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# A five-year performance review of field-scale, slow-release permanganate candles with recommendations for second-generation improvements

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## Highlights:

- We developed slow-release permanganate-paraffin candles for field scale use.
- We compared two methods of inserting the candles into a low permeable aquifer.
- Field-scale results document efficacy of oxidant candles to degrade VOCs.
- Second-generation oxidant candles were developed and tested.
- Adding anti-scaling agent improve oxidant candle release characteristics.

## Abstract

In 2009, we identified a TCE plume at an abandoned landfill that was located in a low permeable silty-clay aquifer. To treat the TCE, we manufactured slow-release potassium permanganate cylinders (oxidant candles) that had diameters of either 5.1 or 7.6 cm and were 91.4 cm long. In 2010, we compared two methods of candle installation by inserting equal masses of the oxidant candles (7.6-cm vs 5.1-cm dia). The 5.1-cm dia candles were inserted with direct-push rods while the 7.6-cm candles were housed in screens and lowered into 10 permanent wells. Since installation, the 7.6-cm oxidant candles have been refurbished approximately once per year by gently scraping off surface oxides. In 2012, we reported initial results; in this paper, we provide a 5-yr performance review since installation. Temporal sampling shows oxidant candles placed in wells have steadily reduced migrating TCE concentrations. Moreover, these candles still maintain an inner core of oxidant that has yet to contribute to the dissolution front and should provide several more years of service. Oxidant candles inserted by direct-push have stopped reducing TCE concentrations because a  $\text{MnO}_2$  scale developed on the outside of the candles. To counteract oxide scaling, we fabricated a second generation of oxidant candles that contain sodium hexametaphosphate. Laboratory experiments (batch and flow-through) show that these second-generation permanganate candles have better release characteristics and are less prone to oxide scaling. This improvement should reduce the need to perform maintenance on candles placed in wells and provide greater longevity for candles inserted by direct-push.

**Keywords:** Second-generation permanganate candles, Chlorinated solvents, TCE, Slow-release oxidants, Permeable reactive barrier

## Graphical abstract

Permanganate Slow-Release  
Oxidant Candles in Wells



## 1. Introduction

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 effective oxidant for ISCO applications and is extremely efficient in oxidizing chlorinated ethenes to  $\text{CO}_2$  and  $\text{Cl}$  (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 or another nearby location (i.e., daylighting) 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); since then, a number of publications have documented the efficacy of slow-release oxidants to remove groundwater contaminants at the laboratory-scale and in larger flow-tank systems (Lee and Schwartz, 2007a, 2007b; Lee et al., 2008a, 2009, 2008b; Yuan et al., 2013; Liang et al., 2014).

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 that mapped the lithology of the landfill and guided groundwater sampling. Because TCE was found to be located in a low permeable zone of the aquifer, we hypothesized that using slow-release permanganate would be effective at treating the TCE. In 2010, we manufactured and deployed slow-release permanganate candles (oxidant-wax cylinders) at the landfill and reported those results in 2012 (Christenson et al., 2012). In this paper, we report on how well the oxidant candles have performed since installation and provide additional chemical formulations for second-generation oxidant candles that are less prone to scaling and display a more consistent rate of chemical release.

## 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 and other VOCs were deposited into the landfill from the surrounding community. The facility was closed in 1989 after TCE (non-aqueous and solution phase) was found in monitoring wells down-gradient from the refuse cells. Remedial attempts to date have included a dual-phase extraction facility, poplar tree plantings to induce phytoremediation, and volatilization ponds. Despite these efforts, TCE contami-

nation remains and the migrating plume has not been contained.

To characterize the landfill and identify the location of the plume, we made several spatial measurements that included: electrical resistivity imaging (ERI), 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 are described in detail in Christenson et al. (2012).

### 2.2. Field testing of field-scale oxidant candles

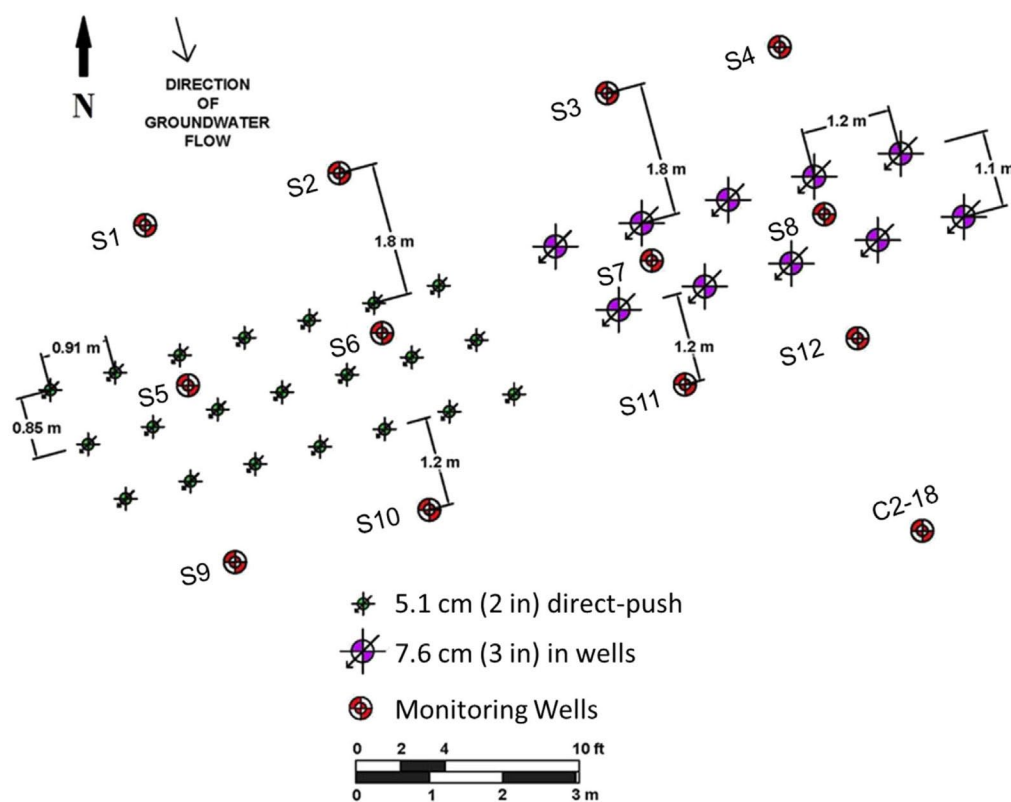
Treatment of the TCE plume occurred by installing a permeable reactive barrier (PRB) of permanganate candles perpendicular to the direction of contaminant flow. Location of the PRB was primarily chosen with the intent to intercept the contaminant plume where TCE concentrations were greatest and the plume was narrow and shallow (Fig. SM-1). Other considerations included choosing a location that was accessible, reasonably level, and up gradient from previously existing monitoring wells.

To compare methods of deployment, we inserted equal masses of the two types (i.e., diameters) of oxidant candles. Specifically, 50 of the 7.6-cm dia versus 105 of the 5.1-cm dia candles were inserted into the 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 (Fig. 1). Each drive point received five candles stacked on top of each other, covering an aquifer thickness of 4.6 m. One reason for utilizing two different diameter candles included the logistics of deployment. Inserting the 5.1-cm candles required using an 8.26-cm outside diameter direct-push rod. Inserting the 7.6-cm candles by direct-push would have required even larger rods (11.43 cm); larger rods are more difficult to direct-push and thus installation would have been more difficult. Since installation, the 7.6-cm candles have been refurbished approximately once per year by using the specialized tools designed specifically for installing and extracting the candles screens (Fig SM-2). In brief, the screens housing the candles were brought to the surface and the candles removed and placed on a water-resistant tarp. Then a hand-held wood planer was used to gently remove the outside layer (1.5–2 mm) of the oxidant candles (Fig. 2). The candles were then reinserted into the screens and lowered back into the wells. This activity requires moderate physical exertion and personal protective equipment of Tyvek suits, safety glasses and rubber gloves. Using a team of 3–4 people, we have been able to remove, refurbish and reinsert all 50 candles within 4–5 h.

### 2.3. Groundwater sampling and analysis

Our standard operating procedure for sampling wells associate with the oxidant candles has been to use low-flow-sampling so as to not artificially pull permanganate from the oxidant candles into the monitoring well and bias results. To accomplish this, we used a peristaltic (GeoTech, Geopump) pump with a flow-through water quality monitor (YSI 556 MPS) to analyze water samples for pH, conductivity, dissolved oxygen, temperature, and oxidation/reduction potential. Once water quality parameters stabilized, groundwater samples were placed in 40-mL volatile organic analysis (VOA) vials with no headspace. Groundwater samples were analyzed for VOCs on an Agilent Technologies 6890N gas chro-

**Fig. 1.** Field plot of the permeable reactive barrier (PRB) of oxidant candles and monitoring wells.



matograph/mass spectrometer using EPA method 8260B. When permanganate was visibly detected (purple color) separate samples were taken and permanganate concentrations were determined with a UV spectrophotometer (Hatch DR 2800). For the 12 monitoring wells specifically installed for this study (S1–S12, Fig. 1), groundwater samples were obtained from 5.3 to 7.3 m (17.5, 24 ft) bgs; with the concentration averages of both depths presented for each well. For monitoring well C2-18 (community landfill monitoring well), only one depth was sampled (0.3–0.6 m below static water level).

#### 2.4. Second-generation oxidant candle testing

To minimize  $\text{MnO}_2$  formation on the permanganate candles and improve the release characteristics, sodium hexametaphosphate (SHMP) was added as an anti-scaling agent. Because SHMP is a polyphosphate that is routinely used in potable water treatment and not considered a groundwater contaminant, the new candle formulations included adding varying masses of sodium hexametaphosphate (Table 1) to the original ratio used to make the candles (4.6:1, w/w;  $\text{KMnO}_4$  to wax). Specifically, paraffin wax was heated ( $\sim 95^\circ\text{C}$ ) in a beaker using a hot plate. Then  $\text{KMnO}_4$  crystals were added and mixed to a “milkshake” consistency. SHMP was then added to give the desired percentage concentration (0–6%, w/w) and the mixture was then poured into a mold and allowed to cool. To test the candles, both flow-through and batch experiments were conducted. For the flow-through experiment, small cylindrical (i.e., miniature) candles were created using a mold drilled into a plastic block (0.7 cm diam, 1.9 cm length). For the batch experiments, larger candles were created (2.54 cm diam, 1.27

cm length) using round silicone molds purchased at a local craft store (Fig. SM-3). Three replications of each treatment (% SHMP) were created for experimentation.

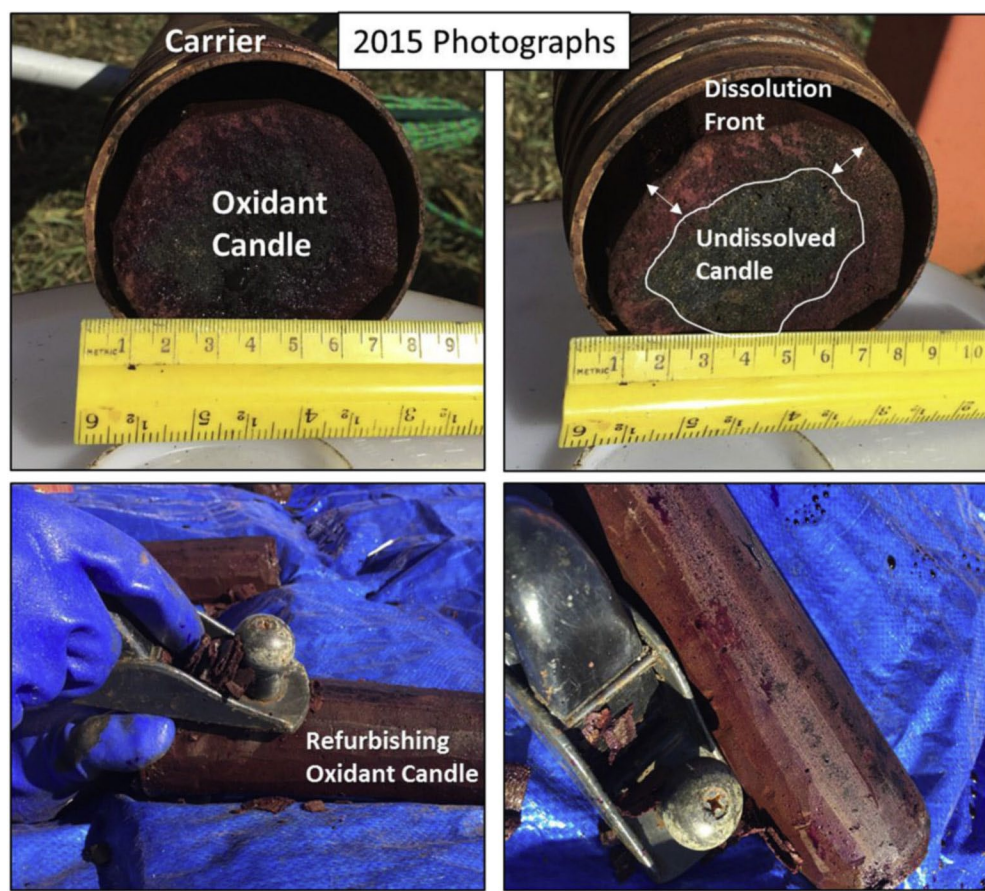
##### 2.4.1. Flow-through experiments

The oxidant released from the miniature oxidant candles was determined with a flow-through system (Fig. SM-4). This system consisted of a peristaltic pump that continuously pumped ( $0.55\text{ L min}^{-1}$ ) either distilled water or  $1\text{ mg L}^{-1}$  TCE solution through neoprene tubing into small syringes that contained miniature versions of the oxidant candles. The influent was housed in 3-L collapsible (i.e., zero headspace) Tedlar bags (Zefon, Ogala, FL) (Huang et al., 2002) equipped with stainless steel valve fittings to minimize TCE volatilization and adsorption. The residence time of water in the plastic syringes was approximately 22 min. Outflow from candle holders went into 2-L glass bottles where oxidant concentrations and volume of outflow was quantified every 2–3 d. The concentration of  $\text{MnO}_4^-$  released was determined by using a UV spectrophotometer (Hach DR 2800) and the cumulative mass released was calculated and plotted over time. Following the conclusion of the flow-through experiment, the oxidant candles were crushed, ground and extracted with water to determine the mass of permanganate remaining within the wax matrix.

##### 2.4.2. Batch experiments

Oxidant candles were suspended 4–5 cm above the bottom of 1-L glass Mason jars (Fig SM-3). All jars were filled with 975 mL of distilled water and half of the jars were dosed with 0.5 mL of pure, non-aqueous phase TCE. The candles were allowed to soak for one week then removed and placed in similar jars containing distilled

**Fig. 2. A.** Photograph of 7.6-cm. dia. permanganate candles in screen; **B.** Candle broken in half to show dissolution layer of oxidant candle; **C.** Removing outside layer with wood planer; **D.** Refurbished candle.



**Table 1.** Candle formulations used for flow-through and batch experiments.

Experiment	Treatment % SHMP <sup>a</sup>	Mass KMnO <sub>4</sub> (g)	Mass wax (g)	Mass SHMP (g)	Mean candle weight <sup>b</sup> (g)
Flow-through	Control (0%)	1.15	0.25	0.0	1.30
	2%	1.15	0.25	0.028	1.39
	4%	1.15	0.25	0.056	1.42
	6%	1.15	0.25	0.084	1.44
Batch	Control (0%)	15	3.33	0.0	16.89
	2%	15	3.33	0.366	17.26
	4%	15	3.33	0.733	17.62
	6%	15	3.33	1.10	17.99

a. Percent SHMP calculated as percentage of combined mass of KMnO<sub>4</sub> and Wax.

b. Recovered mass following removal from candle molds.

water for 1 h. Following 1 h, the candles were removed, the solution mixed and the concentration of MnO<sub>4</sub><sup>-</sup> released determined with a spectrophotometer. Following measurements, the candles were then placed back into freshly prepared jars of distilled water or jars of water dosed with 0.5 mL of TCE. This procedure was repeated for a total of seven weeks (49 d).

### 3. Results and discussion

#### 3.1. Field results

Temporal groundwater sampling over the last five years has revealed differences in candle performance. By comparing monitor-

ing wells up gradient, inside and down gradient of where the candles were located, the efficacy of the candles to reduce TCE and associated degradation products can be determined. For the candles emplaced with direct-push equipment, up gradient concentrations (S1, S2) have ranged between 600 and 800 mg L<sup>-1</sup> TCE. Concentrations inside the barrier (S5, S6) were lower for the first year after installation (through 10/13/11, Table 2) but have since become higher and increased over time. For the wells down gradient of the PRB (S9, S10), the concentrations have generally been consistently lower than the up gradient wells. For instance, at the 2015 sampling (10/20/2015), concentrations up gradient were between 524 and 611 µg L<sup>-1</sup> (S1, S2) while wells located down gradient were between 344 and 571 µg L<sup>-1</sup> (S9, S10), which would

represent a 19% reduction. Despite this, there is no trend showing any steady temporal decreases in TCE (Table 2) or associated daughter products (Table 3).

In 2015, we attempted to recover some of the original oxidant candles that were emplaced in 2010. By sending direct-push rods

**Table 2.** Temporal changes in TCE concentrations in monitoring wells up gradient, inside and down gradient of direct-push candles and candles in wells.

Sampling date	Position <sup>a</sup>	TCE concentration in monitoring wells <sup>a</sup>			
		Direct-Push Candles		Candles in Wells	
		S1	S2	S3	S4
7/25/2010	Up Gradient	378.0	432.4	215.4	147.6
10/10/2010		NS <sup>b</sup>	NS		NS
07/6/2011		850.8	768.6	265.5	233.6
10/13/2011		864.2	619.5	134.5	166.4
11/23/2013		761.7	656.4	461.0	230.4
10/22/2014		751.8	727.8	558.5	351.9
10/20/2015		610.5	523.9	373.5	203.1
		S5	S6	S7	S8
07/25/2010	Inside Barrier	469.0	525.8	315.0	169.8
10/10/2010		425.9	504.4	144.7	99.3
07/06/2011		699.8	595.0	53.9	136.5
10/13/2011		632.1	554.9	33.5	54.3
11/23/2013		808.1	805.4	14.5	202.1
10/22/2014		611.3	515.6	2.3	217.0
10/20/2015		580.2	498.8	5.7	116.4
		S9	S10	S11	S12
07/25/2010	Down Gradient	566.0	377.2	371.0	115.9
10/10/2010		NS	NS	NS	NS
07/06/2011		282.0	526.6	249.0	87.4
10/13/2011		289.9	514.2	136.9	25.6
11/23/2013		666.3	640.9	29.2	110.9
10/22/2014		512.7	540.9	2.4	89.1
10/20/2015		343.7	571.4	6.4	58.4
		C2-18			
10/28/2009	Down Gradient	436.0			
11/03/1010		174.0			
11/16/2011		96.0			
03/27/2014		15.4			
10/22/2014		27.3			
10/20/2015		60.0			

a. See Fig. 1 for well locations.

b. NS = not sampled

down some of the original drive points, we recovered a small fragment of the 5.1-cm diameter candle. The outer circumference of the candle was covered with a very thin brown oxide layer that was impenetrable to water (Fig. 3). The inner section of this candle however, still contained undissolved permanganate that readily released permanganate when wetted. Thus, failure of the direct-push candles to continue to release permanganate and provide treatment for the migrating VOC plume can be tied to oxide scaling (see Sec. 3.2 *Second-generation oxidant candles*).

For candles placed in wells, the up gradient concentrations (S3, S4) or influx of TCE entering the PRB have generally been lower than the concentrations in wells S1 and S2 but still ranged between 135 and 559 µg L<sup>-1</sup>. TCE concentrations in well S7 (inside) have shown a fairly steady decrease in TCE concentrations with time, with concentrations starting at 315 and falling to 5.7 µg TCE L<sup>-1</sup>. Similarly, well S11 (down gradient) has also continued to decrease. These two wells have consistently shown the presence of permanganate during low-flow sampling with permanganate concentrations ranging from 18 to 322 µg L<sup>-1</sup> in 2014; and from 86 to 342 µg L<sup>-1</sup> in 2015. The other wells associated with the candles in wells (S8 and S12) do not show consistent temporal trends but have consistently been lower than the incoming concentrations observed in wells S3 and S4 (Table 2). Using the same comparison of averaging the up gradient (S3, S4) versus down gradient concentrations (S11, S12), we observed that incoming concentration in 2015 was 288.3 µg L<sup>-1</sup> and the down gradient concentration was 32.4 µg L<sup>-1</sup>, which represents an 89% reduction.

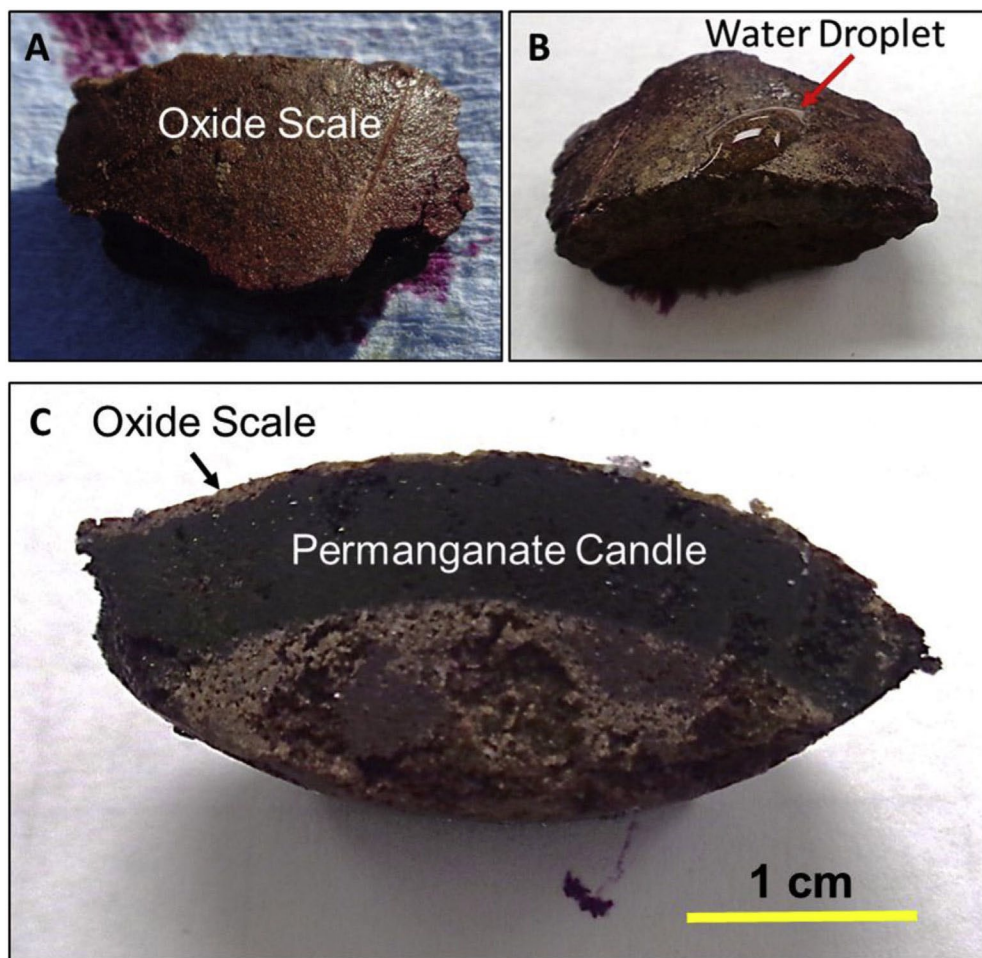
Comparisons of concentrations for the other associated VOCs showed that for the direct-push candles in 2015, the only other contaminant beside TCE that had significantly lower concentrations in the down-gradient wells (S9, S10) than the up-gradient wells (S1, S2) were 1,1-DCE (20% reduction) and 1,1,1-TCA (35% reduction, Table 3). However, for the oxidant candles placed in wells, many VOCs were significant lower in wells down gradient of the PRB (Table 3). It is noteworthy that for the chlorinated ethenes (TCE, VC, 1,1-DCE, cis 1,2-DCE) decreases between the average up gradient concentrations (wells S3 and S4) and down gradient concentrations (S11,S12) ranged between 89 and 100% (Table 3). Decreases in the chlorinated ethanes (1,1-DCA, 1,1,1-TCA), which permanganate is not as an effective oxidant, ranged between 4 and 54% (Table 3). Finally, well C2-18 is a monitoring well used by the city landfill for annual monitoring. This well is located approximately 3.9 m down gradient from well S12 (Fig. 1). This well has also shown a decrease in VOC concentrations, which was unex-

**Table 3.** VOC concentrations in monitoring wells (10/20/2015) up gradient, inside and down gradient of direct-push candles and candles in wells.

Candle type	Well	Position <sup>a</sup>	µg L <sup>-1</sup>							
			TCE	VC	1,1-DCE	Trans 1,2-DCE	Cis 1,2-DCE	1,1-DCA	1,2-DCA	1,1,1-TCA
<b>Direct-push (5.8 cm)</b>										
	S1	Up	611	5	409	ND <sup>b</sup>	253	58	ND	315
	S2	Up	524	4	411	ND	131	50	ND	281
	S5	Inside	580	4	488	ND	214	69	ND	378
	S6	Inside	499	4	395	ND	128	52	ND	298
	S9	Down	344	4	352	ND	187	40	ND	129
	S10	Down	571	7	301	ND	280	69	ND	254
<b>In Wells (7.6 cm)</b>										
	S3	Up	374	4	327	ND	206	32	ND	176
	S4	Up	203	2	175	ND	76	15	ND	43
	S7	Inside	6	ND	3	4	ND	35	ND	178
	S8	Inside	116	ND	90	ND	112	15	ND	40
	S11	Down	6	ND	2	4	ND	35	ND	76
	S12	Down	58	ND	32	ND	23	10	ND	24
	C2-18	Down	60	ND	32	ND	23	23	2	15

a. Position indicates location of wells relative to PRB (See Fig. 1 for well locations): Up = up gradient; Inside = inside PRS; Down = down gradient of PRB.

b. Non-detect.



**Fig. 3.** **A.** Top view photograph of 5.1-cm diam. permanganate candle taken right after recovery in field; **B.** Photograph of candle with water droplet placed on oxide layer; **C.** Side view of candle sliced open showing thickness of oxide layer (shown in A and B) over undissolved permanganate candle.

pected given that this well is also screened in the low permeable zone of the aquifer. The fact that the PRB has impacted this well indicates that some preferential movement of the oxidant must have occurred because the calculated linear velocity of groundwater for this section of the aquifer is only  $0.42 \text{ m yr}^{-1}$ .

Despite the annual refurbishing and length of time the candles have been in contact with the aquifer (5 yr), there is still ~80% of the candle remaining. At the onset of the experiment the 7.6-cm dia candles just barely fit inside the carriers (Fig. 2). A 2015 photograph shows a candle with a diameter of approximately 6.80 cm, which upon conversion to area, represent a 21% loss. Due to the fact that the dissolution front of the oxidant emanates from within the candle and that the wax matrix does not readily slough off on its own (unless physically removed), we recognize that the candle area and mass of oxidant remaining are not equivalent. Upon closer examination of a candle that was broken open, the dissolution front emanates from ~1 cm within the candle and 4.5 cm of the inner portion of the candle has yet to contribute to the dissolution front. Therefore, it appears that the current candles could last five more years and possibly longer. This treatment longevity undoubtedly offers one advantage over liquid oxidants by providing a continuous stationary source of oxidant to control a migrating plume.

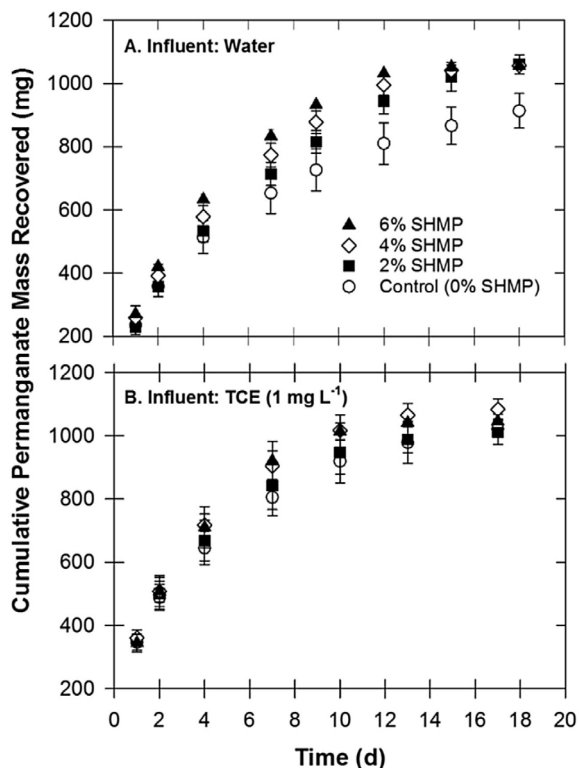
### 3.2. Second-generation oxidant candles

The fact that the annually refurbished candles in wells provided

protection against the migrating TCE front but the direct-push candles did not indicates that improvements must be made if direct-push candles are to be a viable option for remediation.

SHMP is considered a dispersant or stabilization aid, which means it stabilize colloids by inhibiting particle aggregation and precipitation. The multiple mechanisms by which this occurs with  $\text{MnO}_4^-$  have been detailed elsewhere (Freeman and Kappos, 1985; Crimi and Ko, 2009; Crimi et al., 2009) but in brief the colloidal stability of hydrous oxides is strongly dependent on their net charge. The higher the net charge of the oxide surface, either positive or negative, the greater the repulsive forces of the individual colloid to oppose other colloids and inhibit aggregation (i.e., greater stability). Given that manganese oxides are amphoteric ( $\text{pH}_{\text{zpc}} \sim 2.3$ , Murray, 1975), the net surface charge of the oxide can be altered to negative, zero, or positive. Under most environmental conditions (i.e., pH), manganese dioxide ( $\delta\text{MnO}_2$ ) is an important adsorbent of phosphate in natural waters (Yao and Millero, 1996) and SHMP is a polyphosphate that can supply soluble phosphate ions. This phosphate can then bind with colloidal oxides, alter the surface charge (i.e., stabilize) and slow the particle coagulation process.

One way researchers have combated scaling is by recognizing that soluble Mn(IV) and colloidal Mn(IV) precede the aggregation and formation of the insoluble  $\text{MnO}_2$  product. This has given rise to the use of stabilization aids. Mata-Perez and Perez-Benito (1985) found that the conversion rate of soluble Mn(IV) to  $\text{MnO}_2(\text{s})$  could be delayed when phosphate was present. Kao et al. (2008)



**Fig. 4.** Effect of SHMP on cumulative permanganate released in flow-through experiments. **A.** H<sub>2</sub>O influent; **B.** TCE (1 mg L<sup>-1</sup>) influent.

found that ~82% of MnO<sub>2</sub> production could be inhibited by including Na<sub>2</sub>HPO<sub>4</sub> with MnO<sub>4</sub><sup>-</sup> without affecting TCE loss. Christenson (2011) also formulated tetrapotassium pyrophosphate (TKPP), a polymeric phosphate similar to SHMP, into slow-release permanganate candles and observed a more linear release of permanganate. Chokejaroerat et al. (2013, 2014) also observed that by including SHMP with permanganate in the treatment of dissolved and nonaqueous phase TCE, less MnO<sub>2</sub> rinds formed around the DNAPL and permanganate coverage of the treatment zone (i.e., sweeping efficiency) increased. For these reasons, we attempted to improve the permanganate candle performance by incorporating SHMP into the formulation.

### 3.2.1. Flow-through experiments

Miniature permanganate candles with varying SHMP concentrations were subject to a constant inflow of either H<sub>2</sub>O or 1 mg TCE L<sup>-1</sup>. Cumulative mass recovered was recorded and graphed. Candles flushed with H<sub>2</sub>O showed that as the concentration of SHMP increased in the candle, so did the mass of permanganate released (Fig. 4). A clear distinction between the control (0% SHMP) and the other candles with SHMP was evident by the end of the experiment (Fig. 4).

For oxidant candles exposed to a constant inflow of 1 mg TCE L<sup>-1</sup>, treatment differences were not as great but the control again had the lowest mass of permanganate released during the first 10 d, after which, only slight differences between treatments were evident (Fig. 4).

Following termination of the flow-through experiments, the candles were weighed, crushed and extracted to determine the mass of permanganate remaining. Results from this procedure showed that for candles exposed to H<sub>2</sub>O, the biggest differences were between the mass of permanganate left in the control ver-

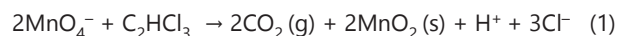
sus the SHMP treatments. The control treatment had 6.1% of the permanganate remaining while the candles with SHMP had 0.83% (2% SHMP), 0.34% (4% SHMP) and 0.26% (6% SHMP) permanganate remaining (Table 4). As observed with the release curves (Fig. 4), less permanganate remained in the candles with increased SHMP. For candles exposed to 1 mg TCE L<sup>-1</sup>, comparatively less permanganate remained in all treatments and the overall range observed was between 1.94% (0% SHMP) and 0.16% (6% SHMP). This smaller difference also corresponds with the smaller treatment effects observed in the release curves (Fig. 4B).

### 3.2.2. Batch experiments

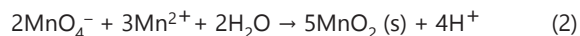
Given that permanganate recovered in the flow-through experiments were controlled by two processes, namely oxidant release and oxidant consumption (especially when TCE was the influent), we designed a different 2-phase experiment to isolate these processes. In this test, permanganate candles were first allowed to soak in H<sub>2</sub>O or TCE-contaminated water for multiple 7-d intervals (Phase 1). Then, once a week, the candles were placed in distilled water for 1 h to record the mass of permanganate released (Phase 2). By taking this approach, the temporal changes in release rates between candles soaked in H<sub>2</sub>O versus TCE-contaminated water could be compared and the effect of contamination on the process quantified. It is also noteworthy that the batch tests ran 49 d versus only 18 d for the flow-through experiment.

Results of the two-phase test showed large differences in release rates. For candles soaked in H<sub>2</sub>O, the effect of SHMP on release rates was fairly stark with the 6% SHMP treatment producing a four-fold greater release of permanganate than the candles without any SHMP after one week of soaking (5 vs 20 mg L<sup>-1</sup>, Fig. 5). With time, release rates decreased for all treatments but the candles containing SHMP consistently released more permanganate. Differences among the four SHMP treatments were fairly consistent for candles stored in H<sub>2</sub>O but for candles stored in TCE-contaminated water, the 4 and 6% SHMP treatments performed similarly, and much better than the control, which stopped releasing permanganate after approximately 2 weeks (Fig. 5). Results also showed that even 2% SHMP in the candle formulation improved the release characteristics dramatically over the control (Fig. 5).

As observed in the flow-through experiment, there were larger differences among SHMP treatments for candles soaked in H<sub>2</sub>O versus TCE (Fig. 5A). One reason for this observation may be due to the pH ranges produced by the treatments. While the presence of TCE undoubtedly facilitated MnO<sub>2</sub> production (Eq. 1), oxidation of TCE by permanganate results in an acidic pH, especially in unbuffered systems (Yan and Schwartz, 1999, 2000, Eq. (1)).



A test of temporal changes in solution pH showed that candles soaked in TCE became acidic within 24 h regardless of whether SHMP was present (pH ~2.4, Table SM-1). This lower pH can influence MnO<sub>2</sub> stability, aggregation and speciation. Previous studies have reported greater stability of colloid manganese oxides (i.e., less precipitation) at pH 3 versus pH 7 (Siegrist et al., 2002). Stability diagrams of Mn speciation under varying pH and Eh values also show that a lower pH favors soluble Mn<sup>2+</sup> (McBride, 1994). In the absence of SHMP, the presence of Mn<sup>2+</sup> will only accelerate the formation of additional MnO<sub>2</sub> by acting as an autocatalyst (Eq. (2)) (Gates-Anderson et al., 2001).





**Table 4.** Mass of permanganate recovered from candles following flow-through experiment.

Influent	Treatment % SHMP	Initial KMnO <sub>4</sub> Mass in candle (mg)	Mass KMnO <sub>4</sub> recovered from candle (mg)	Percent permanganate left in candle (%)
Water	Control (0%)	1150	70.09	6.10
	2%	1150	9.52	0.83
	4%	1150	3.92	0.34
	6%	1150	3.05	0.26
	TCE	Control (0%)	1150	22.34
TCE	2%	1150	2.46	0.21
	4%	1150	6.06	0.53
	6%	1150	1.85	0.16

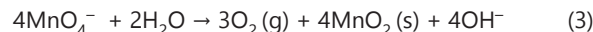
The continuous supply of permanganate dissolving from the candles combined with an acidic pH and presence of soluble Mn<sup>2+</sup> likely explains why the oxidant candles without SHMP showed the most scaling and only released permanganate for about two weeks (Fig. 5).

For candles containing SHMP, the colloidal stability of hydrous manganese oxides forming on or within the candle matrix is strongly dependent on their net charge. Under the acidic conditions caused by TCE oxidation during our closed batch experiments (Eq. (1)), phosphates from the SHMP likely adsorb directly to the hydrous manganese oxides that were at, or below the colloids point of zero charge (pH<sub>zpc</sub> ~2.4). This phosphate adsorption would increase the net charge of the colloids and inhibit aggregation. As a result, higher permanganate release rates for candles containing SHMP were observed under acidic conditions (Fig. 4).

Fortunately, the effects of SHMP in preventing MnO<sub>2</sub> precipitation under acidic conditions can also be observed at neutral and alkaline pHs. Evidence for this was observed for candles soaked in

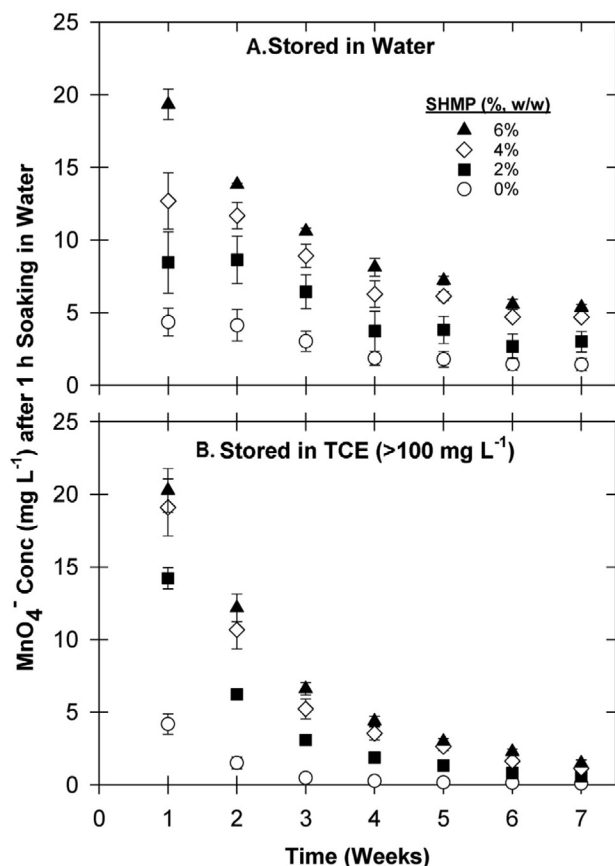
water, where a higher and wider range in pH among SHMP treatments was observed (6.9–9.3). At higher pH values (pH > pH<sub>zpc</sub>) adsorption of Mn<sup>2+</sup> (or other cations) to the negatively charged MnO<sub>2</sub> colloid surface can reverse the surface charge and allow for subsequent phosphate adsorption. Kawashima et al. (1986) showed that alkaline earth cations and transition metals cause manganese dioxide to strongly adsorb phosphate between pH 6 and 9. These phosphate ions can then bind with colloidal oxides, alter the surface charge (i.e., stabilize), slow the particle coagulation process and inhibit MnO<sub>2</sub> aggregation (Perez-Benito, 2002).

In our batch experiments using only H<sub>2</sub>O, the pH became alkaline for candles not containing SHMP (pH > 9) but for candles containing 6% SHMP, the pH of the solution stayed near neutral (Table SM-1). Under alkaline conditions, the permanganate (VII) ions can become reduced to manganate (VI) and eventually to solid manganese (IV) oxide (MnO<sub>2</sub>). While permanganate will preferentially react with reductants such as organic contaminants, natural organic matter or reduced metals, permanganate can also react with water (Eq. (3)), albeit more slowly (Rees, 1987).



Once MnO<sub>2</sub>(s) forms, it can catalyze the above reaction (Eq. (3)) and lead to the decomposition of MnO<sub>4</sub><sup>-</sup>, even when target reductants are absent (Siegrist et al., 2001). Thus, as MnO<sub>2</sub> forms on the outside of the candle, the propensity for more to form likely increases. When SHMP was formulated into the candle, the pH of the candles soaked in H<sub>2</sub>O stayed neutral. Given that phosphate adsorption to MnO<sub>2</sub> starts to dramatically decline once the pH > 6 (Yao and Millero, 1996), the neutral pH observed with 6% SHMP would favor more phosphate adsorption than the alkaline pH (pH 9) observed with the control (0% SHMP). Thus by decreasing the mass of MnO<sub>2</sub> forming on the outside of the oxidant candle with SHMP, the release rates of the slow-release oxidant candles were dramatically improved under neutral to alkaline pHs (Fig. 5).

One final consideration regarding the installation of oxidant candles via direct-push may be whether or not to encase the candles in a protective screen and what effect that might have on oxide formation. If the candles are simply placed directly into the formation, the direct contact of the candle surface with the surrounding soil could facilitate oxide formation. The presence of organic carbon or reduced metals directly in contact with candle surface would facilitate MnO<sub>2</sub> formation. Siegrist et al. (2002) showed that increasing the presence of silt/clay sized particles in batch reactors increased the mass of permanganate consumed and solids produced. By contrast, if the oxidant candle was placed in a screen, mass action would allow some of the permanganate to diffuse away from the candle surface before reacting with any electron donors. This added space along with incorporating SHMP into the formulation may help minimize the amount of oxide scaling that forms on the candle. Evidence to support using a protective screen is presented in supplementary material (Fig. SM-5).



**Fig. 5.** Effect of SHMP on permanganate released into H<sub>2</sub>O from oxidant candles when stored in **A.** H<sub>2</sub>O or **B.** TCE (>100 mg L<sup>-1</sup>) for 7-d intervals.

#### 4. Conclusions

To our knowledge, the deployment of slow-release oxidant candles in 2010 by Christenson et al. (2012) represented the first field-scale trial of treating a contaminated aquifer with slow-release permanganate candles. In this paper, we provide five years of data demonstrating the efficacy of the oxidant candles to treat a migrating plume. Results show that oxidant candles placed in wells and refurbished yearly, steadily reduced migrating TCE concentrations by 89%. Moreover, these 5-year old candles still maintain an inner undissolved core that should provide several more years of service. Oxidant candles inserted by direct-push (no wells) stopped reducing TCE concentrations because a water impermeable scale developed on the outside of the candles. To counteract oxide scaling, we fabricated a second generation of oxidant candles that contain sodium hexametaphosphate. Laboratory experiments show that these second-generation permanganate candles have better release characteristics and are less prone to oxide scaling. This improvement should reduce the need to perform maintenance on candles placed in wells and provide greater longevity for candles inserted by direct-push.

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**Appendix A. Supplementary data** — Supplementary data related to this article follows the *References*.

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1 **A five-year performance review of field-scale, slow-release**  
2 **permanganate candles**

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16 **Supplementary Material**

17 -7 pages –

18 1 Table

19 5 Figures

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**Table SM-1.** Temporal changes in solution pH for candles soaked in H<sub>2</sub>O versus TCE, with and without 6% SHMP

Medium	SHMP Conc	Solution pH				
		Time (h)				
		0	24	96	144	312
H <sub>2</sub> O	0%	7.61	9.40	9.19	9.25	9.26
	6%	6.76	6.71	6.81	6.81	6.91
TCE	0%	5.04	3.03	2.84	2.64	2.48
	6%	6.62	2.84	2.51	2.41	2.41

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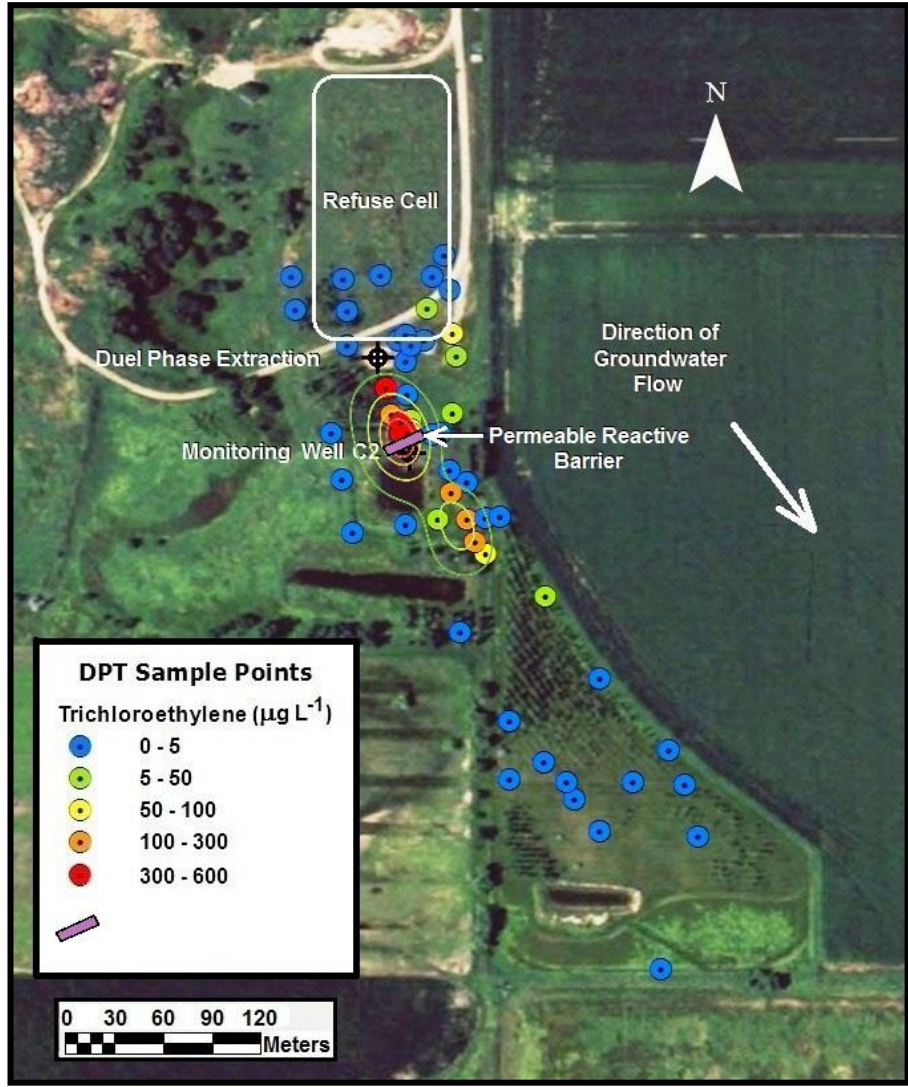


Figure SM-1. Location of permeable reactive barrier containing 5.1 and 7.6-cm diam oxidant candles in relation to TCE concentrations ( $\mu\text{g L}^{-1}$ ) determined via direct-push sampling.

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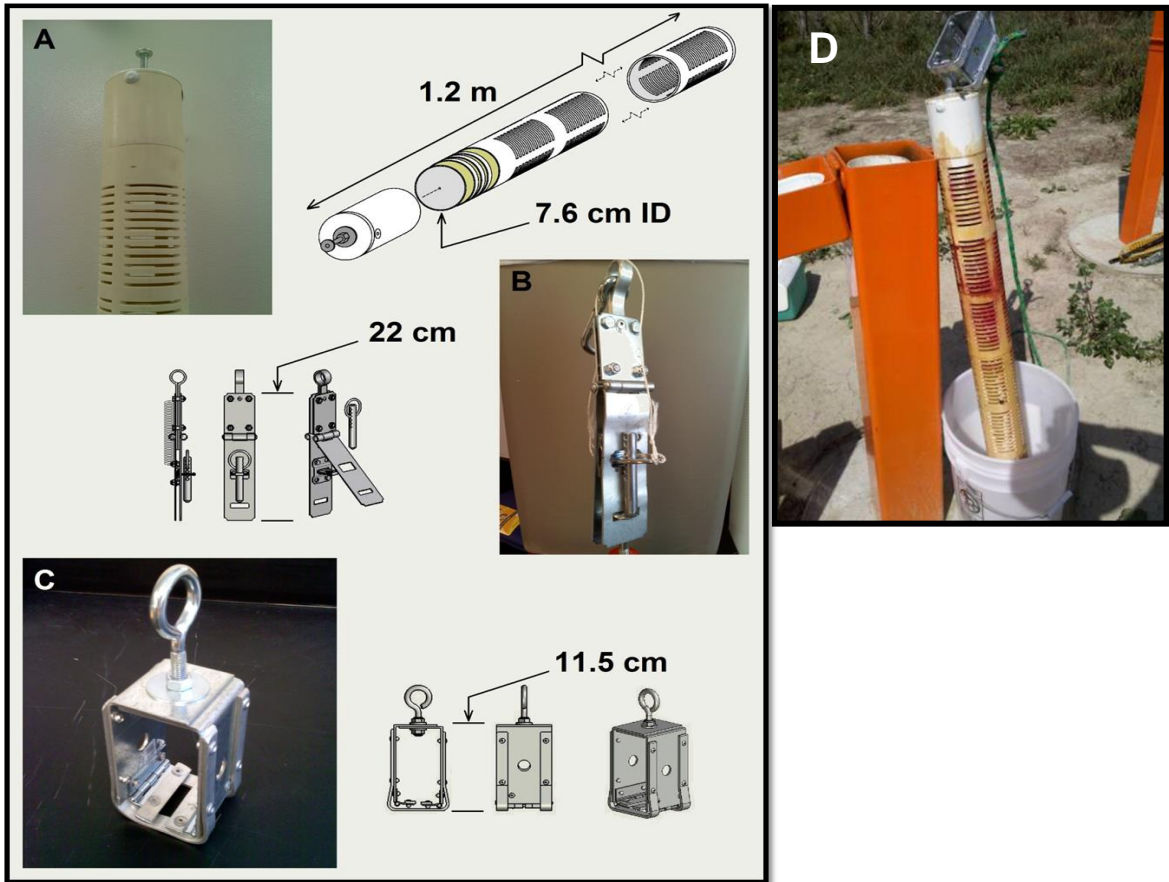


Fig. SM-2. Photographs and schematics of field hardware developed and used with PRB at field site: (A) PVC screened candle carrier for 7.6-cm diam. oxidant candle; (B) Candle Insertion Tool; (C) Candle Removal Tool; (D) Candle Removal Tool attached to Carrier. Each carrier was lowered into a 10-cm diam 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. The candle removing tool is equipped with a trap door that latches onto the carriage bolt on top of the candle carrier.

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Fig. SM-3. Photograph of experimental unit used in batch experiment showing suspended oxidant candles. Insert shows photograph of oxidant candle used in batch tests.

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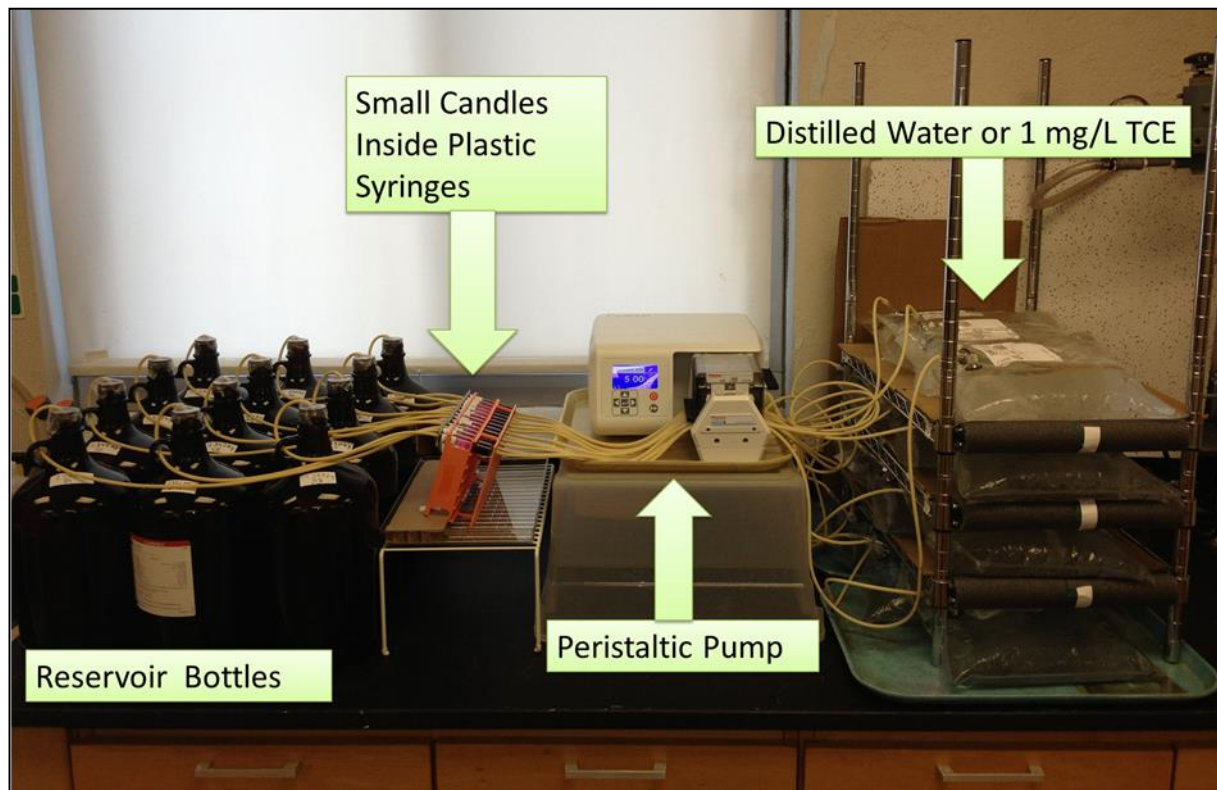


Fig. SM-4. Photograph of flow-through system showing peristaltic pump, zero headspace inlet bags, candle holders and effluent receptacles.



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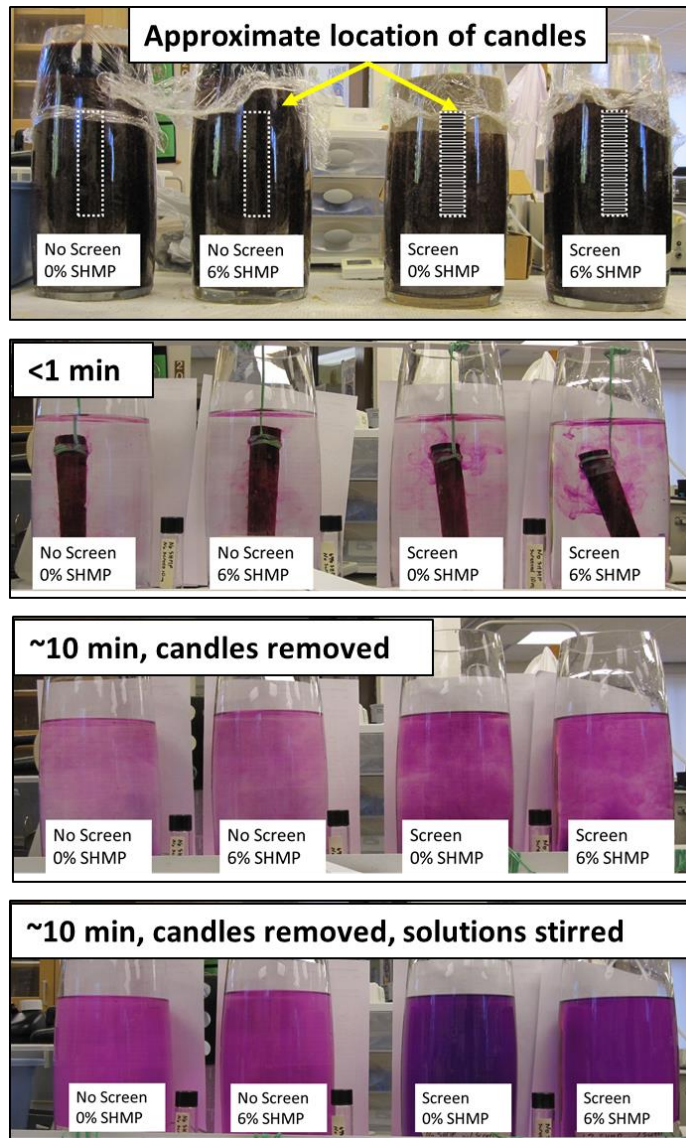


Fig. SM-5. Photographs of water-saturated sand microcosm incubated with permanganate candles, with and without 6% SHMP, and with and without outside screens. Top photograph shows sand microcosms after ~ 21 d. Remaining photographs show temporal release of permanganate from candles after removal from sand and placed in water. Results show candles incubated without screens initially released less permanganate than candles incubated with screens.