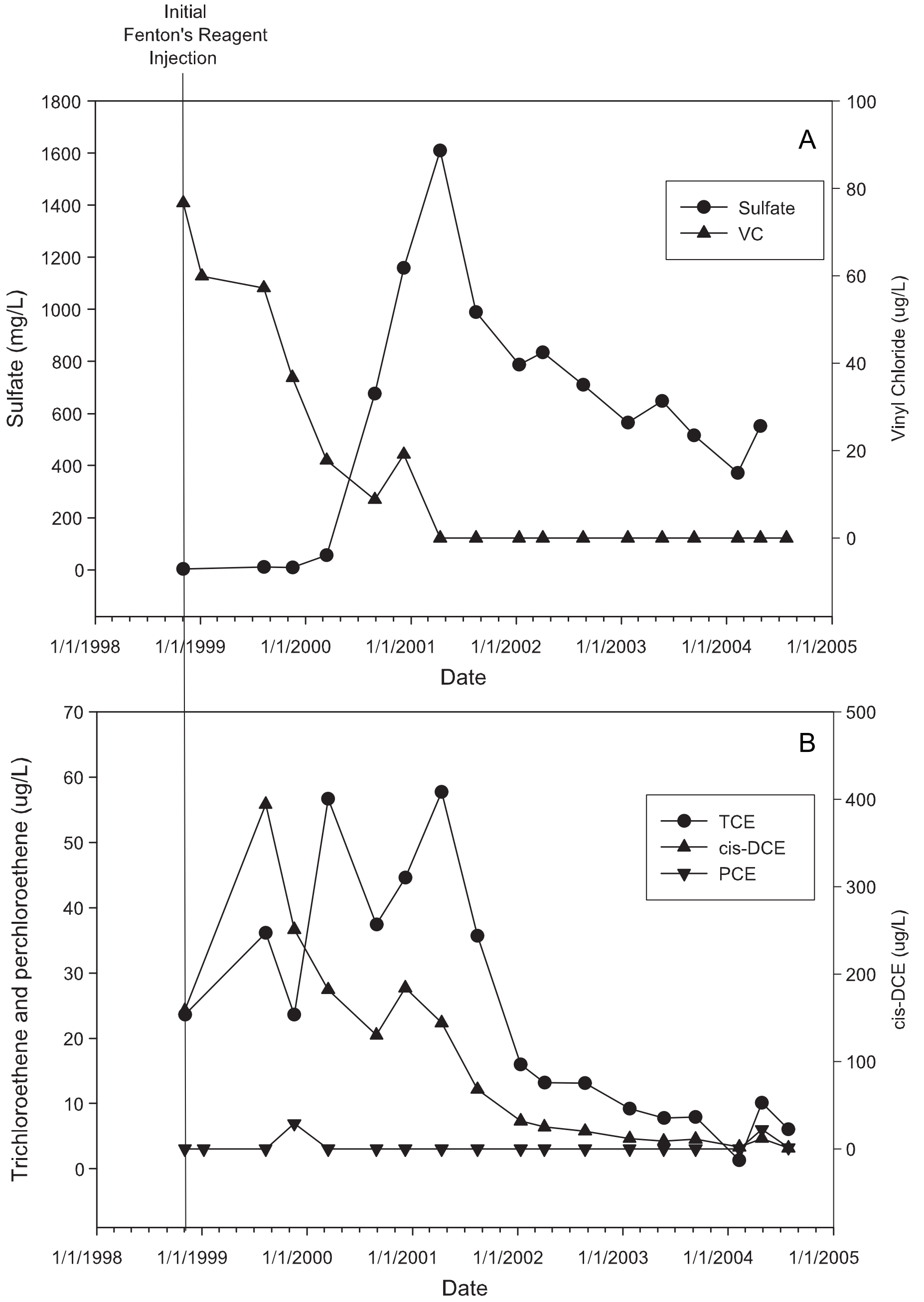

Figure 5. Concentration changes of sulfate and chlorinated ethenes at well KBA-13A between 1998 and 2004.

significantly over time. This may indicate that the Fenton's injection has pushed untreated, chlorinated ethene–contaminated water slightly to the north near the zone of injection, and that this untreated high–*cis*-DCE water is now moving through well USGS-4 (Figure 6).

As of August 2004, high sulfate–treated water has not arrived at the most downgradient line of wells (USGS-8 to USGS-14, Figure 1). Given the observed velocity of the treated water (~10 m per year), and the distance from the treatment zone to the downgradient wells (~75 m), it would take between 7 and 8 years following initial Fenton's treatment for treated water to arrive at the downgradient wells. Nevertheless, significant changes in contaminant concentrations in water produced from these downgradient wells have been observed. At well USGS-9 (Figure 7), concentrations of *cis*-DCE and VC were observed to decrease below detectable levels between 1998 and 2001. In contrast, concentrations of these contaminants were observed to increase at well USGS-11 (Figure 7) during the same time period. Prior to 1998, a pump-and-treat system designed to intercept the contaminant plume was in operation as an interim remedial measure but was not effective in capturing the plume. This downgradient pumping well was located near USGS-9. When pumping ceased in August 1998, the downgradient portion of the plume responded by shifting slightly to the south. This apparently decreased contaminant concentrations at well USGS-9 while increasing concentrations at well USGS-11 (Figure 7).

These monitoring data show that, in the upgradient part of the plume affected by Fenton's-treated water,

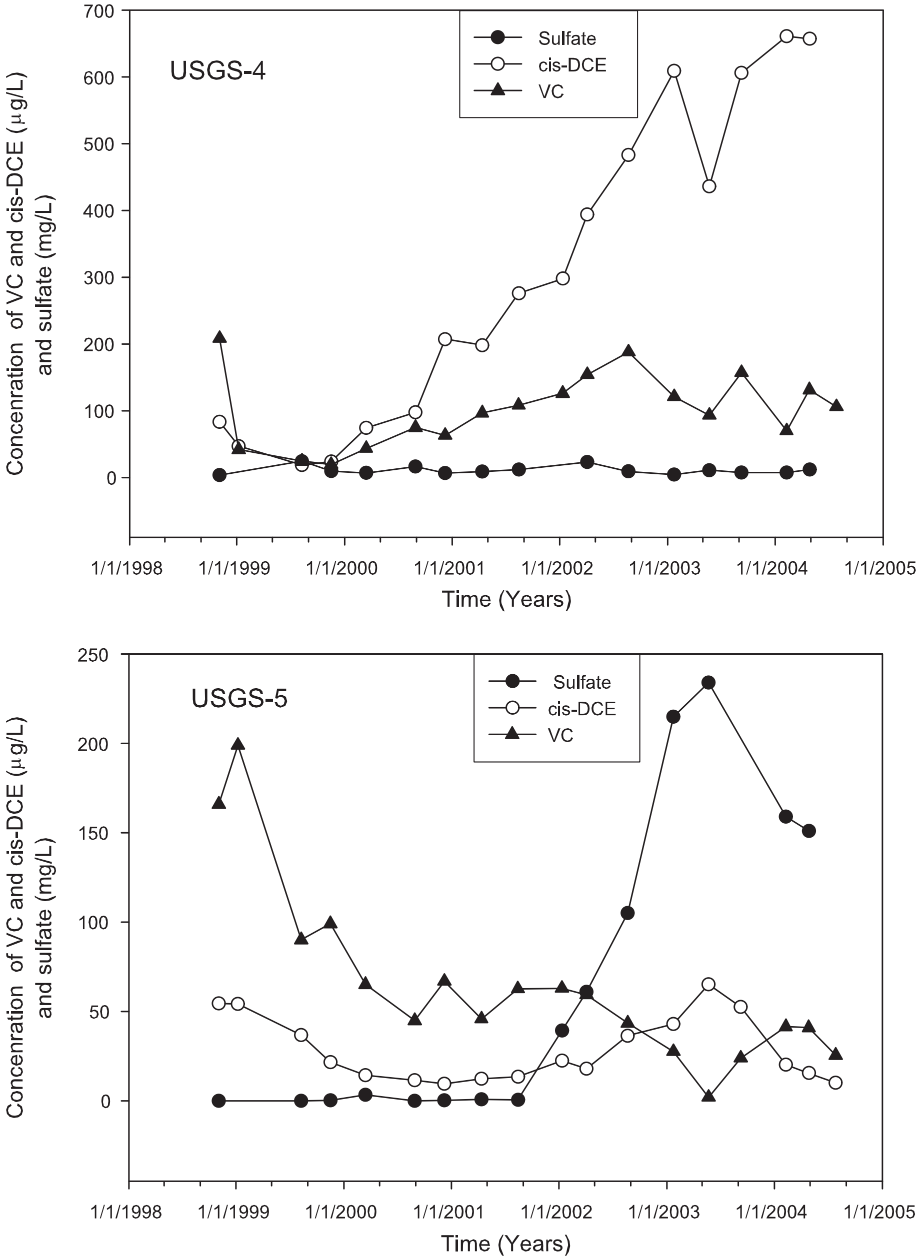

Figure 6. Concentration changes of sulfate and chlorinated ethenes at wells USGS-4 and USGS-5 between 1998 and 2004.

contaminant concentrations have decreased markedly over time. The association between the arrival of high-sulfate water with decreasing concentrations of chlorinated ethenes is the evidence that the Fenton's treatment has been effective in removing contaminants from ground water. The observed contaminant concentration declines in the most downgradient part of the plume, where treated ground water has not yet arrived (Figure 7), are more difficult to explain. One effect of the pump-and-treat system was to increase rates of ground water flow, and thus contaminant transport, from the source area toward the downgradient pumping well located near USGS-9. This may have increased the rates of contaminant transport, thus increasing contaminant concentrations at the pumping well. Once pumping ceased, however, and ground water flow rates slowed, ongoing natural attenuation processes would have more time to operate over a given length of aquifer flowpath, possibly leading to the observed contaminant concentration decreases at the downgradient wells.

Effects of In Situ Oxidation on Microbial Activity

Fenton's reagent, which is used to destroy organic contaminants during in situ oxidation, consists of a mixture of H_2O_2 and a ferrous iron sulfate catalyst that is injected into the aquifer under pressure. H_2O_2 is a powerful oxidizing agent that is toxic to microorganisms. In fact, H_2O_2 is widely used as a sterilizing agent to kill microorganisms in medical practice. The injection of H_2O_2 into the aquifer underlying site 11 raises the possibility that indigenous microbial processes converting chlorinated ethenes to nontoxic carbon dioxide and chloride may be wholly or partially inactivated. This possibility was assessed at the Kings

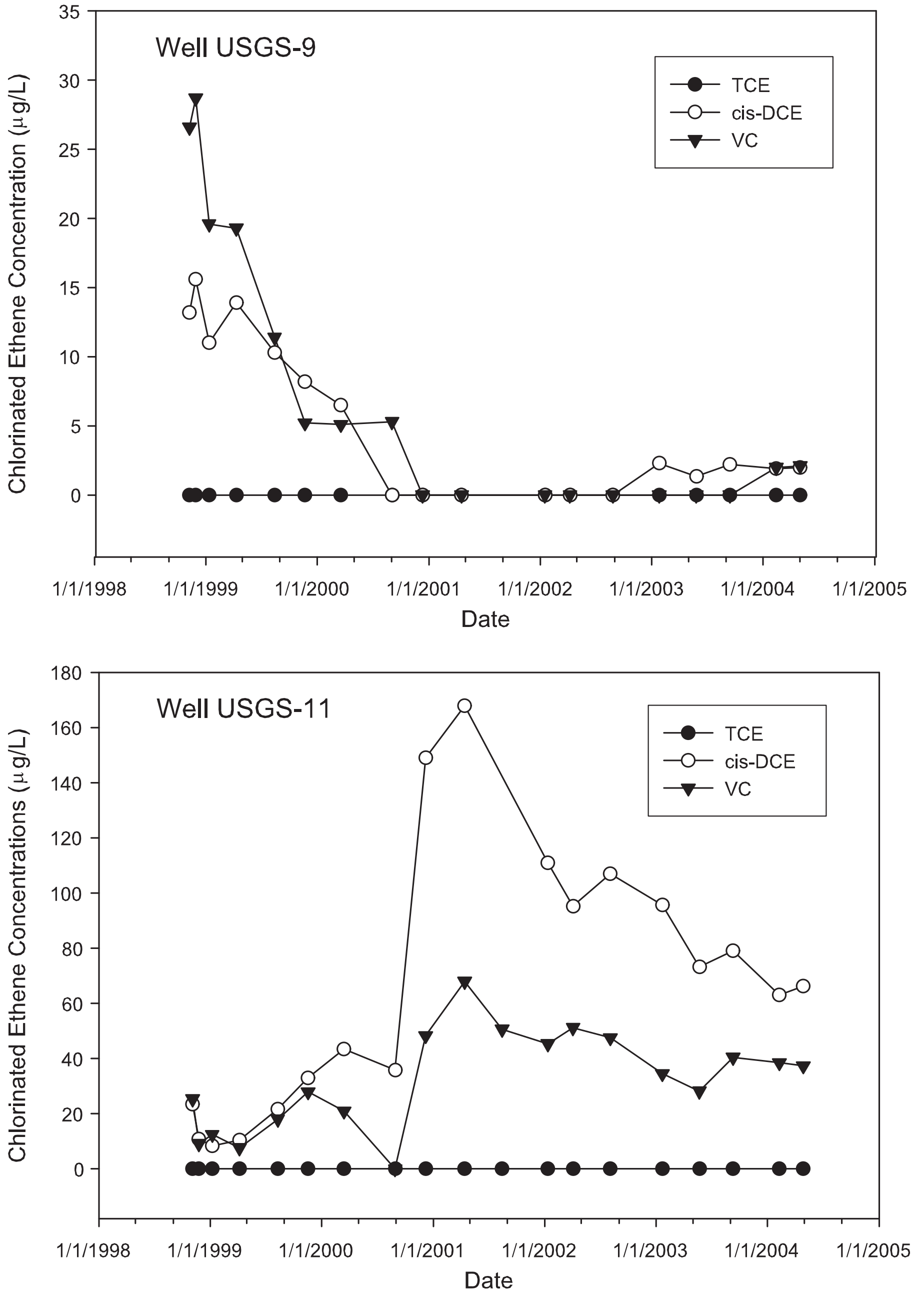

Figure 7. Chlorinated ethene concentrations at downgradient wells USGS-9 and USGS-11 between 1998 and 2004.

Bay site using a combination of field and laboratory methods. Aquifer sediments were cored at the site prior to, immediately after, and 6 months after Fenton's reagent treatment near the location of well KBA-34 (Figure 1). These sediment samples were then analyzed in the laboratory for numbers of bacteria using acridine orange direct counts and microbial activity by following ^{14}C acetate conversion to ^{14}C carbon dioxide.

Prior to in situ oxidation, bacterial counts in aquifer sediments were ~10^6 cells/g sediment (data not shown). Sediment samples taken in the same location 2 d after in situ oxidation showed <10^4 cells/g. This shows that, as expected, the Fenton's reagent decreased the number of bacterial cells in the aquifer. However, sediment samples taken 6 months after in situ oxidation showed that bacterial numbers had rebounded and were about an order of magnitude higher than they were prior to treatment. Measurements of overall microbial activity were consistent with the results of the bacterial cell counts. Prior to in situ oxidation, aquifer microorganisms rapidly converted ^{14}C acetate to ^{14}C carbon dioxide (Figure 8A), whereas sterilized controls showed no ^{14}C carbon dioxide production (Figure 8B). In contrast, sediment samples cored 2 d after Fenton's treatment showed virtually no ^{14}C acetate conversion to ^{14}C carbon dioxide (Figure 8B). Sediment samples taken 6 months later in this same location, however, showed that rates of ^{14}C acetate conversion to ^{14}C carbon dioxide activity had rebounded to levels greater than observed prior to in situ oxidation (Figure 8B). These data indicate that the injection of H_2O_2 initially decreased the

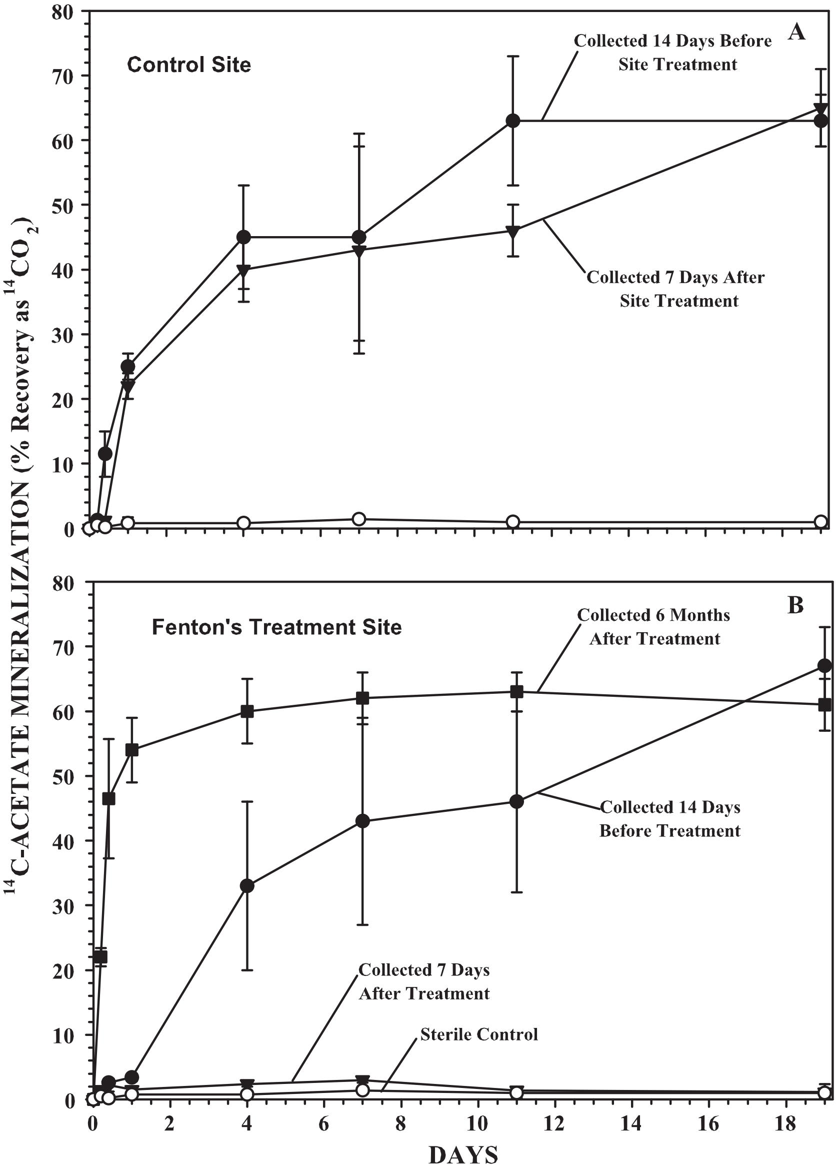

Figure 8. Microbial activity in aquifer sediments before and after Fenton's reagent treatment of the source area.

numbers and activity of microorganisms present in the aquifer. However, these data also indicate that microbial numbers and activity rebounded within a matter of months.

Ground water chemistry data suggest that the injection of Fenton's reagent has modified ambient redox processes at the site. Prior to Fenton's reagent treatment, the source area was predominantly sulfate reducing as indicated by the depletion of dissolved sulfate and hydrogen concentrations in the 2- to 4-nM range characteristic of sulfate reduction. Downgradient of the sulfate-reducing source area, the system was predominantly Fe(III) reducing (Chapelle and Bradley 1998). Following Fenton's treatment, concentrations of D.O. at well KBA-34 increased from below detectable levels (0.05 mg/L) to above 7 mg/L. Within 3 months, however, ground water at KBA-34 was once again anoxic but hydrogen concentrations have remained in the 0.2- to 0.8-nM range characteristic of Fe(III) reduction. Similarly, as Fenton's-treated water has moved downgradient through the location of KBA-13A, concentrations of D.O. remained below detection levels (Figure 9A), concentrations of ferrous iron and sulfate increased rapidly (Figure 9B), and concentrations of dissolved sulfide and methane have decreased (Figure 9C). Prior to the arrival of Fenton's-treated water, hydrogen concentrations varied seasonally between levels characteristic of sulfate reduction (1 to 4 nM) and levels characteristic of Fe(III) reduction (0.2 to 0.8 nM). Since the Fenton's-treated water has arrived at KBA-13A, however, there has been a trend of decreasing hydrogen concentrations into the range characteristic of Fe(III) reduction. These data imply that the delivery of ferric iron to the aquifer via Fenton's reagent has shifted the predominant microbial metabolism toward Fe(III) reduction. Because VC has been shown to oxidize to carbon dioxide under Fe(III)-reducing conditions (Bradley and Chapelle 1996), buffering the redox of this system at Fe(III) reduction may have the effect of enhancing VC oxidation in the plume. Conversely, the establishment of Fe(III)-reducing conditions may also decrease the

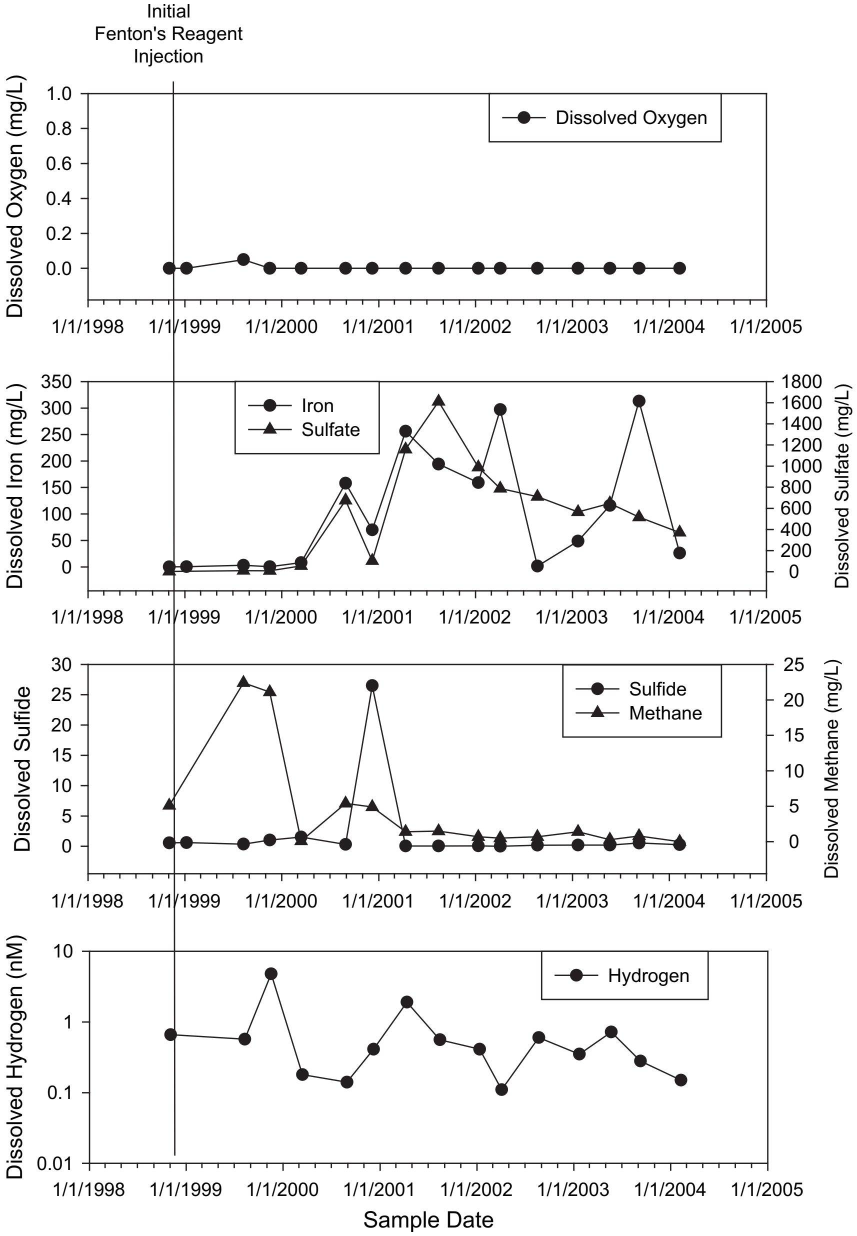

Figure 9. Concentrations of dissolved redox-sensitive parameters at well KBA-13A between 1998 and 2004.

efficiency of reductive dechlorination for PCE (Chapelle 1996). Because of that possibility, the final step in site treatment included the injection of a carbon source (emulsified vegetable oil) in the former contaminant source area (CH2MHill Contractors Inc. 2002). Presently, available data are not sufficient to assess the effects of the vegetable oil injection on ambient redox processes in the former source area.

Conclusions

Ground water monitoring data collected over a 6-year period provide evidence that, under favorable conditions, source-area treatment by Fenton's reagent can lead to significant contraction of chlorinated ethene plumes. There is considerable variability in the pattern of concentration decreases, however, that reflect a variety of hydrologic and microbiologic factors. In the upgradient part of the plume, for example, much of the observed concentration decline can be attributed directly to contaminant destruction by Fenton's reagent (well KBA-34). Furthermore, the movement of high-sulfate, Fenton's-treated water downgradient also leads to declines in chlorinated ethene concentrations (wells KBA-13A and USGS-5). However, movement of low-sulfate, chlorinated ethene–contaminated ground water, possibly in response to Fenton's reagent injection, has served to increase chlorinated ethene concentrations in places (well USGS-4). Concentration changes observed in the downgradient part of the plume appear to reflect hydrologic changes induced by the cessation of pump and treat in the fall of 1998. Cessation of pumpage appears to have increased the effectiveness of ambient biodegradation process by slowing the rate at which contaminants were being transported downgradient.

These observations suggest that the efficiency of natural attenuation is an important factor in determining how contaminant plumes will respond to source-area treatment actions. Theoretical considerations have suggested that DNAPL removal action would have to be highly effective in order to significantly affect contaminant concentrations downgradient of the source zone (Sale and McWhorter 2001). The results of this study are consistent with that expectation. However, the results of this study also suggest that source-area removal actions will be more effective in aquifer systems characterized by a significant natural attenuation capacity.

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