Ground Water Monitoring&Remediation

Permanganate Treatment of an Emplaced DNAPL Source

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Abstract

In situ chemical oxidation (ISCO) using permanganate is one of the few promising technologies that have recently appeared with the capability of aggressively removing mass from nonaqueous phase liquid (NAPL) source zones. While NAPL mass in regions of the treatment zone where delivery is dominated by advection can be removed rather quickly, the rate of mass removal from stagnant zones is diffusion controlled. This gives rise to partial mass removal and a concomitant reduction in the NAPL mass, downgradient ground water concentrations, and the dissolution rate associated with the source zone. Therefore, monitoring the performance of a permanganate ISCO treatment system is important to maintain the desired efficiency and to establish a treatment end point. In this paper, we illustrate the use of various monitoring approaches to assess the performance of a pilot-scale investigation that involved treatment of a multicomponent NAPL residual source zone with permanganate using a ground water recirculation system for 485 d. Ongoing treatment performance was assessed using permanganate and chloride concentration data obtained from extraction wells, 98 piezometers located approximately 1 m downgradient from the source, and ground water profiling. At the completion of treatment, 23 intact soil cores were extracted from the source zone and used to determine the remaining NAPL mass and manganese deposition. Based on the data collected, more than 99% of the initial NAPL mass was removed during treatment; however, remnant NAPL was sufficient to generate a small but measurable dissolved phase trichloroethene (TCE) and perchloroethene (PCE) plume. As a result of treatment, the ambient-gradient discharge rates were reduced by 99% for TCE and 89% for PCE relative to baseline conditions. The lack of complete source zone oxidation was presumed to be the result of dissolution fingers, which channeled the permanganate solution through the source zone preventing direct contact with the NAPL and giving rise to diffusion-limited mass removal.

Introduction

Sites contaminated with dense nonaqueous phase liquids (DNAPLs) are problematic, and there have been no reported cases of restoring a saturated source zone to acceptable regulatory drinking water standards or maximum contaminant levels (U.S. EPA 2003). This lack of success has spawned the development of a variety of technologies that enhance the rate of mass removal that is vital to attain DNAPL site restoration. Enhancing the rate of mass transfer from the DNAPL into the aqueous phase can be achieved by increasing the solubility of the contaminant (e.g., using a cosolvent or surfactant) or by decreasing the concentration of the contaminant in the bulk aqueous phase either through biological or chemical reactions (e.g., using a chemical oxidant, or through biodegradation).

In situ chemical oxidation (ISCO) is a potentially effective technology that enhances the rate of DNAPL mass removal by injecting a reagent into the subsurface that oxidizes aqueous phase contaminants to nontoxic products. Proposed aqueous oxidants for ISCO include hydrogen peroxide (H_2O_2), persulfate ($S_4O_8^{2-}$), and permanganate (MnO_4^-) (U.S. EPA 1998; Interstate Technology & Regulatory Council [ITRC] 2005). Due primarily to its longevity in situ, permanganate has received perhaps the greatest attention. In a series of proof-of-concept experiments, Gonullu and Farquhar (1989) and Schnarr et al. (1998) emplaced a DNAPL source within sand-packed columns and were able to demonstrate that the removal of the free phase zone was accelerated under permanganate flushing conditions. Careful pilot-scale efforts reported by Schnarr et al. (1998) involving the continuous flushing of well-defined residual source zones placed in unconsolidated media showed more than 99% mass removal. These encouraging research findings and many others in the last 10 years (e.g., Siegrist et al. 2001; Lowe et al. 2002; ITRC 2005; U.S. EPA 2006) have led to the accelerated use of permanganate in larger pilot-scale trials and in a host of full-scale applications (e.g., Battelle 2002; ITRC 2005; U.S. EPA 2007).

Typically, posttreatment performance monitoring consists of several rounds of ground water samples collected within months of permanganate injection from an existing monitoring network. Such short-term ground water monitoring is likely to significantly overestimate the benefit of permanganate addition since residual permanganate is still present in the subsurface and available to react with the low-target contaminant concentrations often observed in ground water monitoring wells. This overestimation of treatment performance may, in some situations, lead to a false sense of treatment effectiveness and perhaps termination of the ISCO application activities. Accordingly, it is not surprising to see a rebound of target contaminant concentrations as residual permanganate is slowly consumed (U.S. EPA 2006). A recent review of ground water monitoring data from 59 sites where DNAPL source depletion technologies were implemented indicted that rebound was observed in 81% of observation wells at seven sites where ISCO was the selected treatment technology (McGuire et al. 2006). While contaminant rebound may result from a number of factors (e.g., inadequate site characterization, insufficient oxidant loading, and geological heterogeneity), the use of ground water monitoring data alone does not provide a clear understanding of the treatment system performance and insight into potential technology limitations. Recognizing that the use of point measurements alone is not an adequate indication of treatment performance, the U.S. EPA (2003) grouped performance metrics into three categories: (1) those that are in widespread use and can, in general, be measured reliably (e.g., change in downgradient ground water quality); (2) those that are not in widespread use but can be measured (e.g., mass remaining, change in source zone architecture, or change in nonaqueous phase liquid [NAPL] composition); and (3) those that in theory can be measured but are in the research and development stage (e.g., change in downgradient contaminant mass flux or rate of discharge).

The primary objective of this study was to investigate the utility of various monitoring techniques to assess the treatment of a residual DNAPL source zone with permanganate through the use of a detailed pilot-scale field investigation conducted over 2 years. Specifically, we focused on simple techniques to monitor both the progress of permanganate treatment and the overall impact of permanganate treatment on the mass of DNAPL destructed in the source zone and the capability of the remaining mass to generate a dissolved phase plume. While not all of the approaches used in this investigation are possible at full scale, the complexities of monitoring this technology should be appreciated and limitations acknowledged. We suggest that the use of multiple performance criteria to establish a reliable end point for the treatment are essential and should be considered in the performance assessment design of permanganate ISCO treatment systems.

Site Description

This pilot-scale field investigation was conducted in the approximately 10-m-thick unconfined sand aquifer at a location known as the Emplaced Source (ES) Site (Rivett et al. 2001) at the Canadian Forces Base Borden near Alliston, Ontario, Canada. The water table at the ES Site is 2 to 3 m below ground surface and the aquifer is underlain by a regional silt and clay unit. The aquifer is characterized as a homogeneous, well-sorted glaciofluvial fine-to-medium sand with distinct horizontal layering that is parallel and near-horizontal, although some cross-bedding and convolute bedding has been observed (Mackay et al. 1986). Based on numerous measurements, a dry bulk density of 1.75 g/cm^3, porosity of 0.33, and a total organic carbon (TOC) content of 0.021% were obtained (Rivett et al. 2001). Permeability varies between 10^{-10} to 10^{-14} m^2 on the millimeter scale (Tomlinson et al. 2003) with a mean hydraulic conductivity of 6.34×10^{-3} cm/s. The mean ambient hydraulic gradient at the ES Site is 0.0051 m/m (range 0.003 to 0.006), which yields a mean ground water velocity of 8.5 cm/d; however, the flow direction varies over an approximately 40° range annually (Rivett et al. 2001). Background ground water quality is aerobic, and both sulfate and chloride (<10 mg/L) are present and are associated with a leachate plume generated by an inactive municipal solid waste landfill located upgradient (Rivett et al. 2001).

To investigate the development of a dissolved chlorinated solvent plume from a residual DNAPL source, a block-shaped source zone (0.5 m in the direction of ground water flow, 1.0 m high, and 1.5 m wide) was emplaced approximately 1 m below the water table (Figure 1). Source material was mixed aboveground in batches and, in total, 720 L of wet sand, 72 kg of gypsum powder, and 12.54 kg of perchloroethene (PCE), 8.99 kg of trichloroethene (TCE), and 1.45 kg of trichloromethane (TCM) comprised the source zone. This mass of solvent resulted in an initial volumetric DNAPL saturation of 5%. The gypsum was added to provide an inorganic tracer of dissolved sulfate. Additional details on the source construction procedure are provided by Rivett et al. (2001). Portions of the resulting plume were monitored on 30 occasions over 1030 d (~3 years) with the majority of this effort focused near the source (Rivett et al. 2001; Rivett and Feenstra 2005). After 450 d, remediation efforts that did not interfere with the near-source dissolution process consisted of the first field test of a zero-valent permeable reactive barrier (O'Hannesin and Gillham 1998) and a pump-and-treat plume capture system (Rivett 1993).

This well-characterized residual source zone provided an excellent opportunity to evaluate the treatment capabilities of permanganate and to assess various performance metrics applicable to permanganate ISCO applications. The permanganate treatment of the ES discussed in this paper began 6 years after the source was emplaced and almost 3 years after the extensive plume monitoring was terminated. Findings reported by Rivett and Feenstra (2005) that are relevant to this remedial investigation are as follows: (1) the hydraulic conductivity of the source zone is at least 3.2 times lower than the adjacent aquifer material due to the fine powder gypsum added to the source and the reduced relative permeability as a result of the DNAPL presence; (2) the concentration of TCM emanating from the source had declined significantly; (3) observed

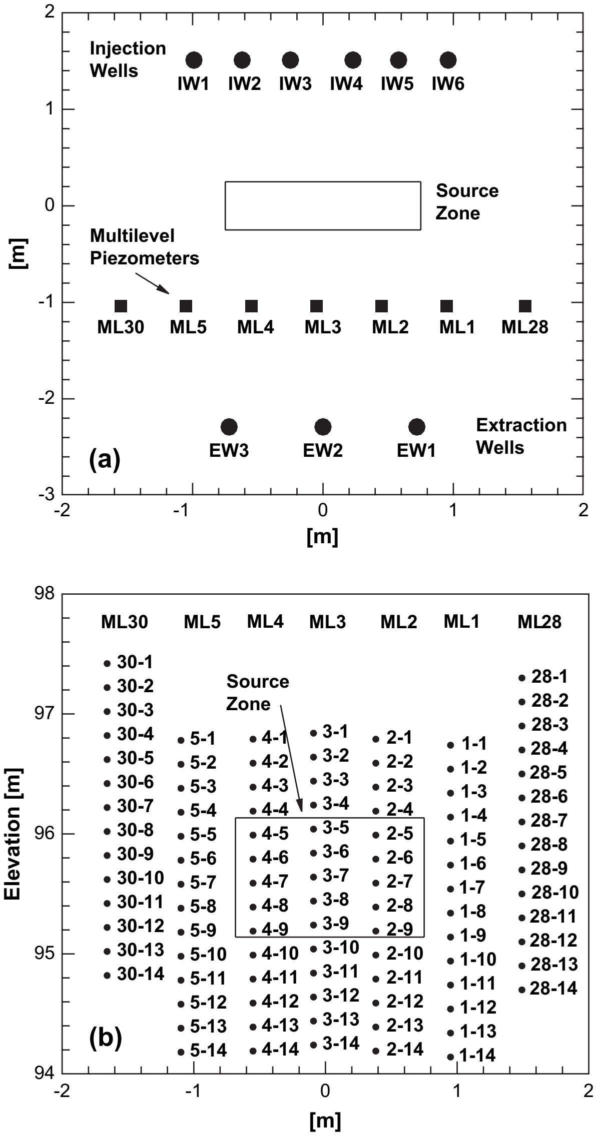

Figure 1. Location of injection and extraction wells and the 1-m multilevel sampling fence line relative to the multicomponent residual source zone: (a) plan view and (b) profile view through the 1-m fence line. Multilevel sampler monitoring points are indicated. Elevations are relative to an arbitrary ground surface datum set at 100 m.

enhanced dissolution of the upper surface of the source indicative of bypass flow; and (4) evidence of preferential dissolution flow paths within the source. As noted by Rivett and Feenstra (2005), the outcome of the lower source zone hydraulic conductivity results in significantly flow bypassing as the ES behaves like a block-shaped physical heterogeneity in the aquifer. While the unique construction of this ES zone gave rise to this situation, similar flow bypassing can occur at actual sites depending on the source zone architecture (Lemke et al. 2004; Fure et al. 2006), and hence a comprehensive assessment of the ability of a permanganate ISCO system to treat this highly characterized source zone has widespread applicability.

Based on the extensive plume monitoring reported by Rivett and Feenstra (2005), 82%, 37%, and 7%, respectively, of the initial mass of TCM, TCE, and PCE had dissolved over the initial 3-year monitoring period. Using a comprehensive three-dimension flow and transport model, Frind et al. (1999) were able to match the observed peak concentrations assuming equilibrium-controlled mass transfer and a homogenous source zone hydraulic conductivity that was 10 to 25 times less than the adjacent aquifer. Modeling results from Frind et al. (1999) were used to estimate the DNAPL mass present in the source zone at the beginning of permanganate treatment. These data suggested that the source contained approximately 9 kg of PCE and approximately1.6 kg of TCE as free phase 6 years after emplacement (day 0 of this investigation), and that TCM had been completely removed due to its high aqueous solubility. Given the low TOC content of the aquifer solids (0.021%), the sorbed mass of PCE and TCE in the source zone is less than 10 g and was ignored.

It has become apparent that a critical design parameter for a permanganate ISCO system is knowledge of the permanganate natural oxidant demand (NOD), which represents the consumption of permanganate by the naturally occurring reduced species, organic carbon, and reduced minerals containing Fe(II), Mn(II, III), and S(-I, -II) associated with the aquifer material (Honning et al. 2007; Mumford et al. 2005; Siegrist et al. 2001). NOD results from well-mixed batch reactor tests using Borden aquifer material produced a value of 0.5 g $KMnO_4$/kg in a 2-d test (Mumford et al. 2004), 1.2 g $KMnO_4$/kg in a 147-d test (Mumford et al. 2005), and 2.1 g $KMnO_4$/kg in a 196-d test (Xu et al. 2004). A recently developed modified chemical oxygen demand test using permanganate to determine the maximum NOD of Borden aquifer material resulted in a value of 3.5 ± 0.85 g $KMnO_4$/kg (Xu et al. 2004). While these results vary in magnitude, they indicate that consumption of permanganate by Borden aquifer material is expected to be between 0.5 and 3.5 g $KMnO_4$/kg, a value that is relatively low compared to the NOD reported for other aquifer materials (Xu et al. 2004). This permanganate NOD is consistent with the low TOC and mineralogy of the Borden aquifer material (calcite, quartz, plagioclase, and feldspar minerals with surface coatings of iron and manganese oxyhydroxides) (Ball et al. 1990). Permanganate consumption from upgradient ground water was expected to be minimal except if mixing with the underlying leachate plume occurred.

Methods

To minimize downgradient migration of the injected permanganate solution, reduce the flow bypassing effects of the lower hydraulic conductivity source zone, and sustain elevated permanganate concentrations within the source zone to maximize the reaction rates and diffusion-related concentration gradients, a ground water recirculation or recycling system comprised of a network of injection and extraction wells was used. This type of delivery system also provides hydraulic control across the source zone and allows for increased flow rates through the target treatment zone (Lowe et al. 2002). While a delivery system of this type has clear advantages over other delivery methods such as injection probes, its choice should be based on site-specific conditions and treatment goals. Guided by results from ground water flow simulations using MODFLOW-2000 (Harbaugh et al. 2000), six injection and three extraction wells were installed (Figure 1). All wells were installed by a direct push technique and constructed from 6-cm diameter polyvinyl chloride tubing and screened between 95.0 and 96.2 m.

The surface components of the recirculation system included a settling/equalization tank (2100 L), permanganate dosing system, and in-line filtration (2 μm). The permanganate dosing system consisted of a diaphragm pump, which circulated a fraction of the total flow rate through a 110 L storage column packed with flowing grade potassium permanganate (Quadra Chemical, Burlington, Ontario). The permanganate concentration in the effluent from this column was near the solubility limit of approximately 45 g/L and was mixed back into the recirculated flow and then reinjected. The flow rate of oxidant dosing pump was used to control the oxidant concentration in the injected solution and was manually adjusted in the field as required. At the maximum system flow rate (360 mL/min), the equalization tank provided a residence time of 2 d, which was sufficient to oxidize any aqueous constituents in the effluent. Flow from the settling/equalization tank into the injection wells was controlled using six peristaltic pumps. A transect of 98 multilevel piezometers installed approximately 1 m downgradient of the source (denoted here as the 1-m fence line) was used to monitor the progress of permanganate treatment and characterize the dissolved phase plume generated by the DNAPL source (Figure 1). Piezometer spacing was 0.2 m vertically and 0.5 m horizontally (see Rivett and Feenstra [2005] for construction details). During permanganate injection, the objective of the monitoring strategy was to determine the effectiveness of the injection system in flooding the source zone with permanganate and to determine if a chloride signature, a zone of elevated chloride concentration indicative of DNAPL mass removal, was present.

Six months prior to initiating permanganate treatment, a baseline assessment of the TCE and PCE plume was performed under ambient-gradient conditions (velocity of ~8.5 cm/d) by collecting a round of samples from the 1-m fence line. Samples for TCE and PCE analyses were collected into 15-mL sample vials using the manifold system described by Mackay et al. (1986). These data were used to establish an estimate of the mass loading from the source zone to the plume and the peak concentration emanating from the source zone under ambient-gradient conditions. The mass loading or dissolution rate (i.e., the rate of TCE or PCE mass crossing the plane defined by the 1-m fence line) was calculated by integrating the spatial distribution of the aqueous mass flux over the 1-m fence line (Kubert and Finkel 2006; ITRC 2004; Einarson and MacKay 2001; King et al. 1999). Following this sampling episode, the injection/extraction system was activated and a conservative tracer test was initiated 27 d after system startup to estimate travel times and to ensure adequate delivery of the tracer to the source zone. NaBr was mixed with site ground water to a concentration of approximately 300 mg/L and injected for 120 h without recycle. The mean injection flow rate was 348 ± 12 mL/min while the mean extraction flow rate was 386 ± 34 mL/min, similar to the design flow rates for the operation of the permanganate treatment system. Also, during this tracer test, TCE and PCE concentrations in the extracted solution (blended ground water from EW1, EW2, and EW3) were monitored to provide an estimate of the mass loading to the extraction wells from the source zone (total extraction flow rate times either the TCE or PCE concentration) under forced hydraulic gradient conditions (ITRC 2004; Bockelmann et al. 2001; Ptak and Teutsch 2000).

Once the tracer test was completed, active permanganate treatment of the source zone was initiated (day 0). Concentrations of both permanganate and chloride concentrations were routinely monitored at nine multilevel locations (1 to 4, 1 to 7, 1 to 10, 5 to 4, 5 to 7, 5 to 10, 3 to 5, 3 to 7, and 3 to 10; Figure 1b), the extraction wells, and in the injection solution. Six rounds of samples were collected during treatment from all 98 multilevel piezometers in the 1-m fence line to assess the extent of permanganate transport and characterize the chloride signature. In addition, aqueous profiling using the Waterloo profiler (Pitkin et al. 1999) was performed six times within the source and two times just downgradient of the source. At the end of the active permanganate treatment effort (day 485), the injection flow was stopped and the extraction wells were used to remove residual oxidant solution from the treatment zone until day 665. A posttreatment assessment of the TCE and PCE mass discharge was performed under both forced-gradient (day 825) and ambient conditions (day 885) using identical approaches to those used during the baseline assessment.

One month (day 915) after the completion of the posttreatment assessment, 23 intact soil cores were extracted from the source zone in 5-cm inner diameter (ID) aluminum-sealed core tubes and used to characterize the spatial mass distribution of TCE, PCE, and MnO_2(s). Core tubes were stored in a walk-in refrigerator prior to opening to minimize volatilization losses. Within 1 week after extraction, the cores were sliced lengthwise, wrapped in foil, and subsampled by a two-person team working as quickly as possible. Duplicate soil samples (1 cm^3) were collected every 5 cm using a precleaned microsampling tool and the soil was exposed to air for less than 2 min. The first sample was placed in a 20-mL vial containing 10 mL of methanol as an extraction solvent for TCE and PCE analysis, while the second was placed in a 40-mL vial for total Mn analysis. Two of the 23 intact cores were used for hydraulic conductivity measurements at 5-cm intervals using the multiport permeameter system described by Tomlinson et al. (2003).

Analytical Methods

Immediately following collection, ground water samples were transported to the University of Waterloo and stored at 4°C prior to analyses. PCE, TCE, and chloride analyses were preformed within 1 week of collection, and permanganate analysis was typically performed either onsite or the same day. Residual permanganate in samples collected for organic and ion analyses were quenched in the field by adding sodium thiosulfate (~0.5 g/40 mL) immediately after collection. Permanganate concentration was quantified in the field on filtered samples (0.45-μm glass fiber, Pall Corp, Mississauga, Ontario, Canada) by spectrophotometry (Spectronic 20D, Milton Roy Co., Rochester, New York) at 525 nm with a method detection limit (MDL) of 1.3 mg/L. The spectrophotometer was calibrated prior to each sampling event using a standard stock solution (APHA–AWWA–WEF 1998).

Analysis of chloride and bromide was performed using a Dionex DX-300 ion chromatography equipped with a SpectraSYSTEM AS3500 autosampler and a conductivity detector, and operated with a 1.7 mM $NaHCO_3$ and 1.8 mM Na_2CO_3 eluent at a flow rate of 2 mL/min and a 2.5 mM H_2SO_4 regenerant solution at a flow rate of 5 mL/min. The MDLs for bromide and chloride were 0.3 and 0.5 mg/L, respectively.

Aqueous samples for PCE and TCE analyses were prepared using liquid:liquid extraction with reagent-grade hexane (solvent/sample ratio of 1:6). Analysis of the hexane extract was performed using an HP 5890 II gas chromatograph (30 m × 0.53 mm ID HP 624 fused silica capillary column) equipped with an HP 7673 autosampler and both flame ionization and electron capture detectors. Concentrations were determined by external standard calibration with a MDL of approximately 1 μg/L for both PCE and TCE. Bulk TCE and PCE concentrations in soil samples were determined using a similar method except that methanol was used to extract the organic species from a soil sample and an aliquot of the methanol was subsequently analyzed (Sawhney et al. 1988; Ball et al. 1997).

The presence of the bulk manganese concentration in the soil samples was evaluated using inductively coupled plasma emission spectroscopy (Spectro Analytical, Fitchburg, Massachusetts). Soil samples were dried (85°C), reweighed, and then digested using 2 mL of 50% HNO_3 and 10 mL of 50% HCl for 1 h at 100°C (Method 3030F, APHA–AWWA–WEF 1998). In this method, all the manganese species present are converted to Mn^{+2} and the MDL was 0.07 mg/L Mn. For the soil samples evaluated in this investigation, it was assumed that the predominant manganese species was MnO_2 and hence the results from this method are reported in terms of MnO_2 per mass of dry soil; however, we acknowledge that laboratory evidence suggests that the solid reaction product from the oxidation of TCE by permanganate under certain conditions may be potassium-rich birnessite (Li and Schwartz 2004).

Results and Discussion

Baseline Conditions

Based on an analysis of the conservative tracer test breakthrough curve (BTC) data at each multilevel piezometer, the mean travel time (18.9 d) corresponded to an average linear ground water velocity of 13 cm/d between the injection wells and the 1-m fence line. The variation in arrival times of the center of mass at each piezometer indicated some degree of heterogeneity resulting from the lower hydraulic conductivity source zone. This forced-gradient velocity is approximately 50% higher than the mean ambient ground water velocity of approximately 8.5 cm/d for this area of the Borden aquifer. As expected, the longer path length and hence slower velocities along the edge of the treatment zone resulted in distinct tailing of the Br BTC in the extraction wells. The extraction well BTC data indicated that this treatment system recovered approximately 80% of the injected conservative tracer mass and created an effective zone of oxidant delivery of approximately 20 m^3. This incomplete tracer recovery implies that this treatment system was not closed presumably due to nonideal hydraulic conditions. With the exception of the multilevel piezometer positioned just above the source zone (ML3-4), a tracer signature was observed on all sides of the source zone, confirming that the injection wells spanned a sufficient width to flush the entire source zone.

The baseline assessment of the TCE and PCE plume under ambient-gradient conditions indicated peak concentrations of TCE and PCE in the 1-m fence line of 140 mg/L and 60 mg/L, respectively (Figure 2a). Although these concentrations are lower than the peak concentrations observed by Rivett and Feenstra (2005) after 3 years of dissolution (TCE 630 mg/L and PCE 130 mg/L), the spatial distribution is remarkably similar, suggesting unchanged dissolution behavior. Assuming a uniform specific discharge estimated from the average hydraulic gradient and hydraulic conductivity, the dissolution rates of TCE and PCE were estimated to be 860 and 880 mg/d, respectively. In comparison to the dissolution rates calculated by Rivett and Feenstra (2005) using data collected 3 years earlier (TCE 1800 mg/d; PCE 610 mg/d), these dissolution rates are lower and suggest that that the mole fraction of TCE may have decreased over the 3-year period. During the tracer test, the TCE and PCE concentrations in the extracted solution were initially high (10 to 60 mg/L) but gradually stabilized at approximately 5 mg/L. Based on observed concentrations and total flow rates over a 15-d period ($n = 11$), the mass loading from the source zone to the extraction system or dissolution rates of TCE and PCE under forced-gradient conditions were estimated to be 2100 and 2220 mg/d, respectively. Complete mineralization of the average concentration of TCE and PCE over this 15-d period would yield an equivalent concentration of chloride of 6.5 mg/L.

Overall Injection/Extraction System Behavior

Permanganate injection occurred continuously over 485 d and a total of 890 kg of $KMnO_4$ was used (average 8.0 g $KMnO_4$/L (Figure 3). During the period of active permanganate injection, the average extracted permanganate concentration was 2.1 g $KMnO_4$/L, substantially lower than the injected oxidant concentration. In response to detection of permanganate at two downgradient sentry monitoring wells, the injection and extraction flow rates were reduced from approximately 350 to approximately 200 mL/min at day 100 to improve the hydraulics of the injection/extraction system. Once permanganate injection was terminated, the extraction system was run without injection for an additional 180 d to remove residual permanganate and chloride from the subsurface. Measurable permanganate was

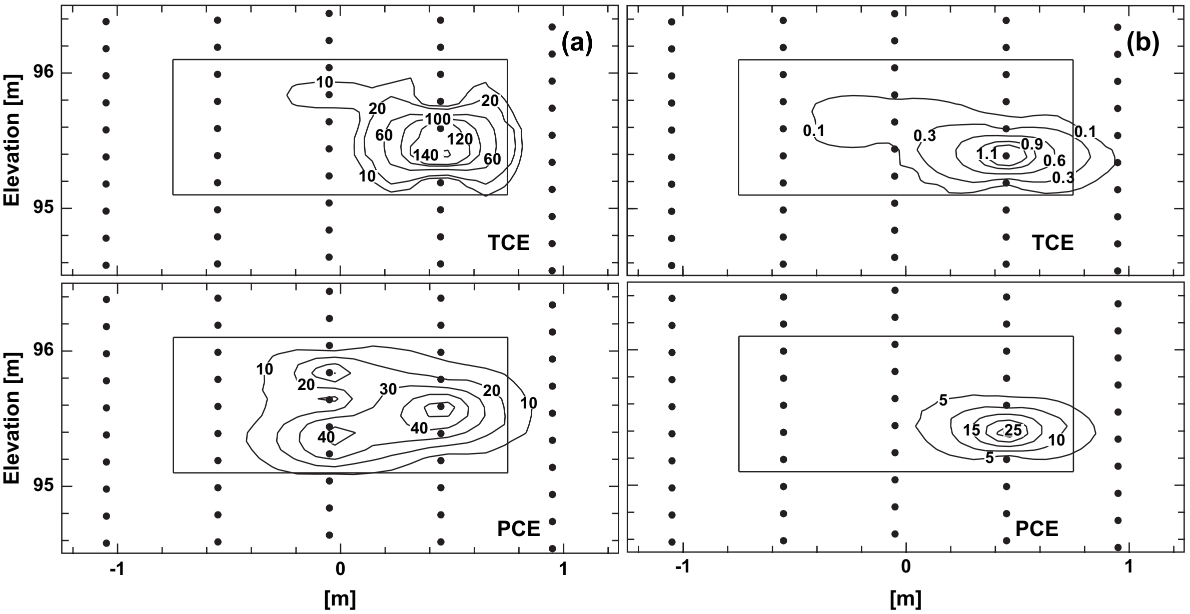

Figure 2. (a) Pretreatment and (b) posttreatment TCE and PCE dissolved phase concentration contours (mg/L) at the 1-m multilevel sampling fence line. The solid circles indicate sampling locations and the rectangle represents the spatial extent of the source zone.

observed in the extracted solution for 100 d and then dropped below the MDL.

Temporal chloride concentration profiles in the extracted and injected solution are presented in Figure 3b. Initial breakthrough of chloride produced by the oxidation of TCE and PCE occurred in EW-2 between 17 to 20 d. The chloride concentration in the extracted solution rose after 50 d to a peak of approximately 150 mg/L and remained at this concentration for approximately 100 d. Subsequently, the extracted chloride concentration slowly decreased until it was indistinguishable from the injected chloride concentration after 300 d. The small differences between the chloride concentration in the injected solution and the extracted solution (<1 mg/L) suggested that little TCE and PCE oxidation was occurring beyond 300 d based on these data. The chloride concentration from day 50 to 150 of approximately 150 mg/L is much higher than the equivalent concentration of chloride of 6.5 mg/L observed during the forced-gradient baseline assessment. This increase in extracted chloride suggests that the maximum rate of DNAPL mass depletion or enhanced dissolution rate as a result of the presence of permanganate occurred during this initial period of treatment and corresponds to an enhanced DNAPL mass depletion rate of 22% (MacKinnon and Thomson 2002). The subsequent drop in chloride concentration after day 150 indicates a concurrent decrease in the DNAPL mass removal rate.

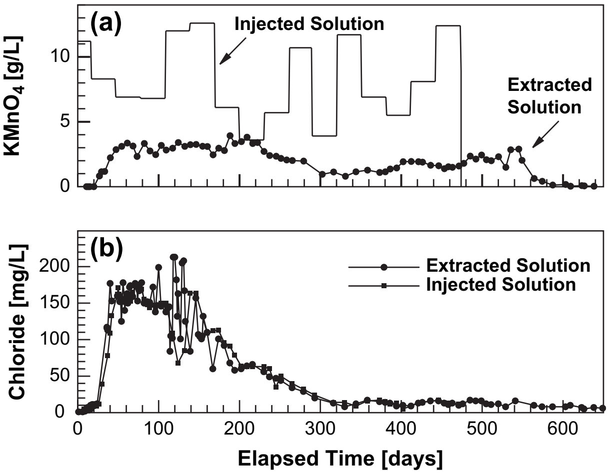

Figure 3. Temporal profiles of (a) extracted and monthly average injected permanganate concentrations and (b) extracted and injected chloride concentrations. Day 0 corresponds to the start of permanganate treatment.

Over the entire duration of this investigation, only 300 kg of $KMnO_4$ were extracted, leaving 590 kg of $KMnO_4$ either consumed by oxidation of TCE, PCE, and reduced components associated with the aquifer solids or unaccounted for. Based on the mass of DNAPL estimated by modeling to be present at the beginning of the permanganate flush, the stoichiometric requirements for complete mineralization of TCE and PCE were 15.4 kg of $KMnO_4$, or approximately 2% of the $KMnO_4$ mass injected. Using the maximum NOD observed from the bench-scale experiments of 3.5 g $KMnO_4$/kg, a bulk density of 1750 kg/m^3 and a treatment zone volume of 20 m^3 consistent with the tracer test data yield an estimated mass of $KMnO_4$ consumed by the aquifer material of approximately 120 kg. Therefore, the fraction of oxidant mass recovered was estimated to be approximately 40%, which is consistent with those observed in other bench and field-scale experiments. For example, MacKinnon and Thomson (2002) recovered approximately 77% of the permanganate mass injected into a two-dimensional model aquifer packed with silica sand containing a PCE DNAPL, while the field experiment conducted by Schnarr et al. (1998), in a completed enclosed sheet-pile cell, recovered only 59% of the injected permanganate mass. In contrast, in our pilot-scale investigation, substantial permanganate may have migrated outside the treatment zone as a result of incomplete closure of the recirculation system. Limited data collected at the downgradient sentry monitoring wells indicated that some permanganate had migrated beyond the extraction wells.

One-Meter Fence Line

Based on the small differences between the chloride concentrations in the injected and extracted solutions (Figure 3b), few inferences about the extent of ongoing TCE and PCE mass destruction could be made. In fact, at this sampling scale, oxidation of the source zone appeared to have been complete after approximately 300 d. To provide additional insight on the extent of ongoing mass removal, chloride concentration temporal profiles from the 1-m fence line were examined (Figure 4). For the multilevel piezometers located immediately to either side of the source (ML1 and ML5), the breakthrough chloride concentrations were comparable to the injected chloride concentration, indicating that only recycled chloride was observed at these monitoring points. Chloride generated by the oxidation reaction within the source zone, however, was consistently observed in the center multilevel (ML3). The upper piezometer (ML3-4) followed a similar trend as the injected concentration, while the central piezometer (ML3-7) had an elevated chloride concentration for a short time then declined to the injected chloride concentration. Ground water samples collected from the lower piezometer ML3-10 consistently indicated that chloride concentrations were well above the injected concentration at this location and included the highest observed chloride concentration of 8360 mg/L at day 52. After 300 d, no difference between chloride concentration in the injection and extraction wells was evident; however, elevated chloride concentrations were measured in ML3-10 up until day 450. This discrepancy between the two sampling scales suggested that after 300 d of permanganate injection, the rate of TCE and PCE removal was slow and produced a small but concentrated chloride plume that was not evident in the extraction wells due to wellbore dilution effects.

Periodically complete sets of ground water samples were collected from the 1-m fence line to evaluate the spatial distribution of permanganate and chloride downgradient of the treatment zone. Figure 5 presents examples of these distributions for sampling episodes conducted on day 120 and 160. These spatial distributions provided fine-resolution sampling data from which the location of the injected oxidant was inferred and the relative rates of DNAPL mass removal assessed. The results from each sampling episode indicated the presence of an asymmetrical permanganate plume extending below the 1-m fence line and high chloride concentrations, relative to the injected concentration, corresponding to the source location. The consistent appearance of the distinct chloride plume in the vicinity of the source, in contrast to the larger spatial extent of the permanganate plume, suggested that the spreading of the permanganate plume occurred upgradient of the source zone. While some of the spreading of the injected permanganate may have resulted from high injection flow rates and density-driven advection, divergence of flow around the source zone was most likely caused by the lower hydraulic conductivity associated with the source zone.

The spatial distributions at day 120 (Figure 5a) correspond to the period of time when the injection/extraction

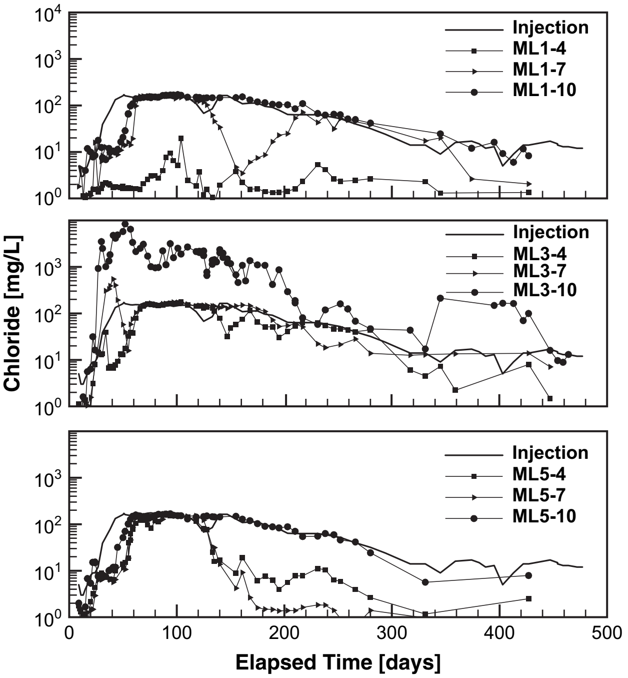

Figure 4. Temporal profiles of chloride concentration at selected locations within the 1-m multilevel sampling fence line (Figure 1 for locations). The injected chloride concentration profile is also shown for comparison (solid line).

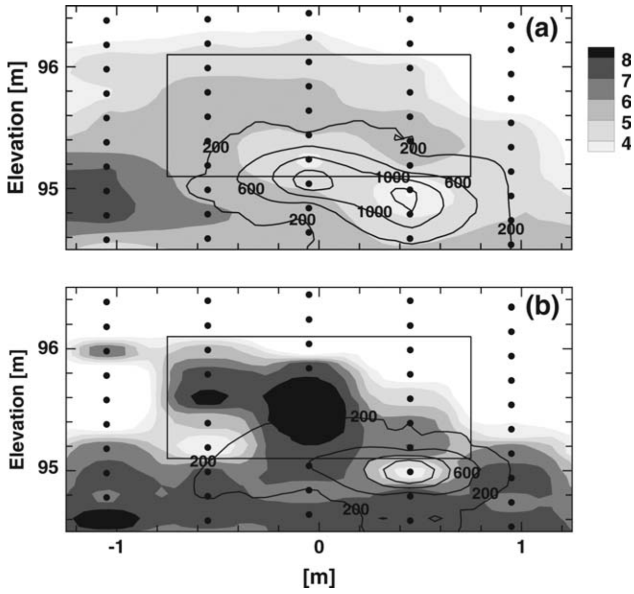

Figure 5. Spatial distribution of chloride (mg/L; labeled lines) and permanganate (g/L; filled zones) at the 1-m multilevel sampling fence line at (a) day 120, and (b) day 160. The solid circles indicate sampling locations and the rectangle represents the spatial extent of the source zone.

system was operating at the highest flow rate and resulted in a wider permanganate plume as compared to day 160 (Figure 5b) when the flow rates were reduced. However, for both sampling episodes, the location of the peak chloride concentration coincided with lowest permanganate concentration consistent with ongoing oxidation of TCE and PCE. This distinct chloride peak persisted until day 280 before decreasing and blending with neighboring zones to form a small chloride plume with a peak concentration of approximately 100 mg/L. By day 450, chloride concentrations across the 1-m fence line decreased to a level that if a distinct chloride plume was present, it was below the spatial sampling resolution (0.2 m vertically and 0.5 m horizontally). This result was consistent with the temporal ML3-10 chloride concentration data (Figure 4b), where elevated concentrations more than 100 mg/L were not observed beyond day 450.

Ground Water Profiling

Once evidence that chloride concentrations were decreasing at the extraction wells, vertical profiles of aqueous permanganate and chloride concentrations were collected from the center and downgradient of the source zone using the profiling tool. Peak permanganate concentrations in the profiles collected from the center of the source zone (Figures 6a through 6d) varied from 4 to 10 g $KMnO_4$/L but indicated that a concentrated permanganate solution was present in the source zone. In general, the permanganate concentrations increased with depth through the source zone consistent with the 1-m fence line data. The chloride signature was consistently located in a narrow interval approximately 0.25 m above the bottom of the source, suggesting the presence of a small DNAPL zone. This peak chloride concentration decreased over time and by day 430 (profile not shown) was indistinguishable from the recycled chloride concentration, indicating that no oxidation was occurring upgradient of the center of the source zone.

Figures 6e and 6f present permanganate and chloride concentration data from two profiles collected at day 480 downgradient of the source zone spaced approximately 0.4 m apart. At these locations, there is evidence that permanganate is present (2 to 10 g $KMnO_4$/L) but more significant is the presence of a distinct chloride signature (~450 mg/L) in one of these profiles. Given that no chloride signature was observed in the profiles collected from the center of the source zone, these data suggest that even at day 480, oxidation was still ongoing in the downgradient portion of the source zone.

Posttreatment Conditions and Performance Assessment

Posttreatment assessment of the TCE and PCE plume performed under ambient-gradient conditions indicated peak concentrations of TCE and PCE in the 1-m fence line of 2.0 and 30 mg/L, respectively (Figure 2b), at a location identical to that observed during the baseline assessment and coincident with the persistent hotspot reported by Rivett and Feenstra (2005). The reductions in peak concentrations relative to the baseline assessment were 99% for TCE and 48% for PCE (Table 1); however, it is unlikely that the peak concentration in the plume was coincident with a sampling piezometer in the 1-m fence line for either the baseline or the posttreatment sampling episodes, so the reliability of these reductions should be considered approximate. Assuming a uniform specific discharge estimated from the average hydraulic gradient and hydraulic conductivity, the source zone mass loading or discharge rate of TCE and PCE to the plume was estimated to be 7.0 and 98 mg/d, respectively. Relative to the baseline assessment, these ambient-gradient discharge rates represent a 99% reduction for TCE and a 89% reduction for PCE.

The forced-gradient source zone mass loading of TCE and PCE to the extraction system was estimated using the observed extraction system flow rate and TCE and PCE concentrations ($n = 5$) to be 17 and 220 mg/d, respectively. In both the baseline and posttreatment assessments, the forced-gradient mass loading to the extraction system was approximately 2.4 times higher for both TCE and PCE than the ambient-gradient mass loading to the plume. This consistent ratio between the two loading estimates indicates that the two methods were reproducible and the

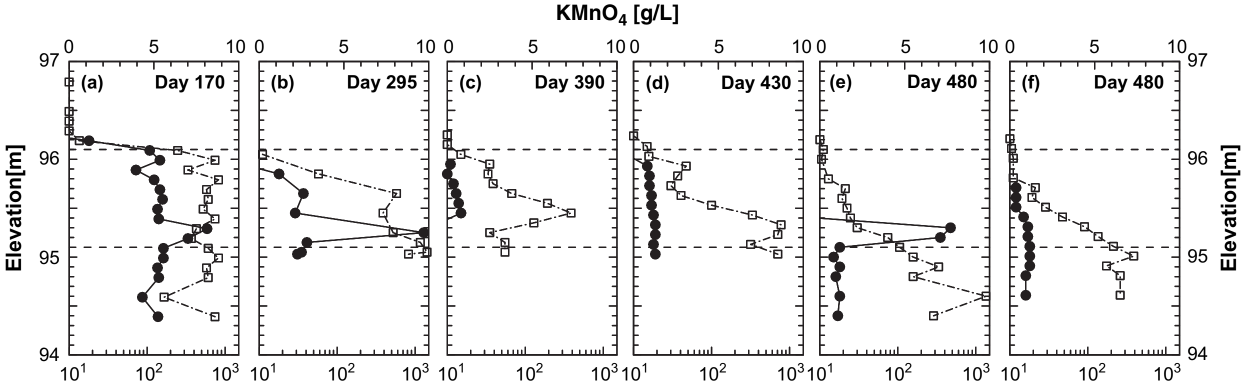

Figure 6. Vertical ground water profiles of chloride (solid circles) and permanganate (open squares) concentrations. The data shown in panels (a) to (d) were collected near the center of the source zone after 170, 295, 390, and 430 d of permanganate treatment, and the data in panels (e) and (f) were collected 0.4 m apart and less than 0.1 m downgradient of the source zone after 480 d of permanganate treatment. The dashed lines represent the vertical extent of the source zone.

Table 1
Summary of Treatment Performance Metrics

	Baseline		Posttreatment		Percent Reduction	
	TCE	PCE	TCE	PCE	TCE	PCE
Peak concentration (mg/L)	140	60	2.0	30	98	50
Ambient-gradient loading (mg/d)	860	880	7.0	98	99	89
Forced-gradient loading (mg/d)	2100	2220	17	220	99	90
Mass in source zone (kg)	9.0	1.6	<0.001	<0.001	>99	>99

assumptions underlying their use reasonable. However, the ambient-gradient mass loading estimate requires spatial interpolation/extrapolation and knowledge of the spatial variability of the fluid flux, which leads to uncertainty associated with this method. Based on an assessment of baseline condition data collected prior to permanganate treatment over a 15-d period, the estimated forced-gradient loadings to the extraction system for TCE and PCE were statistically identical ($n_{\text{TCE}} = 11$; $n_{\text{PCE}} = 11$; $p = 0.01$). In contrast, the average TCE loading after permanganate treatment was 7% of the PCE loading, indicating that the permanganate treatment had disproportionately removed TCE from the source zone. Preferential removal of TCE is consistent with the low TCE fraction in the initial source composition and the higher aqueous solubility (1100 mg/L compared to 200 mg/L) and reaction rate coefficient (8.0×10^{-1} compared to 3.5×10^{-2} L/Ms; Waldemer and Tratnyek 2006) of TCE relative to PCE, which favors faster mass removal. The permanganate treatment resulted in a statistically significant ($n_{\text{pre}} = 11$; $n_{\text{post}} = 5$; $p = 0.01$) decrease in forced-gradient loading of TCE and PCE to the extraction system suggesting that the observed reductions reflect the effect of the permanganate treatment rather than random sampling variations. The reductions in forced-gradient loading to the extraction system were 99% for TCE and 89% for PCE.

Bulk manganese soil concentrations ranged from 200 to 13,500 mg MnO_2/kg with a mean concentration of 1720 mg/kg (428 samples). The majority of the samples with elevated concentrations were located on the upgradient edge of the source zone with the highest concentration near the center, and only low manganese concentrations were observed across the top and bottom 10 cm. Manganese dioxide stains, evident as dark brown-black discolorations of the soil and indicative of permanganate oxidation, were present in distinct lenses, suggesting that DNAPL within these horizons had been oxidized. Some cementation of the soil grains was observed in the most highly stained regions consistent with the finding from MacKinnon and Thomson (2002). The total mass of MnO_2(s) in the source zone was estimated to be approximately 3.3 kg. Complete mineralization of the initial mass in the source zone of 9.0 kg of PCE and 1.6 kg of TCE would have generated 10.1 kg of MnO_2(s), approximately three times higher than estimated from the soil cores. Since the manganese oxides produced as a result of the oxidation of TCE and PCE are initially colloidal in nature and can migrate with ground water, it is not surprising to see a low mass of MnO_2(s) retained in this source zone (MacKinnon and Thomson 2002; Siegrist et al. 2002). The permeameter test results from 2 of the 23 intact soil cores extracted from the source at the completion of this study indicated that the arithmetic mean hydraulic conductivity of the source was 1.9×10^{-5} m/s ($n = 41$), a value consistent with the pretreatment hydraulic conductivity estimate of 2.65×10^{-5} m/s reported by Rivett and Feenstra (2005). This minor change in the source zone hydraulic conductivity over a period of 6 years of dissolution followed by approximately 500 d of active permanganate treatment suggests that hydraulic conductivity changes due to DNAPL depletion, dissolution of carbonate minerals from the acidity generated by the oxidation reactions, and manganese oxide plugging are insignificant or perhaps counteractive at the scale of these observations.

Bulk TCE soil concentrations ranged from less than 0.003 to 30 mg/kg with a mean concentration of 0.2 mg/kg (338 samples; standard deviation 1.7 mg/kg), while bulk PCE soil concentrations were higher and ranged from 0.2 to 160 mg/kg with a mean concentration of 25 mg/kg (345 samples; standard deviation 15.2 mg/kg). The mean TCE concentration was significantly lower than the mean PCE concentration, consistent with the lower mass of TCE present prior to permanganate treatment and the higher aqueous solubility and permanganate reaction rate coefficient of TCE relative to PCE, which would have resulted in a higher relative degree of TCE removal. The highest detections of TCE (five samples > 2 mg/kg) and PCE (seven samples > 50 mg/kg) were scattered on the downgradient side of the source zone in contrast to MnO_2(s), which was primarily deposited on the upgradient side of the source zone. The decrease in the TCE and PCE mass in the source zone was estimated to be more than 99% using the baseline DNAPL mass estimated from the modeling results by Frind et al. (1999) and the posttreatment mass estimated using the soil core data. This posttreatment mass estimate was based on a high density of soil cores (a total of 20 soil cores with a density of 1 core/0.04 m^2 that was subampled every 5 cm), which should provide a reasonably accurate estimate of the mass remaining; however, we acknowledge the potential negative bias associated with the use of bulk soil concentration core data to estimate source zone mass (Pankow and Cherry 1996). Based on the assumed initial mole fraction of the emplaced source material prior to permanganate treatment, linear partitioning calculations (Charbeneau 2000) suggest that a bulk soil PCE concentration of more than 50 mg/kg may indicate the presence of free phase PCE; similar calculations for TCE are problematic since the mole fraction of TCE is expected to decrease during treatment, and thus no minimum bulk soil concentration threshold can be specified without additional data. The five locations where the bulk soil PCE concentration was more than 50 mg/kg were randomly distributed on the downgradient side of the source, indicating that isolated zones of remnant free phase may have been present following permanganate treatment. The high chloride concentrations observed during the downgradient aqueous phase profiling on day 480 and the dissolved phase concentrations observed in the 1-m fence line during the posttreatment assessment support the presence of free phase, and also suggest that perhaps other areas of free phase were missed during the source zone soil coring campaign. In fact, the posttreatment TCE and PCE plume likely resulted from dissolution of a small free phase zone that was below the soil core sampling resolution, and therefore the posttreatment mass estimates from the soil core data underestimate the actual mass remaining in the source zone following treatment.

Removal of the remaining DNAPL mass during permanganate treatment was likely controlled by diffusive transport limitations; however, the mechanism that gave rise to these diffusion limitations is unknown. Presumably, the dissolution fingers with a width of less than 0.2 m as discussed by Rivett and Feenstra (2005) channeled the injected permanganate solution through the source zone, limiting direct contact with regions containing free phase TCE and PCE. The role that the manganese oxide deposits played in shielding DNAPL from direct access by permanganate is unknown.

Summary

In order to reduce the flow bypassing effects of the lower hydraulic conductivity associated with the source zone, and sustain elevated permanganate concentrations to maximize reaction rates and diffusion-related concentration gradients, a ground water recycling system comprising six injection and three extraction wells was implemented. The results from the tracer test indicated that the injected fluid was effectively delivered to the entire source zone but that the recirculation system did not operate as a completely closed-loop system and was able to capture only approximately 80% of the injected tracer mass. This reduced the expected effectiveness of the permanganate delivery system, as approximately 60% of the injected permanganate could not be accounted for and presumably migrated outside the capture zone or was consumed by unknown reactions in the treatment zone.

During permanganate injection, treatment effectiveness and progress were established by monitoring chloride, permanganate, TCE, and PCE concentrations in the extracted solution, at the 1-m fence line, and in aqueous profiles collected at strategic locations within and downgradient of the source zone. The permanganate delivery system was able to sustain an average permanganate injection concentration of approximately 8 g $KMnO_4$/L that was transported through and around the source zone, producing an average permanganate concentration in the extracted solution of approximately 2 g $KMnO_4$/L. Despite the high concentration of chloride in the recirculation system, the extracted solution showed elevated chloride levels relative to the injected solution until day 300, at which point it became indistinguishable from the injected concentration, suggesting that oxidation of the source zone was complete. However, using the data collected from the 1-m fence line, we were able to discern a zone of chloride production coincident with an area of lower permanganate concentration indicating ongoing oxidation of TCE and/or PCE up to day 450. Aqueous phase profiles collected from the center and downgradient of the source zone indicated that permanganate was present at these locations, and more importantly provided clear evidence that a distinct chloride signature was present at day 480. This tiered approach to monitor treatment effectiveness allowed us to optimize data collection efforts by moving to a finer spatial-scale and more focused sampling effort as evidence at the coarser resolution indicated that a potential treatment end point was reached.

Three monitoring techniques were used in this pilot-scale investigation to assess the impact of permanganate treatment on the capability of the remaining source zone mass to generate a dissolved phase plume: (1) the peak plume concentration at the 1-m fence line; (2) ambient-gradient loading across the 1-m fence line; and (3) forced-gradient loading to the extraction system. The reductions in ambient-gradient loading and forced-gradient loading were similar, indicating that they both were representative metrics of the reduction in loading following treatment. This may have been a result of the uncommonly high spatial sampling density employed in this investigation at the 1-m fence line and a sparser sampling network may not have generated similar results; however, the numerical investigation conducted by Kubert and Finkel (2006) suggests that that method we used is largely independent of the number of sampling points. In addition, the ambient-gradient loading estimate requires knowledge of the ground water flux (calculated from hydraulic gradient observations and hydraulic conductivity estimates), which is known to vary seasonally at this site. The forced-gradient loading measurement provides a direct measure of the ability of the source to generate a ground water plume and assumes that a comparable fraction of the plume was extracted during both the baseline and posttreatment measurements; however, this is considered minor in comparison to the limitations associated with the measurement of ambient-gradient loading. Moreover, the uncertainty in the ambient-gradient loading can be determined only by collecting replicate data sets, while the forced-gradient loading measurement requires far fewer samples and readily permits a statistical analysis of the uncertainty. Surprisingly, the percent reduction in peak PCE concentration did not agree favorably with the reduction in the two loading estimates, likely as a result of the sampling resolution in the 1-m fence line and temporal variability in the direction of ground water flow. To use concentration reduction at individual monitoring points as a meaningful assessment of treatment performance requires that similar hydraulic conditions are present during baseline and posttreatment sampling episodes. Even if this were possible, point concentration measurements provide less information about the extent or potential impact of a source zone on downgradient receptors than plume loading estimates. Finally, we feel that using reductions in bulk soil concentration as a treatment performance metric may be problematic since NAPL heterogeneity at some sites makes collection of representative samples difficult and expensive, and measurement errors related to subsampling and analyses can affect sample representativeness (Siegrist et al. 2006).

This study involved permanganate treatment of a homogenous residual DNAPL source emplaced within a uniform fine-to-medium sand aquifer. The known physical location of this source zone provided an opportunity to install a ground water recirculation system immediately upgradient and downgradient of the source area. This recirculation system allowed for elevated permanganate concentrations to be sustained within the source zone in order to maximize reaction rates and diffusion-related transport, and for an increased flow rate and hence oxidant loading to be delivered to the source zone. In addition, the manner in which this source zone was constructed represents perhaps a best-case condition for dissolution. Given these clear advantages relative to actual contaminated sites and the lengthy period of permanganate injection (485 d), there remained a distinct chloroethene plume 400 d after active permanganate treatment was terminated. The presence of this remaining plume under these near-ideal treatment conditions suggests that partial source mass removal is a likely outcome of permanganate treatment, and hence, performance expectations should be accordingly tempered.

Acknowledgments

Funding for this research was provided by the University Consortium, Solvents-in-Groundwater Research Program, which is sponsored by Boeing, Ciba-Geigy, General Electric, Eastman Kodak, Laidlaw Environmental Services, the Natural Sciences and Engineering Research Council of Canada, and the Ontario University Research Incentive Fund. This manuscript was significantly improved by comments provided by two anonymous reviewers.

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