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Application of a Persistent Dissolved-phase Reactive Treatment Zone for Mitigation of Mass Discharge from Sources Located in Lower-Permeability Sediments

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Abstract

The purpose of this study is to examine the development and effectiveness of a persistent dissolved-phase treatment zone, created by injecting potassium permanganate solution, for mitigating discharge of contaminant from a source zone located in a relatively deep, low-permeability formation. A localized 1,1-dichloroethene (DCE) source zone comprising dissolved- and sorbed-phase mass is present in lower permeability strata adjacent to a sand/gravel unit in a section of the Tucson International Airport Area (TIAA) Superfund Site. The results of bench-scale studies conducted using core material collected from boreholes drilled at the site indicated that natural oxidant demand was low, which would promote permanganate persistence. The reactive zone was created by injecting a permanganate solution into multiple wells screened across the interface between the lower-permeability and higher-permeability units. The site has been monitored for nine years to characterize the spatial distribution of DCE and permanganate. Permanganate continues to persist at the site, and a substantial and sustained decrease in DCE concentrations in groundwater has occurred after the permanganate injection. These results demonstrate successful creation of a long-term, dissolved-phase reactive-treatment zone that reduced mass discharge from the source. This project illustrates the application of in-situ chemical oxidation as a persistent dissolved-phase reactive-treatment system for lower-permeability source zones, which appears to effectively mitigate persistent mass discharge into groundwater.

Keywords

Remediation; ISCO; Oxidation; Permanganate; Source zone; Mass flux; Source containment

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INTRODUCTION

Contaminant source zones located in relatively deep, lower-permeability formations provide special challenges for remediation. This remains true even when organic-liquid (i.e., NAPL) contamination has been depleted or was never present, and contamination exists as only dissolved and sorbed mass. These secondary sources, often comprising lower concentrations, typically have poor hydraulic accessibility yet may discharge mass in quantities sufficient to sustain groundwater contaminant plumes.

Many of the treatment technologies available for source zones, such as enhanced in-situ flushing, in-situ chemical oxidation, and enhanced bioremediation, rely on reagent delivery and hydraulic accessibility of the contamination. Such methods are typically ineffective for sources residing in lower-permeability domains. For example, the results of prior research have shown that standard flood injection of permanganate solution does not fully treat contamination residing in lower-permeability domains (e.g., Seol et al., 2003; Heiderscheidt et al., 2008; Marble et al., 2010). Technologies that can more specifically target the contamination within the lower-permeability domains, such as in-situ thermal or electrokinetic methods, are generally expensive and/or impractical for deeper sources. Hydraulic containment is not considered practical due to the lower permeability, lower hydraulic accessibility, and diffusive mass-transfer limited constraints. Hence, new approaches are needed to address these sources of contamination.

One possible approach for such conditions is to focus on mitigating contaminant discharge rather than on enhancing contaminant removal. This could be accomplished for example by injecting a material (vegetable oil, silica) to decrease permeability at the interface between the higher and lower permeability zones, thereby reducing discharge (e.g., Durmusoglu and Corapcioglu, 2000; Coulibaly and Borden, 2004; Borden, 2007; McCartney et al., 2011). Another possible option is to create a persistent, dissolved-phase treatment zone by injecting a solution containing an oxidizing or reducing agent into the lower-permeability domain to reduce contaminant discharge from the source.

The objective of this study was to examine the effectiveness of a persistent dissolved-phase treatment zone for mitigating discharge of contaminant from a source zone located in a relatively deep, lower-permeability formation. The study was conducted in a section of the Tucson International Airport Area (TIAA) Superfund Site. The treatment zone was created by injecting a potassium permanganate solution into the target domain. The concentrations of the contaminant of concern and the presence of permanganate in groundwater were monitored for approximately nine years to evaluate the effectiveness of the approach.

MATERIALS AND METHODS

Study Site

The site that was the focus of the study is part of the Tucson International Airport Area (TIAA) federal Superfund site in southern Arizona (Leake and Hanson, 1987; Brusseau et al., 2007, 2011a, 2013). A large, multiple-source trichloroethene plume exists in the upper portion of the regional aquifer, which is a secondary source of potable water for the Tucson

metropolitan area. A large-scale in-situ chemical oxidation project was conducted at two source zones in the southern portion of the regional plume (Brusseau et al., 2011b). The current work is focused on the Samsonite Building Area (SBA), which is a part of the Tucson Airport Authority's domain in the central portion of the TIAA site (Figure 1).

A localized 1,1-dichloroethene (DCE) source zone comprising dissolved- and sorbed-phase mass is present in a lower permeability stratum that is adjacent to sand/gravel layers. DCE contamination at the SBA site was initially discovered through soil-gas surveys from 1988, 1993, and 2000 that identified the presence of DCE and delineated the potential source area (a 30 by 25 meter zone near monitoring well S-31). The site consists of the small source area and a groundwater contaminant plume extending approximately 70 m to the west. Concentrations of DCE in groundwater samples collected from monitoring wells S-31 and S-42 averaged approximately 40 and 5 µg/L, respectively, before the remedial action. The source of the DCE contamination is unknown. Based on current data and site historical records, it has been hypothesized that no organic-liquid DCE is currently present, if it had indeed ever been, and that all contamination is present as dissolved and sorbed mass (Whillier, 2004).

Based on prior characterization efforts (CRA, 2003), the majority of the contamination resides in a lower permeability layer of a ~30-m thick unit termed the shallow groundwater zone (SGZ) (Figure 2). This layer, comprised primarily of silt and clay, resides between approximately 28 and 34 below land surface (bls). A thin (~3-m thick) laterally discontinuous sand and gravel unit, termed the gravel sub-unit (GSU), is present in the lower portion of the SGZ, between approximately 34 and 37 m bls, adjacent to the lower-permeability layer. A layer of sand with silt and gravel resides above the lower-permeability layer. The potentiometric surface for the shallow groundwater zone is approximately 25 m bls in the vicinity of the source area, resulting in an approximately 13-m thick saturated zone. The GSU serves as the primary domain for contaminant transport and the attendant plume migration. The natural hydraulic gradient is towards the northwest, with a value of approximately 0.004. The SGZ is considered to act as a leaky confined aquifer system of limited areal extent. The GSU appears to have some hydraulic connection to the deeper regional aquifer. Thus, mass discharge from the source within the lower permeability SGZ into the higher permeability GSU could impact the regional aquifer system (CRA, 2003).

Bench-Scale Experiments

Several sets of bench-scale experiments were conducted to quantify KMnO_4 consumption, sediment oxidant demand, DCE oxidation, and possible mass loss (e.g., volatilization). The KMnO_4 solution used in the bench-scale experiments and the field test was prepared using RemOx™ -ISCO reagent (98.8% pure) obtained from Carus Chemical Company (Peru, IL). A 1 M sodium thiosulfate pentahydrate solution was added to the vials prior to sampling to quench further oxidation (e.g., Hood et al., 2000; Johnson et al., 2012). DCE used in bench-scale experiments was ACS grade (Aldrich Chemical Co., Inc., Milwaukee, WI). The initial DCE concentration for all experiments was 100 µg/L, which was used to represent the upper end of anticipated concentrations at the site. Synthetic groundwater designed to represent natural site groundwater, with an ionic strength of 0.01 M and pH of 7.7, was used in all

bench experiments. The composition is presented in Johnson et al. (2003). A representative sediment sample collected from the site (borehole IW-05, 23 to 24 meters bls) was used for the experiments.

Experiment A did not contain sediment and was designed to examine DCE transformation kinetics at three different initial permanganate concentrations (19, 1, and a replicate for 1 mM). Synthetic groundwater was added to 20-mL borosilicate vials followed by DCE stock solution and finally stock permanganate solution. At the scheduled sampling time, subsamples were removed and transferred into a GC headspace vial with sodium thiosulfate and then analyzed. Experiment B also did not contain sediment and served as the system controls (DCE in synthetic groundwater) to quantify DCE loss from the reactors due to volatilization and other possible loss mechanisms.

For experiments C and D, five grams of sediment were added to the vials. Experiment C examined permanganate oxidant demand of the sediments, and contained no DCE. Experiment D examined the kinetics of DCE transformation in the presence of the sediment. Four different initial permanganate concentrations were tested including 1.0, 3.8, 20, and 29 mM (0.02 to 0.5%).

Sample times spanned from 1 minute to 20 hours. Triplicate samples were collected and analyzed each sampling period. The samples were analyzed by gas chromatography (Shimadzu GC-17A) with an electron capture detector (ECD) and Tekmar 7000 headspace sampler for DCE, with a detection limit of approximately 1 µg/L. KMnO₄ was analyzed using a ultraviolet-visible spectrophotometer (Shimadzu UV-VI Model 1501), with a detection limit of approximately 1 mg/L.

Permanganate Injection and Performance Monitoring

Fourteen boreholes were drilled at the SBA site to characterize the DCE contamination source zone before ISCO treatment application. They were drilled using a hollow stem auger CME-85 (St. Louis, Missouri). The boreholes were completed as wells for injection or monitoring (Figure 1). Preliminary mathematical modeling was conducted using MODFLOW-2000 (Harbaugh, et al., 2000) and MT3D3 (Zheng and Wang, 1999) to support selection of the injection design and evaluate potential persistence of the injected solution. The results of the simulations indicated that the selected design would support the development of a permanganate zone that would persist for several years.

Nine of the wells (IW-01 through IW-09) were spaced in a regular areal grid pattern, with approximately 9-meter intervals, located in the center of the source area. The other five boreholes were located ~40 m downgradient. The wells were screened across the interface between the higher-permeability and lower-permeability layers (23 to 29 m bls). With the presence of the sand and silt layer at the top of the injection zone, it was anticipated that the injected solution would migrate through this interval relatively quickly during the injection (with the attendant higher gradients). After the injection and initial migration, it was then expected that lateral migration would be slow, and that the solution would migrate primarily downward into the lower-permeability layer.

Continuous cores of sediment were collected in ~1 meter increments from 22 to 32 meters bls for each borehole, using clear 7.6 cm outer diameter acrylic tubes. Sediment subsamples were collected from the cores when noticeable changes in stratigraphy were apparent and averaged 2 subsamples per core. Windows of approximately 6 cm² were cut into the side of the acrylic tubes with a utility knife, into which were inserted plastic 10-mL syringes with the tips cut off. The syringes were pressed into the core until filled. Sediment samples were then extruded into 40-mL borosilicate vials that contained 20 mL of HPLC/ACS grade methanol. The samples were stored on ice and transported to the laboratory.

The samples were placed on a shaker table and agitated for 12 hours and then centrifuged. Subsamples of the extractant fluid were then analyzed for DCE by gas chromatography, with a quantifiable detection limit (QDL) of 4.5 µg of DCE per kg of dry sediment. Selected sediment subsamples were dried, ground, and digested with acid before being analyzed with a N/C/S Analyzer (Model NA 1500, Carlo-Erba Strumatazione, Milan, Italy) for measurement of total organic carbon.

Groundwater samples were collected from all monitoring and injection wells prior to, during, and after the permanganate injection. The samples were analyzed for temperature, pH, oxidation reduction potential (ORP), total dissolved solids (TDS), and conductivity using a field-portable unit (Myron L Company Ultrameter II 6P) that was calibrated daily. Additional samples were collected with dedicated Model QED Micropurge bladder pumps (Ann Arbor, MI), and analyzed for chloride, chromium (VI), and DCE. Chromium concentrations were monitored to assess if oxidant addition caused mobilization of resident chromium. Analysis of drill cuttings revealed total Cr concentrations of approximately 8 mg/kg. Chromium (VI) concentrations in groundwater were analyzed using EPA method 8023, with a detection limit of approximately 30 µg/L. DCE concentration in groundwater samples was determined using GC/MS, with a detection limit of 0.5 µg/L. Long term monitoring included analysis of MnO₄ and DCE (the latter only when no MnO₄ was present).

Injection of the permanganate solution spanned two months (July 26-August 15) in 2005 (Table 1). The injections included three wells at a time, and the series of wells were switched every few days to complete injection in all wells. The injection flow rates averaged 2.3 to 4 gpm (8.7 to 15 L/min), which was achieved through a flexible hose and rigid PVC piping manifold where injection rates, total flow, and well-head pressures were monitored with flow meters and magnehelic pressure gauges, respectively. A total of 3289 kg of permanganate was injected with an average concentration of 1.7% (ranging from 0.7–1.7%). Note that permanganate solution was not injected into IW-07 so that it could be used as a monitoring well.

RESULTS AND DISCUSSION

Pre-Injection Sediment and Groundwater Data

A total of 66 solvent-extraction subsamples were collected from the IW-01 to IW-09 borehole cores. Of the 66 samples, four had detections above the QDL (>4.5 µg/kg), 18 had detections below the QDL, and 44 were non-detect for DCE. DCE was detected above the

QDL for cores from IW-01, IW-03, and IW-09. DCE was detected but below the QDL for all cores except IW-05 and IW-06. These latter two cores are on the southwest edge of the source area. Sediment subsamples from IW-05 were used for the bench-scale experiments. The sediment material for which the DCE was detected was predominantly clay with some silt and sand, which suggests that the remaining DCE contamination was primarily distributed within the lower-permeability sediment materials. Removal of this contaminant mass via standard hydraulic-based remedial actions would be expected to be significantly limited by mass-transfer constraints.

The mean total sediment organic carbon for all samples was 0.03%. This value is consistent with previous results reported for sediment collected in the area (Johnson et al., 2003, 2009), and is typical for alluvial sedimentary systems in arid regions. The TOC did not vary significantly as a function of sediment grain size. Prior research shows that sorption of chlorinated aliphatic compounds by the sediment is very low, with retardation factors of ~ 1.1 (Johnson et al., 2003, 2009).

Long-term groundwater data are available for two monitoring wells at the test site, S-31, which is located in the center of the source area, and S-42, which is downgradient of the source area. DCE concentrations ranged from approximately 20 to 50 $\mu\text{g/L}$ for S-31 and from approximately 3 to 10 $\mu\text{g/L}$ for S-42 prior to the permanganate injection (Figure 3). Note that the DCE concentrations for these two wells generally increase during the nine years prior to the injection. These results indicate that it is unlikely that natural attenuation is significantly influencing DCE behavior. This is consistent with general site conditions and observations from prior site characterization. DCE samples were collected from the injection wells prior to injection. DCE concentrations ranged between 28 and 53 $\mu\text{g/L}$, consistent with the long-term results obtained for S-31.

Bench-Scale Investigation

DCE concentrations decreased rapidly in the presence of permanganate (Figure 4a). First-order rate coefficients of 0.22 and 1.3 min^{-1} were obtained for the 1 and 19.25 mM permanganate experiments, respectively. The very short half-lives observed for these experiments are consistent with the results of prior experiments for DCE (Huang et al., 2001). The results of the control experiments (Expt B) indicated no measurable loss.

Experiment C examined the natural oxidant demand associated with the sediment (Figure 4b), which was determined to be ~ 0.1 gram of permanganate per kg of sediment based on standard molar conversion. This value is at the low end of the range of reported values (e.g., Mumford et al., 2004). This low level of oxidant demand is attributed to the low organic carbon content and the absence of other oxidizable materials. The low natural oxidant demand, combined with the low permeability and resultant low groundwater velocities, is expected to contribute to significant persistence of the injected permanganate solution.

Experiment D investigated the rate of DCE degradation in the presence of sediments for several concentrations of permanganate (Figure 4c). For all the permanganate concentrations used in the experiments (0.99 mM, 3.75 mM, 19.9 mM, and 29 mM), DCE concentrations decreased below detection in all cases in less than 25 minutes. For permanganate

concentrations >1 mM, DCE was oxidized in less than 5 minutes. At an initial permanganate concentration of 29 mM, DCE was oxidized in less than 2 minutes. Note that this largest permanganate concentration is lower than that used for the field test (108 mM, 1.7%). The first-order rate coefficients obtained for these experiments with sediment present are similar to those obtained for the prior experiments conducted in the absence of sediment. This is consistent with the low natural oxidant demand and low sorption of DCE by the sediment.

Permanganate Application and Short-Term Response Monitoring

The average pH of groundwater prior to injection was 7.0 for all wells and 7.2 post-injection. It is likely that sediment-associated carbonate buffered the majority of the protons produced through the oxidation reaction. Pre-injection electrical conductivity values ranged from 826 $\mu\text{S}/\text{cm}$ in IW-09 to 2891 $\mu\text{S}/\text{cm}$ in IW-05 and averaged 2153 $\mu\text{S}/\text{cm}$. Post-injection conductivity values increased up to a maximum of 11,880 $\mu\text{S}/\text{cm}$ twenty days post-injection, and averaged 9809 $\mu\text{S}/\text{cm}$. Chromium (VI) samples were collected from IW-07 and S-31 and in all cases were below the detection limit.

The ORP measurements indicate significant alteration of the aqueous redox conditions upon injection of permanganate into the treatment zone (Figure 5a). The ORP averaged 203 mV prior to injection, while it averaged 634 mV after injection. ORP has remained relatively steady within the treatment zone since injection. The results show that DCE concentrations decreased to nondetect with the arrival of permanganate, as expected. For example, the arrival of permanganate and the increase in ORP was coincident with the observation of the DCE decrease from 30 $\mu\text{g}/\text{L}$ to nondetect at well IW-07 (Figure 5b).

Monitoring of well CRA-13 showed that a four-fold increase in ORP and the presence of purple coloration of groundwater was observed within three months of the injection. This shows that the permanganate solution migrated to at least as far as CRA-13 within that time, indicating relatively rapid migration during that time period. This is consistent with the anticipated behavior of rapid migration in the sand/silt layer during the injection. Within a year of the injection, ORP had decreased by approximately half and the groundwater was clear for CRA-13.

Long-Term Monitoring, Contaminant Concentration Reductions, and Permanganate Persistence

Monitoring of DCE concentrations and permanganate has continued for approximately nine years since the injection period. Figure 1 presents the areal extent of permanganate within the treatment zone since injection based on colorimetric measurements and visual observations, wherein the footprint of the permanganate plume was estimated by determining the best-fit distribution for the available measurements at each time period. The extent of the permanganate plume decreased significantly within the first two years, but appears to have stabilized in the last several years. These data indicate that the 2005 injections created a plume of permanganate that encompassed the entire source zone and which has persisted for approximately nine years. This persistence is attributed to the low oxidation demand associated with the sediments and contaminants (no NAPL), in combination with the low groundwater velocities. Any permanganate that migrates outside

the lower-permeability sediments is presumably transformed through the oxidation of resident DCE, organic matter, or other oxidizable material.

Figure 3 presents the DCE concentrations over time in the monitored wells. Note concentrations at well S-31 are plotted on the secondary y-axis because concentrations are significantly higher than those at wells S-42, CRA-13, and MWS-1. DCE concentrations have decreased since permanganate injection to below the regulatory standard (7 µg/L) at all well locations, and concentrations are below detection at wells S-31, CRA-13, and MWS-1. Inspection of the results for CRA-13, located downgradient from the treatment zone, indicate that DCE concentrations have remained near the detection limit for the entire monitoring period. This suggests that the permanganate injection has prevented further migration of the DCE plume.

SUMMARY

Injection of ISCO reagent solutions into a lower-permeability source zone can be used to create a dissolved-phase reaction zone to contain and treat residual or persistent contaminant sources. The application of this approach was tested through a pilot-scale study that developed a treatment zone through injection of permanganate solution at the Samsonite location of the TIAA Superfund site. Pre-injection TOC and DCE contaminant distributions were obtained from analysis of core material. Core materials were also used in a series of bench-scale experiments to determine natural oxidant demand, which was very low, and DCE transformation rates, which were very high. A multiple-well injection scheme with moderate distance between wells was used to enhance coverage between wells. Cycling of injection between different wells was also used to elicit hydraulic gradients in different directions to support a more uniform distribution.

The results of groundwater monitoring for nine years after injection shows that a persistent treatment zone of permanganate solution was developed. Since the injection, DCE concentrations in groundwater have decreased to below the regulatory standard for all well locations, and it appears that the permanganate injection has prevented further migration of the DCE plume. The results of the pilot test illustrate the successful development of an in-situ reactive treatment zone to mitigate persistent mass discharge into groundwater.

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Figure 1. Map of the test site and areal distribution of permanganate present throughout the shallow groundwater zone over time after injection

Figure 2.

Simplified schematic of simplified cross-section for the shallow groundwater zone. The red arrow shows the position of the screened intervals for the monitoring and injection wells.

Figure 3.
DCE concentrations over time at all monitoring wells screened in the shallow groundwater zone.

b.

c.

Figure 4.

a. Results of Experiment A: DCE relative concentration versus time with oxidation rates (k) upon addition of permanganate at initial concentrations of 0.99 mM and 19.25 mM without sediment.

b. Results of Experiment C: Permanganate relative concentration versus time upon reaction with sediment illustrating the impact of sediment oxidant demand.

c. Results of Experiment D: DCE relative concentration versus time with oxidation rates (k) upon addition of permanganate at initial concentrations of 0.99, 3.75, 19.88, and 29 mM with sediment.

a.

b.

Figure 5.

a. Oxidation-reduction potential (ORP) during and after permanganate injection for several wells.

b. 1,1-DCE concentration and ORP monitoring during and after permanganate injection for IW-07.

Table 1

Summary of permanganate solution injections within the source area of the Samsonite Site.

Well #	Date Range (2005)	Amt of H ₂ O (liters)	Amt KMnO ₄ (kg)	Cumulative Amt KMnO ₄ (kg)	% KMnO ₄ solution
IW-01	Jul 26 –Aug 15	28,139	517	517	0.7 –1.7
IW-02	Aug 4 –Aug 9	14,557	233	750	1.7
IW-03	Aug 9 –Aug 11	11,710	192	943	1 –1.7
IW-04	Aug 11 –Aug 15	18,444	203	1,146	1 –1.7
IW-05	Aug 11 –Aug 15	17,636	203	1,349	1 –1.7
IW-06	Aug 4 –Aug 10	14,557	233	1,582	1.7
IW-07	Observation well only				
IW-08	Aug 9 –Aug 11	11,710	192	1,774	1.7
IW-09	Aug 9 –Aug 11	11,710	192	1,967	1.7
IW-10	Jul 28 –Aug 2	22,342	284	2,251	1.2 –1.6
IW-11	Jul 28 –Aug 2	22,342	284	2,534	1.2 –1.6
IW-12	Jul 28 –Aug 2	22,342	284	2,818	1.2 –1.6
IW-13	Aug 2 –Aug 4	15,356	236	3,054	1.7
IW-14	Aug 2 –Aug 4	15,356	236	3,290	1.7
		226,200	3,290		

Note: Injection configuration: 1, 2 or 3 wells