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Using slow-release permanganate candles to remove TCE from a low permeable aquifer at a former landfill

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Abstract

Past disposal of industrial solvents into unregulated landfills is a significant source of groundwater contamination. In 2009, we began investigating a former unregulated landfill with known trichloroethene (TCE) contamination. Our objective was to pinpoint the location of the plume and treat the TCE using in situ chemical oxidation (ISCO). We accomplished this by using electrical resistivity imaging (ERI) to survey the landfill and map the subsurface lithology. We then used the ERI survey maps to guide direct push groundwater sampling. A TCE plume (100–600 $\mu\text{g L}^{-1}$) was identified in a low permeable silty-clay aquifer ($K_{it} = 0.5 \text{ m d}^{-1}$) that was within 6 m of ground surface. To treat the TCE, we manufactured slow-release potassium permanganate candles (SRPCs) that were 91.4 cm long and either 5.1 cm or 7.6 cm in dia. For comparison, we inserted equal masses of SRPCs (7.6-cm versus 5.1-cm dia) into the low permeable aquifer in staggered rows that intersected the TCE plume. The 5.1-cm dia candles were inserted using direct push rods while the 7.6-cm SRPCs were placed in 10 permanent wells. Pneumatic circulators that emitted small air bubbles were placed below the 7.6-cm SRPCs in the second year. Results 15 months after installation showed significant TCE reductions in the 7.6-cm candle treatment zone (67–85%) and between 10% and 66% decrease in wells impacted by the direct push candles. These results support using slow-release permanganate candles as a means of treating chlorinated solvents in low permeable aquifers.

Keywords: permanganate, chlorinated solvents, TCE, slow-release oxidants

1. Introduction

The disposal of solid waste into unregulated landfills has resulted in numerous examples of groundwater contamination throughout the United States. Although federal regulations have been enacted to promote safe disposal of nonhazardous waste (e.g., Federal Resource Conservation and Recovery Act, Subtitle D), not all landfills have been in compliance. For example, from 1972 through 1991, small communities in the state of Nebraska with populations of 5000 or less were exempt from solid waste rules and regulations (NDEQ, 1990). These small landfills were not required to have liners, conduct

groundwater monitoring, or take appropriate steps to prevent the disposal of industrial solvents. Although this original exemption was intended to limit the financial burden on small communities, the consequences of not requiring preventative actions have resulted in widespread groundwater contamination. In 1990, Nebraska had 294 unregulated landfills, of which, 135 were identified as having groundwater concerns (Woldt et al., 1998). While many of these solid waste disposal facilities have since closed, several local communities are now strapped with the financial costs of removing industrial solvents such as tetrachloroethene, trichloroethene, and 1,1,1-trichloroethane from their groundwater.

During the past decade, significant efforts have been devoted to developing innovative remedial technologies to treat contaminants at the source. One technology that is relatively mature is the injection of liquid oxidants into contaminated aquifers or in situ chemical oxidation (ISCO) (Watts and Teel 2006). Permanganate is widely accepted as an efficient oxidant for ISCO applications and is extremely efficient in oxidizing chlorinated ethenes to CO_2 (Yan and Schwartz, 1999, 2000). While the chemistry is sound, the application and delivery of permanganate to the contaminants is still a challenge at many sites. Most ISCO treatments to date have involved injecting oxidants into aquifers as liquids. A common problem with any chemical injection however, is that certain sites have finer textured soils that do not readily accept liquid injections. When this occurs, the chemical oxidant can be observed coming back out of the injection borehole because it offers the path of least resistance. Difficulty in addressing contamination in low permeable soils may be alleviated to some degree by taking a passive approach where a controlled-release oxidant is inserted into the formation and allowed to dissolve and intercept the contaminant over many years.

The idea of encapsulating permanganate for sustained release was first proposed several years ago (Kang et al., 2004; Ross et al., 2005; Schwartz, 2005; Swearingen and Swearingen, 2008) and since then, a number of publications have documented the efficacy of slow-release oxidant dispersal systems to remove chlorinated solvents at the laboratory-scale and in larger flow-tank systems (Lee and Schwartz, 2007a, 2007b; Lee et al., 2008a, 2008b, 2009). Although excellent results have been reported, examples of field-scale applications by practitioners have been limited, in part because commercial sources of slow-release oxidants have not been readily available.

In 2009, we began investigating a former unregulated landfill with known TCE contamination. Our objective was to pinpoint the location of the plume and implement an ISCO remedial strategy. This was accomplished by using a geophysical approach, which characterized the lithology of the landfill and guided groundwater sampling. Because TCE was found to be located in a low permeable aquifer, we hypothesized that using slow-release permanganate candles would be effective at reducing TCE concentrations in the contaminated aquifer. This paper reports the manufacturing and deployment of slow-release permanganate candles (SRPCs) and provides results from both laboratory and field testing aimed at demonstrating the release rates and radius of influence of the SRPCs as well as their efficacy in reducing TCE concentrations.

2. Materials and methods

2.1. Site history and characterization

The former Cozad Solid Waste Disposal Facility is a small community landfill in western Nebraska (Cozad, NE) that operated for 20 yr. During this time, unknown quantities of TCE were deposited into the landfill from residential, commercial, and industrial sources. The facility was closed in 1989 after TCE was detected in monitoring wells located down-gradient from the refuse cells at concentrations above the USEPA's Maximum Contaminant Level (MCL). Remedial attempts to date have included a dual phase extraction facility, poplar tree plantings to induce phytoremediation, and volatilization ponds. Despite these efforts, TCE contamination remains and the migrating plume has not been contained.

To characterize the landfill and identify the location of the plume, several spatial measurements were made. These included: electrical resistivity imaging (ERI, Figure 1), direct push electrical conductivity logging, hydraulic conductivity measurements and the measurement of soil texture, soil oxidant

demand and groundwater chemistry. Details of these measurements along with chemical standards, and analytical instruments used are provided in supplementary material (in Supplementary Material (SM) SM Section 1.1–1.6, Figure SM-1).

2.2. Slow-release permanganate candle production

A drying oven (Fisher Scientific-Isotemp Oven 630F), hot plate (Fisher Scientific-Isotemp Hot Plate 11-100-49SH), 6-quart electric skillet and a 2-quart ceramic cooker were preheated to $93 \pm 5^\circ\text{C}$. Straight solid paraffin wax (Peak Candle Supply-IGI 1343A) was placed into an electric skillet until melted and subsequently transferred to the ceramic cooker to be kept melted and ready for use. Approximately 600 g of KMnO_4 (Carus Corp-RemOxS) were put into glass mason jars and placed into a drying oven to preheat (93°C) for at least 15–20 min. 250 mL of melted wax was added to an aluminum wax pouring pot and placed on the hot plate. A stand-alone mixer with propeller blade was inserted into the wax, and 600 g of preheated KMnO_4 were quickly added to the melted wax. The mixture was stirred at approximately 2000 rpm until all KMnO_4 particles were blended with the wax. Additional melted wax and/or KMnO_4 was added to the mixture to achieve a mixture with a milkshake like consistency that was just barely pourable. The final ratio by mass of KMnO_4 to paraffin was on average 4.6:1 (w/w). Additional text discussing how the 4.6:1 ratio was chosen is provided in supplementary material (in SM Section 1.7). If the mixture cooled too quickly it was briefly placed back into the drying oven to reheat to $93 \pm 5^\circ\text{C}$. The mixture was then poured into a 7.6 cm (3 in.) or 5.1 cm (2 in.) by 91.4 cm (36 in.) stock cardboard tube (Yazoo Mills) with a poly tube plug inserted at the bottom. The cardboard tube was gently tamped to remove trapped air bubbles. Once filled, the candle was set aside to cool vertically at room temperature for at least 12 h. Material costs (US\$) per candle (91.4 cm long) were approximately \$18 (5.1-cm dia) and \$40 (7.6-cm dia).

2.3. Laboratory testing of SRPCs

To quantify permanganate release rates and radius of influence, laboratory experiments were conducted with 1.27 cm lengths of the 5.1 and 7.6-cm dia (disc-SRPCs) as well as with miniature candles (mini-SRPCs). The 5.1 and 7.6-cm disc-SRPCs were sealed on the flat top and bottom with a layer of pure wax to ensure diffusion was in the radial direction only, so results could be scaled to any candle length. The miniature candles were prepared in a similar manner to ones used in the field trial but were cast in 0.71-cm dia molds, 2.38 cm in length.

For the mini-SRPCs, we placed individual mini-candles into clear glass jars with 200 mL of deionized water. Sample temperature was maintained at 15°C and room temperature in two separate experiments. Immediately prior to sampling, the solutions were gently swirled to mix. The solution was sub-sampled via pipette every 10 min for the first hour, hourly for the first 4 h, and approximately daily for the remainder of the experiment. Similarly, the disc-SRPCs were placed in 12.5 L of room temperature deionized water and sub-sampled in the same manner as above with the exception that samples were stirred to mix prior to sampling and collected weekly after the first 10 weeks. Samples were diluted when necessary, and analyzed on a Hach DR 2800 Visual Spectrum Spectrophotometer at 525 nm.

To characterize SRPC performance, we determined temporal KMnO_4 release rates (Flux, J) and concentration ratio (C_r). Flux was calculated using the following equation.

$$J = \frac{1}{A_{\text{SRPC}}} \frac{(C_{n+1}V - C_nV)}{(t_{n+1} - t_n)} \quad (1)$$

Figure 1. Composite ERI diagram of the former landfill in Cozad, NE. Figure represents results from 10 of the 19 ERI images obtained. Colored circles in cropped image (Line O) indicates locations and depths from which groundwater samples were obtained and provides an example of how samples were taken from different ERI-identified layers. (A) Results of direct push Electrical Conductivity Survey overlain on Line I in the TCE plume.

where A_{SRPC} is the exposed surface area of the cylindrical SRPC, C_{n+1} the concentration of MnO_4^- in solution at time t_{n+1} , C_n the concentration of MnO_4^- in solution at time t_n , V the volume of the solution, $t_{n+1} - t_n$ is the elapsed time between MnO_4^- measurements. Concentration ratio was calculated using the following equation.

$$C_r = \frac{CV}{M} \quad (2)$$

where M is the initial mass of $KMnO_4$ in the SRPC (Ross et al., 2005). Plots of both J and C_r versus time were fitted using non-linear regression to a 2-parameter power function with SigmaPlot scientific analysis and graphing software. The fitted equations were used to project the performance of the SRPCs with time.

2.3.1. Radius of influence

To ensure the gap between SRPCs at the Cozad field site would be closed, the permanganate radius of influence achievable through diffusion was estimated. Saturated aquifer material collected from sample cores was cut and packed into a $14 \times 14 \times 2.5$ cm 2D tank. A steel cylinder slightly larger than the diameter of the mini-SRPCs was pressed into the low permeable aquifer material to create a pseudo borehole. One mini-SRPC was placed into the bottom of the borehole, sand was poured around the SRPC and the top of the borehole was sealed with bentonite. The saturated tank was then sealed and the diameter of the MnO_4^- distribution was visually observed, measured, and photographed daily. Individual photographs were digitally enhanced with Microsoft Video Editing software (Windows Live Movie Maker) to intensify the color contrast so as to more easily quantify diffusion distances. To estimate the mass of permanganate released from the mini-SRPCs in the 2D tank, a parallel experiment in H_2O was conducted as described in Section 2.3 to determine release rates.

2.3.2. Permanganate distribution from SRPC in sand tank with and without a pneumatic circulator

Fine washed sea sand (VWR) was packed into the same 2D tank described above. A well assembly was fabricated using a 1.6 cm id $\times$ 2.0 cm OD polypropylene tube slotted along 10 cm, starting 2 cm from the bottom of the assembly. The tube was sealed on the bottom and sheathed in fine mesh polyester fabric. The tank was filled with deionized water and the well assembly was centered on the bottom of the tank. Sand was then poured into the tank and allowed to settle under gravity. After the tank was filled with sand, the entire tank was sonicated for 5 min to remove air pockets. Between tests, the tank and well assembly was unpacked, cleaned, and repacked with new sand.

During circulator tests, air was gently bubbled into the water column of the well. Compressed air, supplied by a PETCO AC9903 aquarium air pump, was pumped through a 3.2 mm id $\times$ 6.4 mm OD polyethylene tube connected to a sintered diffusion stone at the bottom of the well assembly. A series of three mini-SRPCs with embedded fishing line were tied to each other and to the diffusion stone to ensure they would remain stationary throughout the experiment. For the non-circulator test, three new mini-SRPCs were suspended at the same depth without a circulator. Migration of the MnO_4^- was observed and recorded in 5 min intervals for the circulator test and daily for the non-circulator test. Additional experiments demonstrating the utility of pneumatic circulator in facilitating permanganate distribution are described in supplementary material (SM, Section 1.8).

2.4. Field testing of SRPCs

Treatment of the entire TCE plume was considered impracticable due to the cost to treat the plume in its entirety. Therefore, we installed a permeable reactive barrier (PRB) of permanganate candles perpendicular to the direction of con-

Figure 2. (A) Field plot of the permeable reactive barrier of SRPCs and monitoring wells; each SRPC location received five candles stack on top of each other; and (B) photograph of permanganate candles.

taminant flow. Location of the PRB was primarily chosen with the intent to intercept the contaminant plume where TCE concentrations were greatest and the plume was narrow and shallow (Figure SM-2). Other considerations included choosing a PRB location that was accessible, reasonably level, and up gradient from previously existing monitoring wells.

For comparison, we inserted equal masses of the two diameter SRPCs (50 7.6-cm dia SRPC versus 105 5.1-cm dia) into a low permeable aquifer in staggered rows that intersected the TCE plume. The 7.6-cm candles were placed on 1.2 m centers in two rows while the 5.1-cm candles were inserted via direct push on 0.91 m centers in three rows (Figure 2, Figure SM-3). Each SRPC location received five candles stacked on top of each other, covering an aquifer thickness of 4.6 m.

The 7.6-cm SRPCs were removed from cardboard molds and inserted into specially manufactured slotted PVC carriers (Titan Industries, Aurora, NE) and then lowered into 10-cm dia wells. The specially designed tools we used to lower and remove the slotted carriers in and out of the wells are described in supplementary material (Figure SM-4). In year 2, pneumatic circulators (Figure SM-5) were placed at the bottom of the 10 wells housing the 7.6-cm SRPCs to improve the distribution of permanganate. Additional details of the procedures used to install the permanganate candles, monitoring wells and sampling and analysis are provided in supplementary materials (SM, Section 1.9–1.10).

3. Results and discussion

3.1. ERI and site characterization

Inversion modeling (2D) of ERI data identified four resistivity regions that were assigned different colors for visual interpretation. These resistivity regions had resistivity measure-

ments (ohms-meter) that ranged from 0 to 7 (orange); >7 to 15 (green); >15 to 35 (blue) and >35 to 95 Ω m (gray) (Figure 1). The lowest resistivity region (highest electrically conductive region) consisted of a layer beginning at or near the ground surface and was prominent throughout most of the refuse cell (orange layer, Figure 1). Beneath the orange region was a layer with higher resistivity properties, represented in green (Figure 1) that intermittently protruded upward into the orange layer creating some discontinuities. The thickest areas of both the orange and green layers were at the highest elevations, near the refuse cell. These layers then decreased moving south and west toward a floodplain near the property boundaries (Figure 1). Beneath the green layer were two more electrically distinct layers represented by the blue and gray regions. Both layers vary in thickness throughout the site and the gray layer extends beyond the depth of the ERI images (i.e., >16.5 or 22 m).

We found that the ERI survey, soil core analyses, direct push electrical conductivity logging, and slug tests provided complementary results. For example, when ERI images were overlain with direct push electrical conductivity logs, the ERI color regions and EC values match reasonably well (Figure 1a). Electrical conductivity logging indicated finer sediments in the upper 6 m followed by a transitional region from 6 to 8.2 m. Beneath 8.2 m conductivity values were indicative of coarser sediments. Analysis of soil cores for texture indicated that the orange and green ERI layers were silt loams but between 3 and 7.6 m there was an increase in silt and a decrease in sand content while clay remained relatively constant.

Despite somewhat similar textures among orange and green ERI layers, slug tests from the upper three ERI layers indicated three distinct hydraulic conductivities (Table SM-1). The highest hydraulic conductivity (K_h) was in the blue ERI layer consisting of fine to medium sands as indicated by drilling logs. The average K_h in the blue layer was 20 m d⁻¹. The

Figure 3. TCE occurrence in groundwater samples as a function of (A) depth and (B) ERI layer; insert provides example of ERI map.

lowest K_h was in the green ERI layer. The average K_h in the green ERI layer was 0.04 m d⁻¹. The orange ERI layer, lying above the green and blue layers in most surveys, had an average K_h of 0.5 m d⁻¹. Slug test results reaffirmed what was observed during manual groundwater sampling where the ease of obtaining water samples from the different ERI regions followed the order of blue (readily obtainable), orange (moderate) and green (difficult).

3.2. Groundwater contamination

Analysis of 146 groundwater samples obtained from 64 sampling locations revealed a distinct relationship between TCE contamination and ERI classifications. Nearly all groundwater samples with detectable TCE (and degradation products) were obtained from the orange ERI layer (Figure 3). It is important to note that not all groundwater samples obtained from the orange ERI layers were contaminated but the majority of samples with detectable TCE were from the orange regions. TCE was only detected in six samples obtained from the green ERI layer. TCE was not detected in any of the blue and gray ERI layers. Thus, in most cases TCE and its degradation products were located within 6 m of the ground surface (Figure 3). Coupled with the hydraulic conductivity results, we believe that the low permeable zone below the orange region, represented by the green ERI layer, is acting as an aquitard and preventing TCE transport into the underlying sands.

On a mass basis, more degradation products were present than TCE indicating that natural attenuation was occurring. 1,1-dichloroethene and *cis*-1,2-dichloroethene were the most commonly detected degradation products and present at the highest concentrations. A map of the degradation product detections is presented in supplementary materials (Figure SM-6). The highest TCE detected at the site was 521 μg L⁻¹ immediately south of the dual phase extraction facility. From this high point, TCE values decreased along a southeast transect to below the MCL before reaching the southern property boundary (Figure SM-2).

Figure 4. (A) Observed permanganate concentrations, flux (J; mg d⁻¹ 2.54 cm⁻¹ of SRPC) and C_r from disc-SRPCs (5.1-cm dia) in water. (B) Observed J and C_r with values projected out for 2 years.

3.3. SRPC longevity and radius of influence: laboratory results

Two important questions regarding the efficacy of using slow release permanganate candles are: how long will they last? And what is their radius of influence? In an attempt to answer these questions, laboratory experiments were performed with 1.27 cm segments of the candles used in the field (disk-SRPCs) and placed in 12.5 L of H₂O. Chemical dissolution rates from slow-release oxidants can be characterized as an initial flush followed by a slower and sustained release (Kang et al., 2004; Lee and Schwartz, 2007a). Results from the disk-SRPCs showed permanganate concentrations reaching ~200 mg L⁻¹ within the first 10 d and gradually increasing afterward (Figure 4a). We found these concentrations would be sufficient to remove TCE within a few hours (Figure SM-7).

Several equations have been used to fit dissolution data to predict longevity. Examples include first-order decay (Lee and Schwartz, 2007b) and power function (Kang et al., 2004). Depending on the equation used, the projected longevity can vary by many years. Attempts at fitting our flux and C_r data to previously used equations also showed considerable variability in projected longevity. For simplicity, we picked 2 years as a timeframe and then predicted flux and C_r from our disk-SRPCs. Results showed a 20.8 mg d⁻¹ flux per 2.54 cm of candle length. Also, we project that only ~20% ($C_r = 0.195$) of the 5.1 cm candle would be released after 2 years (Figure 4).

To determine radius of influence, we inserted mini-SRPC into the low permeable aquifer material (orange ERI region) and then visually measured permanganate distribution. Results showed that within 1 d, the permanganate distribution had a diameter of 3.9 cm (Figure 5). By dividing the permanganate distribution in half and accounting for the radius of the mini-SRPC (0.355 cm), the permanganate had migrated 1.6 cm beyond the candle after 1 d. Subsequent measurements showed

Figure 5. Temporal changes in diffusion distances (radius of influence) from miniature candles when placed in water-saturated, static, 2-D tank packed with low permeable aquifer material (i.e., orange ERI region). Estimates of mass released were obtained from parallel experiments conducted in H_2O (Section 2.3). Photos with dashed outlines show original photo (top) and digitally enhanced photo (bottom).

radius of influences of 3.7 cm after 7 d, 4.6 cm after 14 d and 5.25 cm after 35 d, the time when the majority of the permanganate had been estimated (from parallel experiments, Section 2.3) to be released from the mini-SRPC (Figure 5). Scaling results from mini-SRPCs to field SRPC is not straightforward because both candle diameter and permanganate mass differ. Given that diffusion rates are dependent on concentration gradients, it is reasonable to assume that the field-scale SRPCs will impart a greater radius of influence because they can sustain a higher concentration gradient and should not become mass limiting for years as opposed to days for the mini-SRPCs. Actual diffusion distances will also be highly dependent on soil textures, oxidant demand, and groundwater flow rates.

Ultimately, the maximum transverse distances permanganate had to travel through the native aquifer material to close the gaps between the SRPCs used in our field test were 12.7 cm (5.1 cm SRPC) and 17.9 cm (7.6 cm SRPC). In an aquifer with similar properties to the Cozad aquifer, solid fracture emplaced permanganate diffused to create a reactive zone >20 cm (radius) in 10 months (Siegrist et al., 1999). Subsequent diffusion experiments utilizing the same aquifer material yielded a diffusion rate of 0.1 cm d^{-1} over 40 d from a $5000 \text{ mg L}^{-1} \text{ MnO}_4^-$ solution (Struse et al., 2002). When we factored out the early time spike in permanganate flux and late time mass limited flux in our laboratory 2D tank experiments, we calculated a mean diffusion rate of 0.17 cm d^{-1} . Using this estimate for our field site indicated that a minimum of 3–6 months would be needed to close the gaps between candle locations.

While horizontal permanganate migration away from the mini-SRPCs was encouraging in the low permeable material, we also recognized that the 2D tank differed from the field conditions because the direct push 5.1-cm SRPCs were surrounded by a small volume of sand and the 7.6-cm SRPCs were inserted into wells that were not in direct contact with the low permeable aquifer material. With regard to slow release oxidants, the downward migration of permanganate is of greatest concern inside the free water of the permanent wells (Lee et al., 2008b). When mini-SRPCs were placed directly in water, we observed a steady stream of permanganate

Figure 6. Temporal changes in permanganate diffusion patterns from three miniature candles placed in water-saturated, static, 2-D tank packed with sand, with and without a pneumatic circulator.

migrating down from the candle; similar results were observed in a denser 10% KCl solution (Figure SM-8). While density driven flow of permanganate has been reported in the past (Lee et al., 2008b), the chemical structure of KMnO_4 also lends itself to intermolecular forces (e.g., dipole-dipole) that are cohesive and cause the molecules to stick together. This cohesiveness can help to exert downward force even in the presence of coarser aquifer material. In 2D tank experiments with sand, we observed uneven permanganate distribution in surrounding media due to sinking of permanganate within the well and out the bottom (Figure 6). To prevent downward migration, the permanganate molecules need to be separated and solvated so that they can hydrogen bond with H_2O . Consequently, we repeated the 2D tank experiment and for comparison, photographed the migration patterns with and without a pneumatic circulator that emitted small air bubbles to physically break apart the permanganate molecules (Figure 6).

Permanganate migration patterns from the mini-SRPC alone formed a Christmas tree shape typical of permanganate plumes in sandy media. It took 5 d for permanganate to be visible throughout the majority of the tank. It is clear that the permanganate was accumulating at the bottom of the 2D tank, and stacking its way toward the top. Thus, in a theoretical “bottomless” tank, the treatment zone surrounding the well assembly may never have become adequately treated with permanganate.

Conversely, when small bubbles were emitted from the circulator, an upside-down Christmas tree distribution pattern was observed. Moreover, the time needed to saturate the tank with permanganate was ~75 min, considerably less than the 5 d required without the circulator (Figure 6). Additionally, the time needed to saturate the treatment zone surrounding the screened interval was only 30 min, and this was the first section of the tank treated instead of the last as observed without the circulator. During subsequent injection tests, circulation of water into the bottom of the well and out the top of the well was clearly evident. Additional photographs demon-

Table 1. TCE concentrations in monitoring wells at Cozad field site. See Figure 2 for location of wells in relation to SRPCs.

Well	Depth (m)	TCE ($\mu\text{g L}^{-1}$)				Well	Depth (ft)	TCE ($\mu\text{g L}^{-1}$)			
		07/25/10	10/10/10	07/06/11	10/13/11			07/25/10	10/10/10	07/06/11	10/13/11
S-1	3.35	378		785	682	S-2	3.35	432		646	582
	5.18			953	701		5.18			642	644
	7.32			814	1209		7.32			1018	632
	AVG	378		851	864		AVG	432		769	620
S-5	3.35	469	416	688	835	S-6	3.35	526	477	496	586
	5.18		428	535	517		5.18		506	561	563
	7.32		434	876	544		7.32		532	728	516
	AVG	469	426	700	632		AVG	526	505	595	555
S-9	3.35	566		281	298	S-10	3.35	377		549	512
	5.18			290	222		5.18			480	499
	7.32			274	350		7.32			551	531
	AVG	566		282	290		AVG	377		527	514
S-3	3.35	215		216	127	S-4	3.35	148		222	82
	5.18			297	132		5.18			240	105
	7.32			284	145		7.32			239	312
	AVG	215		266	134		AVG	148		234	166
S-7	3.35	315	396	123	18	S-8	3.35	170	67	123	31
	5.18		13	24	26		5.18		90	24	46
	7.32		24	15	56		7.32		141	15	86
	AVG	315	145	54	34		AVG	170	99	54	54
S-11	3.35	371		335	90	S-12	3.35	116		89	22
	5.18			219	142		5.18			93	25
	7.32			193	178		7.32			81	29
	AVG	371		249	137		AVG	116		87	26

strating this behavior are provided in supplementary material (Figures SM-9, SM-10). These data indicate that if SRPCs are placed in porous media, additional measures to control density driven flow would likely be needed.

3.4. SRPC: field results

Monitoring wells were sampled 1 d before (7/25/10) and 77, 346 and 445 d after SRPC installation (Table 1). All wells were sampled with a low-flow sampling technique so as to not artificially accelerate permanganate migration into the monitoring wells (SM Section 1.9). Rather, we wanted the permanganate to diffuse and migrate from SRPCs under natural gradients. Given the low permeability of the aquifer and average linear groundwater velocity ($v = 0.42 \text{ m year}^{-1}$), monitoring wells located 1.2 m down gradient from the SRPCs (wells S-9, S-10, S-11, S-12, Figure 2) were not expected to show treatment effects for a few years. Similar calculations for the monitoring wells embedded within the SRPC treatment zone (wells S-5, S-6, S-7, S-8, within $\sim 0.5 \text{ m}$ of the SRPCs) indicate travel times of 1.2 years. These travel times however, do not account for the chemical diffusion of permanganate away from the SRPCs and the fact that wells and SRPCs were packed with sand and thus provided more transmissive zones. When monitoring well results were grouped according to the method in which the candles were inserted into the formation (direct push versus permanent wells), results from the first 15 months after installation provided evidence on the effectiveness of SRPC technology.

3.4.1. Field results: direct push candles

Comparisons of TCE concentrations up gradient versus inside the candle treatment zone show some differences (Table 1). For instance, by comparing TCE concentrations in wells S-1 versus S-5 at our last sampling (10/13/11), we observed a decrease of $232 \mu\text{g L}^{-1}$ (26% reduction). Likewise, TCE concentrations in S-6 were $64.6 \mu\text{g L}^{-1}$ lower than S-2. The last two samplings taken out of S-9 (7/6/11 and 10/13/11) were also significantly lower than the initial baseline value (7/25/10) as

well as the concentrations up gradient in wells S-1 and S-5. In fact, TCE concentrations in S-9 represent the lowest values obtained from this set of monitoring wells; specifically, a 66% reduction in TCE concentration over the up gradient well (S-1).

While TCE concentrations in S-5, S-6, S-9, and S-10 are all lower than the up gradient wells (S-1 and S-2), TCE concentrations have not gone down with time. For instance, TCE concentrations in S-5 and S-6 have not decreased temporally and have either stayed similar or increased over the initial baseline values. Part of this can be explained by fluctuations in TCE concentrations coming into the treatment zone (see temporal variations in S-1 and S-2). It is noteworthy that wells S-4 and S-5 are likely only being influenced by one up gradient direct push candle location (see Figure 2), so any heterogeneity in water flow could cause flow paths to bypass these wells. Monitoring wells S-9 and S-10 on the other hand, have numerous candles (i.e., entire treatment zone) up gradient and may explain the greater reduction in TCE concentrations observed. One potential problem with permanganate is the production of the insoluble MnO_2 , which can cause plugging and flow diversion. This problem however, is generally observed at contaminant and oxidant concentrations that are orders of magnitude higher than those observed in this study. Thus, the candle technology may offer an advantage over liquid injections by providing a sustained release of low concentrations of permanganate.

3.4.2. Field results: candles installed in permanent wells

Incoming concentrations into the permanent well treatment zone were not as high as concentrations observed up gradient of the direct push candle zone. That is, TCE concentrations in monitoring wells S-3 and S-4 have not been as high as S-1 and S-2 (Table 1). Nonetheless, we have observed significant decreases in TCE concentrations in wells S-7 and S-8 with time (i.e., inside treatment zone). TCE concentrations in S-7 and S-8 at our last sampling were significantly lower than initial baseline values and also 67–75% lower than the concentrations in the up gradient wells (S-3 and S-4). Moreover, concentrations in S-11 and S-12 have also decreased with time. As observed in

well S-9, TCE concentrations in the down gradient well S-12, represent the lowest values observed in this set of monitoring wells (an 85% reduction over up gradient well S-4).

Pneumatic circulators were installed in all 10 wells (Figure SM-5) after the 7/6/11 sampling and results indicate they have influenced TCE removal. TCE concentrations in wells S-7, S-8, S-11 and S-12 all decreased from 7/6/11 to 10/13/11. Prior to installation, density driven flow of permanganate appeared to be causing more of a decrease in TCE concentrations in S-7 at the lower depths (7.32 versus 3.35 m); this was also supported by measured permanganate concentrations. After installing the circulators, TCE concentrations were lower at the 3.35 m elevation rather than the deeper depths; this was also observed in well S-11 (Table 1). It is also noteworthy that we visually inspected the 7.6-cm candles 428 d after installation (9/26/11) by removing them from the wells and carriers. Candles were mainly intact and showed very little deterioration but some had an oxidized manganese coating, which we quickly removed with a hand wood planer before reinserting. Whether this refurbishing is needed on a routine basis (i.e., annual or biennial) has yet to be determined but this option is available when candles are placed in wells as opposed to direct push.

While the characteristics of the low permeable aquifer at the Cozad site dictates that additional field monitoring will be needed for several years to fully determine the efficacy of the slow release candles, initial field results and the supporting laboratory results presented indicate that slow-release permanganate candles may be an effective means of treating chlorinated solvents in low permeable zones. Potential advantages to the candle technology are that they negate the need for specialized equipment (mixing trailer, pumps, hoses, etc.), curtail health and safety issues associated with handling liquid oxidants, and when used in a barrier design, could potentially provide a long-term solution for controlling contaminant migration.

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Appendix A. Supplementary material

Supplementary material (21 pages), including Methods and materials, 1 table, and 10 figures, is presented following the References.

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Using slow-release permanganate candles to remove TCE from a low permeable aquifer at a former landfill

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Supplementary Material

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SM 1. Materials and methods

SM 1.1 Direct push electrical conductivity logging

Direct Push Electrical Conductivity Logging (DPT EC) was conducted near monitoring well C2 and on line L (Fig. SM 1), 47 meters down-gradient (south-southeast) from monitoring well C2. A Geoprobe Direct Imaging Electrical Conductivity Probe was pushed to a depth of 10.7 m (35 feet) bgs through the two uppermost ERI layers described in the results section. Depth specific electrical conductivity and probe speed were collected on a Geoprobe FC5000 Data Acquisition System. Services and equipment were provided by the University of Nebraska Conservation and Survey Division (CSD).

SM 1.2 Soil texture

Analyses of soil texture were performed on soil cores collected near monitoring well C2. Cores were sub-sampled at depths of 1.5, 3, 4.5, 6, 7.5 m (5, 10, 15, 20, and 25 feet). Samples were analyzed for bulk density and porosity (Soil Science Society of America, 1986). Additionally, soil texture was determined from sub-samples collected from the same locations stated above (Kettler et al., 2001).

SM 1.3 Soil oxidant demand

We determined soil oxidant demand from the same soil cores used for soil texture analyses. Procedures used are described in ASTM D7262-07. Sub-samples were extracted from depths of 1.5, 3, 4.5, and 6 m (5, 10, 15, and 20 feet). Sample aliquots were centrifuged in a Sorvall T6000B laboratory centrifuge to remove MnO_2 and suspended sediment. Aliquots were then diluted if necessary and analyzed at 525 nm on a Hach DR 2800 Spectrophotometer standardized using Method 4500- KMnO_4 (APHA et al., 2005).

SM 1.4 Electrical resistivity imaging (ERI)

ERI measurements consisted of installing metal stakes (surface electrodes) approximately 15 cm into the ground every 1.5 or 2 m for a total length of either 82.5 or 110 m. The electrodes were attached to a cable and the ERI data was collected with a 56 electrode array using an Advanced Geosciences, Inc., *SuperSting R8* system that induced a current, measured the potential, and stored the data. Data were processed using the Halihan/Fenstemaker processing technique (Halihan and Fenstemaker, 2004). The ERI method measures apparent resistivity with a resolution equal to half the electrode spacing, which in this case was 0.75 or 1 m both horizontally and vertically. ERI imaging depths were 1/5 of the survey line length (16.5 or 22 m).

We collected 22 ERI measurements creating a total of 19 images. Survey locations were based on the locations of: 1) the proposed TCE plume based on existing wells. 2) the refuse cell, 3) phytoremediation plantings, and 4) property lines representing the legal point of compliance. ERI lines were surveyed using a GPS equipped total station to correct for elevation and to allow fencing of images as displayed in Figure 1.

SM 1.5 Groundwater Chemistry Sampling and Analysis

A Geoprobe 6610DT was used to drive an SP16 Groundwater Sampler to desired sample depths. We used a check-ball valve and polyethylene tubing to manually withdraw water from each sample point. At each sampling location, we used new tubing and decontaminated the stainless steel screen of the SP16 sampler with deionized water. Groundwater samples were collected in 40-mL Teflon septa-capped clear glass vials that contained 0.2 mL of hydrochloric acid preservative.

A YSI 556 MPS was used to analyze water samples for pH, conductivity, dissolved oxygen, temperature, and oxidation/reduction potential. Because groundwater samples were manually obtained with a check valve and tubing, water was immediately analyzed in a calibration cup rather than utilizing a flow-through cell. Groundwater samples were

analyzed for VOCs on an Agilent Technologies 6890N gas chromatograph/mass spectrometer using EPA method 8260B.

SM 1.6 Hydraulic conductivity

Slug tests were conducted near the central portion of the TCE plume (near well C2, Fig. SM-1) to determine horizontal hydraulic conductivity (K_h). A Geoprobe GW1600 Pneumatic Slug Test Kit was used to measure isolated water level recoveries at 3, 6, and 10 m. These depths corresponded to the three uppermost ERI layers identified in the ERI survey. We conducted tests in accordance with the GW1600 Standard Operating Procedures (Geoprobe, 2002) with one exception. Rubber electrical tape was used to seal probe rods due to o-ring failures experienced during previous tests at other sites. Slug tests at 3 m (10 ft) and 10 m (32 ft) were conducted in triplicate for two different initial displacements. Due to slow recovery times observed during tests at 6 m (20 ft) we conducted one test at the first displacement and two tests at a second smaller displacement. We used Aqtesolv aquifer test analysis software and the Bouwer-Rice method for interpreting slug test data in unconfined aquifers to obtain values of K_h (Bouwer and Rice, 1976).

SM 1.7 Slow-Release Permanganate Candle Production

Multiple ratios of KMnO_4 to paraffin were initially tested (1:1, 2:1, 3:1, and 4.6:1). Two of the objectives of the candle design were to maximize the mass of KMnO_4 placed into the treatment zone, as well as, maximize the pore connectivity within the matrix to more easily facilitate diffusion from the SRPC. Thus, the higher the ratio of KMnO_4 to paraffin, the closer we were to meeting these objectives. However, as the ratio increases the paraffin film which surrounds and binds the KMnO_4 particles becomes thinner reducing the integrity of the candle. Additionally, as the ratio increases the viscosity of the hot mixture increases making mixing and pouring difficult. We found that a ratio of 4.6:1 yielded an easily manufactured and relatively strong SRPC which could deliver a substantial mass of KMnO_4 into the treatment zone.

Settling of the KMnO_4 in the paraffin matrix was initially a concern. At lower ratios of KMnO_4 to paraffin settling could be seen in mini-SRPCs. However, at the higher ratios (>3:1) space between the particles was minimized leaving very little volume within which the particles could move. Additionally, mixing of the melted paraffin and KMnO_4 with the stand mixer cooled the suspension quickly. Also, the tall and narrow cardboard tubes had a sufficient surface area to volume ratio to cool the candles quickly. Inspections of full scale candles showed a solid wax layer where KMnO_4 particles had settled out at the surface of the poured mixture of no more than 1 cm.

SM 1.8 Additional pneumatic circulator testing

An additional test was conducted to describe the circulation path of water outside the well assembly caused by the circulator. The tank was packed in an identical manner as described in main manuscript and the circulator assembly was inserted into the bottom of the well. Four separate 1 mL injections of a 1000 mg L^{-1} KMnO_4 solution

were injected through injection ports at the back of the tank into the sand surrounding the well assembly. Migration of the MnO_4^- was observed and recorded in 2.5 min intervals for a total of 50 min.

An additional experiment tested a circulator in heterogeneous media to determine if density driven sinking of permanganate from SRPCs would prevent effective distribution of permanganate into a lower permeable zone between two higher permeable layers. To accomplish this, a 12.7 cm (ID) column 38 cm in length sealed on the bottom was filled with 10.8 cm of medium sand followed by 15.2 cm of fine sand and 7.6 cm of medium sand then filled with deionized water. A 1.3 cm (ID) well, screened 10 cm in the center of the fine sand, was inserted into the center of the column to the bottom of the fine sand. For the first experiment a string of three mini-SRPCs were inserted into the well and permanganate migration was observed. In a subsequent experiment the same column conditions were repeated, and a circulator was inserted into the bottom well.

SM 1.9 SRPC installation via direct push

Geoprobe Probe Rods 1.5 m x 8.3 cm OD x 6.7 cm ID (5 ft x 3.25 inch OD x 2.625 inch ID) and an expendable tip without o-rings were inserted into the soil in 1.5 m (5 ft) increments. After each rod was pushed into the ground, SRPCs were removed from the cardboard molds and inserted into the hollow rods. After a total of 4.6 m (15 ft) of probe rods and candles were inserted, one additional probe rod was attached and pushed into the ground to achieve a total depth of 7 m. Expendable point holders were gently lowered down the hollow probe rods onto the top of the candles. This allowed us to visibly determine that the candles remained in place as the probe rods were raised and removed. After all rods were removed, sand was poured around the candles until the hole collapsed near the water table. Probe holes were then sealed above the candles with bentonite.

SM 1.10 Installation of monitoring wells, sampling and analysis

A series of twelve 5.1-cm diam sampling wells were installed to monitor the efficacy of the slow-release oxidant PRB (Fig. 2). Monitoring wells were installed up gradient, down gradient, and inside the PRB. Up gradient wells were placed 1.8 m away from the leading edge of the PRB. Down gradient monitoring wells were placed 1.2 m from the trailing edge of the PRB. Finally, embedded monitoring wells were centered between candles in the PRBs.

Prior to and after completing the PRB installation, all monitoring wells were sampled for VOCs and groundwater chemistry. A GeoTech Geopump II peristaltic pump and Viton tubing were used to sample water 0.3 m below the top of the well screen. Sample water was pumped through a flow-through cell until pH changed by less than 0.1 and conductivity changed by less than 10% over one min. The flow-through cell was then disconnected and VOC samples were collected and quenched with hydrazine (35%) when permanganate was visibly present. This protocol was utilized for all VOC sampling.

In addition to discrete VOC samplings, spatial changes in conductivity throughout the well screen were measured more frequently. This was done to characterize the diffusion front of MnO_4^- and to reduce cost of monitoring the treatment field for VOCs. A Solinst TLC meter was used to measure temperature, conductivity, and static water level in each well. Measurements were taken in 0.3 m (1 ft) intervals starting from the static water level. Upon reaching the bottom of the well the probe was left in place and low-flow sampling of MnO_4^- occurred. Conductivity sampling was conducted prior to MnO_4^- sampling to prevent erroneous results from well mixing.

Low-flow MnO_4^- sampling was conducted to complement the conductivity measurements described above. Samples were collected with a peristaltic pump at a rate of 300 mL min^{-1} . Depths collected were 3.4 m (11 ft), which was 0.3 m (1 ft) below the top of the screen, 5.3 m (17.5 ft) (middle of the screen), and 7.3 m (24 ft) (0.3 m

from the bottom of the screen). Samples were placed on ice and transported to the laboratory for measurement with a Hach DR 2800 Visual Spectrum Spectrophotometer at 525 nm.

Table SM-1. Properties of the electrical resistivity layers at the Cozad former solid waste disposal site.

ERI Region	Approximate Depth (meters)	Soil Texture	K _h (ft d ⁻¹)	K _h (m d ⁻¹)	Greatest TCE Conc. Observed (µg L ⁻¹)	Mean Electrical Conductivity (µS cm ⁻¹)
Orange	0-4	Loess (Silt Loam)	1.52	0.50	521	2225
Green	4-8	Loess (Silt Loam)	0.144	0.04	154	1461
Blue	8-16	Alluvium (Fine-Medium Sand)	65.6	20.0	nd	1103

Figure SM-1. Aerial photo of Cozad Landfill with locations of ERI lines. Six ERI lines (O, A, B, 1, 2, and 3) acquired images that overlapped the refuse cell, the remaining lines were down gradient from the refuse cell. Lines labeled 1 and 3 consist of multiple 110 meter lines overlapping by 55 meters. Overlapping ensured a continuous image across the entire length of the survey line.

Figure SM-2. Location of permeable reactive barrier containing 5.1 and 7.6-cm diam SRPCs in relation to TCE concentrations ($\mu\text{g L}^{-1}$) determined via direct push sampling and ERI lines (Fig. SM-1).

Fig. SM-3. Photographs of (top to bottom): (1) 0.91 m length permanganate candles; (2) candles placed in a carrier for insertion into designated wells and (3) candles being inserted into formation with direct push technology.

Fig. SM-4. Photographs and schematics of field hardware developed and used with SRPCs at field site: (A) 7.6-cm SRPC In Situ Candle Carrier; (B) Candle Insertion Tool (CIT); (C) Candle Removal Tool (CRT). Each carrier was lowered into a 10-cm diam well with a specially built Candle Insertion Tool attached to a rope. Once the PVC carriers were in place, a locking pin (attached to a second rope) was pulled to release the carrier from the CIT and the CIT was removed from the well. The CRT was equipped with a trap door that latched onto the carriage bolt on top of the candle carrier.

Fig. SM-5. (A) Schematic of field-scale well stacked with 4.57 m of 7.6-cm diam permanganate candles and pneumatic circulator connected to a compressor; (B) Photograph of pneumatic circulator; (C) Manifold connected to a compressor and used to service 10 designated wells containing slow-release oxidant candles and pneumatic circulators. Details of pneumatic circulator construction can be found in Christenson (2011).

Fig. SM-6. Aerial view of Cozad landfill with the highest degradation product concentration collected from each sample location.

Fig. SM-7. Temporal changes in TCE concentrations following treatment of 100 mg L^{-1} TCE with three concentrations of potassium permanganate.

Fig. SM-8. Photograph of streams of permanganate flowing downward from mini-SRPC in (A) water and (B) 10% (w/v) KCl.

Fig. SM-9. A 12.5-min time sequence of photographs showing permanganate movement when in the presence of a pneumatic circulator. Experimental setup was identical to results provided in Fig. 6.

Fig. SM-10. Effects of density driven flow on permanganate distribution. Photographs of heterogeneous soil column equipped with three SRPCs placed in a well: (A) Photographs at 1, 7, and 14 d without a circulator, and (B) with a pneumatic circulator at 2, 5, and 7 h. Well is screened between black lines in the central fine sand region.

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