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Remediating Contaminated Groundwater with an Aerated, Direct-Push, Oxidant Delivery System

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Remediating Contaminated Groundwater with an Aerated, Direct-Push, Oxidant Delivery System

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Abstract: One of the biggest challenges to treating contaminated aquifers with chemical oxidants is achieving uniform coverage of the target zone. In an effort to maximize coverage, we report the design and installation of a novel aerated, slow-release oxidant delivery system that can be installed by direct-push equipment. By continuously bubbling air beneath a slow-release oxidant in situ, an airlift pump is created that causes water and oxidant to be dispersed from the top of the outer screen and drawn in at the bottom. This continuous circulation pattern around each drive point greatly facilitates the spreading of the oxidant as it slowly dissolves from the wax matrix (i.e., oxidant candle). Given that the aeration rate controls the outward flow of oxidant from the outer screen in all directions, the radius of influence around each drive point is largely a function of the outward velocity of the oxidant exiting the screen and the advection rate opposing the upgradient and lateral spreading. Temporal sampling from three field sites treated with the aerated oxidant system are presented and results show that contaminant concentrations typically decreased 50–99% within 6–9 months after installation. Supporting flow tank experiments that demonstrate oxidant flow patterns and treatment efficacy are also presented.

Keywords: airlift pump; groundwater remediation; modular oxidant delivery system; oxidant cylinders; oxidant delivery device

1. Introduction

A critical review of two decades of contaminated groundwater sites treated by in situ chemical oxidation (ISCO) has uncovered many examples where liquid oxidant injections have failed to achieve desired cleanup goals [1,2]. Unlike the positive results obtained when chemical oxidants are used in well-mixed reactors, such as during the treatment of municipal wastewaters, direct-push delivery techniques of liquid oxidants into groundwater can fail to deliver uniform coverage. The reason for this is the uncontrolled, unmixed and stratified nature of subsurface environments. Moreover, the volume of oxidant delivered is often too small to allow for complete coverage of the target zone.

Huling et al. [1] systematically reviewed a series of ISCO performance surveys and concluded that poor ISCO performance often corresponds with sites treated with low oxidant volumes (i.e., percentage of contaminant plume). A review of 40 ISCO sites showed that nearly 50% of the ISCO treatments injected liquid oxidant volumes equivalent to 10% of the contaminant plume [2–4]. While diffusion and mass transport will ultimately increase the percentage of the plume impacted following ISCO injections, the heterogeneous and anisotropic nature of aquifers prevents uniform mixing and can leave significant portions of the contaminated aquifer untouched [2].

Advancements in high-resolution site characterizations (e.g., coupled direct-push membrane interface with hydraulic profiling) combined with prescription-type injections has advanced injection technologies by providing for more targeted treatments. While improved profile characterization can direct better oxidant placement, the injected liquid oxidant is still subject to advection and density-driven flow. These two processes, coupled with the presence of residual non-aqueous phase liquids (NAPLs) within low permeable zones often necessitates additional injections as contaminants desorb back (i.e., rebound) into the transmissive regions following declines in contaminant concentrations from ISCO injections [5,6]. McGuire et al. [7] reported that in a review of 23 NAPL sites treated with liquid oxidants, 81% of the wells exhibited rebound with 30% bouncing back to concentrations greater than those observed before treatments began.

While the chemistry of treating groundwater contaminants with chemical oxidants such as permanganate or persulfate is proven, crucial challenges remain. The biggest challenges to contaminant plume treatment appear to be how to more uniformly deliver the chemical oxidants to targeted zones and determining how to make the oxidant remain in place long enough to mitigate rebound. To overcome the limitations associated with liquid injections, researchers began encapsulating oxidants as slow-release treatments for contaminated aquifers several years ago [8–10]. Since these initial reports, increased interest has resulted in a number of publications that have documented the efficacy of slow-release oxidants to remove groundwater contaminants at the laboratory-scale and in larger flow-tank systems [11–23]. In their analysis of peer-reviewed research involving controlled-release materials for groundwater remediation, O'Connor et al. [24] indicated that of the 30 publications identified, most have been published in the last five years.

Christenson et al. [25] was the first to report the use of slow-release oxidants in the field. They treated a former unregulated landfill with known trichloroethene (TCE) contamination by manufacturing and deploying slow-release oxidant candles (oxidant-wax cylinders). Installation involved inserting half of the oxidant candle mass into the aquifer with direct-push technology and the other half by placing the candles in screens and then dropping them down designated wells. For the candles placed in wells, it was observed that the permanganate dissolving from the oxidant-wax matrix was subject to downward density flow and thus producing an uneven oxidant distribution across the well screen. To counteract the downward flow, Christenson et al. [25] began bubbling air at the base of the oxidant. This bubbling action creates what is analogous to an airlift pump where the injection of air into a submerged pipe (i.e., well screen) causes water to rise up and discharge near the top of the screen and enter at the bottom. Kambhu et al. [26] recently simulated these flow patterns by coupling a two-phase bubbly flow model with the Darcy flow model in a wide flow tank (Figure S1). By combining aeration with the slow-release oxidants, Christenson et al. [25,27] created a continuous (i.e., 24 h per day, 7 days per week; 24/7) circulation pattern around each drive point, which over time, greatly facilitated the distribution of the oxidant to the target zone. Results from the initial field study showed that after more than seven years of deployment, the aerated oxidant candles were still functioning and had reduced downgradient TCE concentrations and associated contaminants by 90%. The initial success of combining aeration with oxidant candles to decrease contaminant concentrations subsequently led to a reloadable design that could be installed by direct-push equipment [28]. This modular oxidant delivery system is currently treating a variety of aquifers contaminated with petroleum and chlorinated solvents.

In this paper, we report the groundwater monitoring results from three field sites treated with the direct-push, aerated, oxidant delivery system. Supporting flow tank experiments that demonstrate oxidant flow patterns and treatment efficacy are also presented. This new method of treating contaminated groundwater is a novel combination of an airlift pump with slow-release oxidants. Merging aeration with slow-release oxidants creates a technology that differs from typical ISCO treatments and avoids some of the problems associated with injecting liquid oxidants. By creating a circulation pattern around each drive point, density-driven flow of the oxidant is minimized. Given that the oxidant is added as a solid, no surfacing (i.e., daylighting) of the oxidant will ever occur. Moreover, the stationary and sustained release of an oxidant to a targeted aquifer zone greatly diminishes the chances of rebound. Finally, the reloadable design allows more oxidant to be added as needed with minimal effort or safety concerns; this allows the technology to provide an effective groundwater treatment for months to years.

2. Materials and Methods

2.1. Treatability Studies, Oxidant Manufacturing and Field-Scale Installation and Sampling Procedures

Prior to installing the aerated oxidant delivery system in the field, treatability studies using miniature candles were performed with groundwater from the field sites. Details of the procedures used in the treatability studies are provided in the supplemental materials (SM). The identification of acetone and 2-butonone in one of the treatability studies and at one of the field sites prompted additional investigations to determine the source of the acetone. Methodologies used to manufacture the field-scale wax-based oxidant candles have previously been reported [17,25,27]. Supplementary Materials also contains detailed schematics of the oxidant delivery devices (Figure S2), direct-push installation procedures of the oxidant drive points, groundwater sampling and analysis methodologies, and the methods used to measure the longevity of the persulfate candles under field conditions.

2.2. Generalized Plot Plan and Technology Components

The placement and spacing of drive points containing the aerated oxidant delivery devices are site specific and tailored to the contaminant plume. Regardless of the plume geometry, the treatment technology consists of three components. These include: (i) two or more rows of individual drive points that are offset and spaced 0.9–2.4 m apart (Figure 1A); (ii) a dual manifold system that supplies an aeration tube to the drive points and a ventilation line away from the drive points to a central outlet and (iii) a rocking piston compressor (EasyPro Pond Products, Grant, MI, USA). Rocking piston compressors have routinely been used to aerate lakes and are compact, quiet and able to run 24/7 with minimal maintenance. This three-part modular design is scalable to accommodate most contaminant plumes. Width can be accommodated by adding more drive points and depth can be adjusted by direct-push placement of the oxidant screens.

2.3. Oxidant Delivery System

The drive points used to deliver oxidant to the aquifer consist of an outer screen that is emplaced with direct-push equipment and an inner screen that holds the slow-release oxidant [28]. To cover the treatment zone, the outer screen extends from the targeted depth to slightly above the water table; this allows potential smear zones to be treated as the water table fluctuates. An aeration tube is placed in the gap between the outer and inner screens. For the reloadable design, the outer screen consists of multiple 6.0325 cm OD by 1.52 m SCH 40 PVC pipes with 0.0254 cm screens. The inner screen, which holds the 2.54-cm diameter oxidant candles, consists of 4.2164 cm OD SCH 80 PVC with 0.0254 cm screens (Figure 1B). Compressed air supply and vent line headers were constructed of propylene pipe installed with a hydraulic vibratory plow to a depth of 30–40 cm. Self-tapping branch connections tapped into the headers to connect to each insertion point with 6.35 mm polyethylene tubing (Figure 1C).

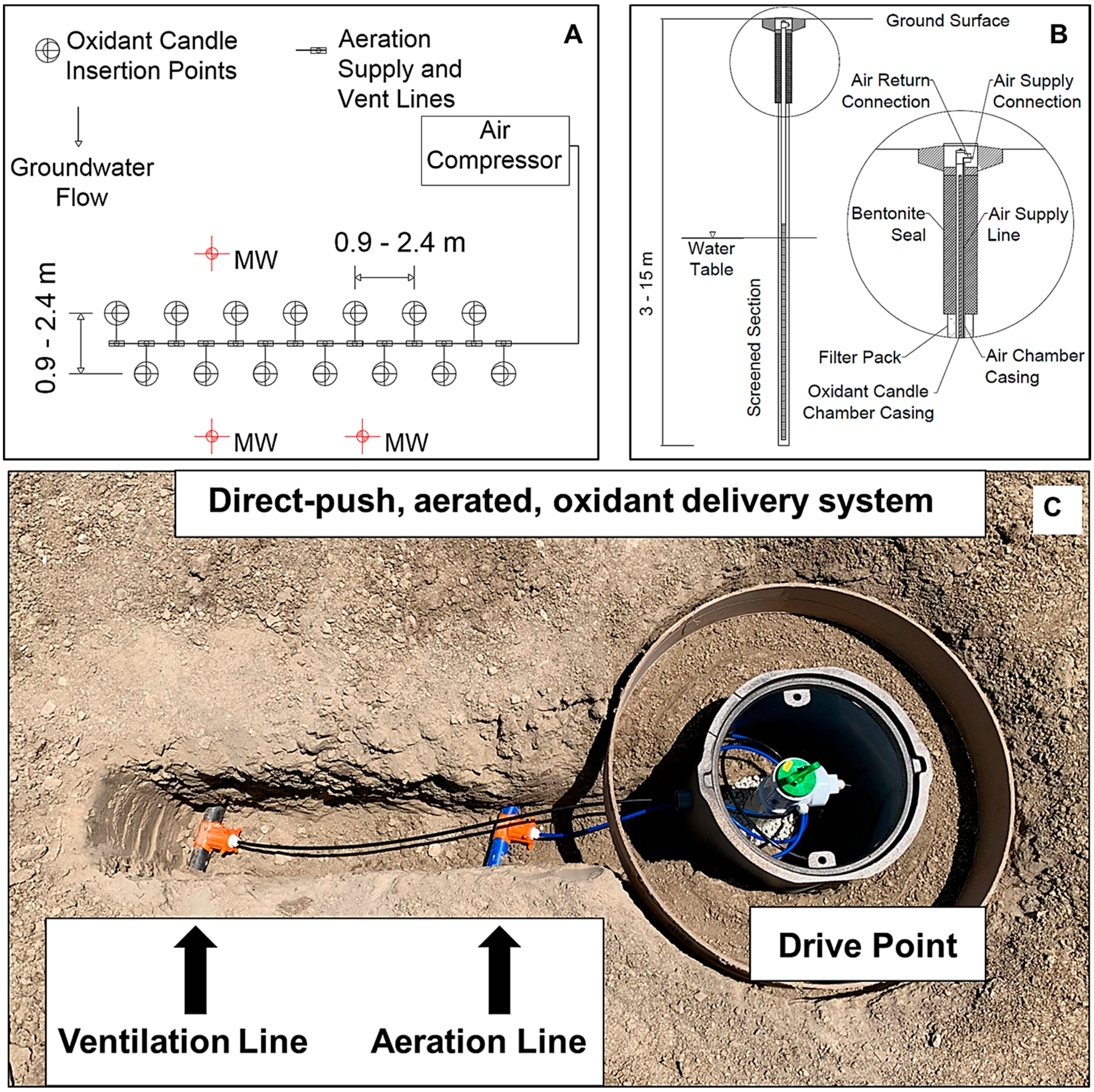

Figure 1. (**A**) Generic plot plan (plan view); (**B**) vertical view of drive points used in deploying the direct-push, aerated, oxidant delivery system and (**C**) photograph of direct-push, aerated, oxidant delivery system.

2.4. *Visualizing Oxidant Dispersal from Aerated Oxidant Candles*

To understand the flow patterns created by aerating the oxidant candles in the double screened assembly (i.e., airlift pump), a large acrylic tank was filled with water and field-scale 1.52-m segments of the outer and inner screen containing permanganate oxidant candles were lowered into the tank and aerated. Temporal photographs were taken as the permanganate dissolved and circulated around the outer screen. To aid in understanding the flow dynamics of the system, we used similarly dimensioned clear outer and inner screens and added dye to specific locations between the outer and inner screen (i.e., screen gap) and recorded water flow directions.

2.5. *Field Testing of Aerated, Direct-Push, Oxidant Candles*

Results from three field sites are presented. The site names and locations include: Freeman (Sargent, NE, USA), Textron (Lincoln, NE, USA) and Hoover (Beatrice, NE, USA). All three sites were treated with aerated oxidant candles that were installed with direct-push equipment. The Freeman site used a non-reloadable design whereas the Textron and Hoover site used a reloadable design that is currently being used at other locations. The number of drive points installed at each site is shown in the individual plot plans provided below; additional plot details and brief site histories are provided in SM.

The aerated oxidant candle drive points were placed in the contaminant source areas for the Freeman and Textron sites while the drive points at the Hoover site were positioned to test a pilot-scale barrier design (Table 1). Each field site was located in a different geographical location within the state of Nebraska (USA) and thus site and groundwater characteristics differed. Individual field site characteristics are presented and include: depth to groundwater; screen depths of oxidant candles and monitoring wells; soil textures; seepage velocity; groundwater quality characteristics and major contaminants of concern (Table 1).

Table 1. General site characteristics of three field sites treated with aerated oxidant candle drive points.

Site Characteristics	Freeman	Textron	Hoover
Treatment type	Source Zone	Source Zone	Permeable Reactive Barrier
Depth to Groundwater (m)	2.0	4.1	4.4
Screened Interval of Oxidant Drive Points (m)	1.5–6.1	1.5–6.1	1.5–6.4
Screened Interval of Monitoring wells (m)	1.2–4.3	1.5–6.1	3.4–6.4
Texture	Layers of Clay and Fine to Coarse Sand	Layers of Clay, Sandy Clay, and Medium to Fine Sand	Lean Clay with various amounts of Fine Sands
Seepage Velocity (cm/d)	16.5	26.5	0.21
Contaminant(s) of Concern	BTEX	BTEX	1,4-dioxane, TCE, BTEX
Dissolved Oxygen (mg/L) Initial Range [1]	0.76–1.64	0.34–3.30	0.32–1.80
ORP (mV) Initial Range	−248.6 to −207.1	−118.9 to 48.0	−167.4 to −48.5
pH Initial Range	6.45–6.78	6.15–6.98	6.47–7.06

[1] Initial range of water quality parameters measured in site monitoring wells (Freeman: SG-10, SG-19 and SG-20; Textron: TX-1, TX-2, TX-3 and TX-4 and Hoover: HV-1, HV-2 and HV-3) prior to initiating the aerated oxidant candle treatment.

2.6. *ISCO with Liquid Oxidant versus Aerated Oxidant Candle*

Given that the Freeman site had been treated by ISCO using a liquid oxidant in a previous investigation and aerated oxidant candles from this research, we compared the efficacy of using oxidant candles versus liquid oxidant in a controlled wide flow box experiment. Tank experiments used Ottawa graded sand (grain size 0.150–0.425 mm) that was packed into the tank by uniformly adding the sand in layers while raising the water level during packing. Additional details of the flow box construction (inlet, soil and outlet chambers) are presented in Supplementary Materials (Figure S4). To compare the two forms of oxidant delivery, we used phenol as the surrogate contaminant and flooded the tank with phenol (50 mg L^{-1}) under constant advection. Once inlet and outlet phenol concentrations stabilized, the tank inlet chamber was switched to tritiated water (^3H_2O) and pumped into the inlet chamber to produce the same advection rate. Effluent samples were collected from the outlet chamber to produce a tritiated water breakthrough curve. For the control treatment, the rise in ^3H_2O corresponded with a decrease in phenol as it was physically flushed out of the tank.

To determine phenol destruction by either the addition of liquid oxidant (injected at 8% of plume volume, with a permanganate concentration of 20,000 or 25,000 mg/L) or the aerated oxidant candles, we repeated this experiment and compared the mass of phenol recovered from the outlet chamber. In brief, the control treatment provided the baseline removal of phenol by advection or simple displacement (by ^3H_2O) whereas the oxidant treatments represented phenol removal by advection and chemical oxidation. We also compared the mass of permanganate used by both the liquid and oxidant candle treatments.

Samples for phenol and ^3H_2O analysis were taken from the outlet reservoir every 6 h while the total mass of effluent eluted from the flow tank was determined by collecting all the effluent in a single reservoir and periodically weighing. One milliliter effluent samples were taken for phenol analysis by high performance liquid chromatography (HPLC; Shimadzu Scientific Instruments Columbia, MD, USA) using a photodiode array detector and AQUASIL C18 column (Thermo Fisher Scientific, Waltham, MA, USA, dia. 250 mm × 4.6 mm, particle size 5 µm) that was coupled to a guard column. An isocratic mobile phase of 50% acetonitrile was used at a 1 mL min^{-1} flow rate. The samples were analyzed at 256 nm by an external calibration curve. A second 2 mL sample was taken and thoroughly mixed with 12 mL of Ultima Gold$^{\text{TM}}$ liquid scintillation cocktail (PerkinElmer, Inc., Waltham, MA, USA) to measure tritium (^3H) activity via liquid scintillation counting (Packard 1900TR scintillation counter, Downers Grove, IL, USA).

3. Results and Discussion

3.1. Visualizing Oxidant Dispersal from Aerated Oxidant Candles

Airlift pumps are historical devices (circa 1800) that have proven to be a reliable and low maintenance way of moving liquids in the petrochemical and oil industries [29,30]. In its simplest form, a compressor was used to inject air into the bottom of a submerged pipe and because air has a lower density than liquid water, it moves upward. In the context of our modular oxidant delivery system, the air bubbles placed in the screen gap created a buoyancy force that lifted and caused water and oxidant to dispel from the upper portions of the screen (Figure 2A). With water exiting the upper half of the screen, equilibrium is maintained by water being drawn in at the bottom of the screen (Figure 2A). Thus, the airlift pump, which has no mechanical or moving parts, provided a simple way of circulating and treating contaminated groundwater in the field.

Using clear screens and colored dye, we observed four distinct flow patterns created in the aerated oxidant delivery system. The flow patterns detected included: (1) water moved upward in the screen gap on the side where the aeration tube was located but moved (2) partially downward on the opposite side, causing an internal circulation within the screen gap; (3) water and oxidant were expelled from the top half of the outer screen and (4) water was drawn into the screen gap in the lower sections of the outside screen (Figure 2A).

Aerating the oxidant candles provides two important functions to the treatment. First, the induced flow patterns around the candle broke the intermolecular forces holding the oxidant together and allowed the oxidant to solvate with water, thus reducing downward density driven flow. Secondly, by aerating the candles inside the reloadable screen, a continuous, 24/7 circulation pattern around the drive point was created. Kambhu [31] simulated this action around miniature aerated double-screened oxidant candles by coupling a two-phase bubbly flow model with the Darcy flow model in a wide flow tank (Figure 2B; Figure S1). Kambhu et al. [26] showed that the aeration rate controls the outward flow of the oxidant from the outer screen in all directions and that the radius of influence around each drive point is largely a function of the outward velocity of the oxidant exiting the screen and the advection rate opposing the upgradient and lateral spreading of the oxidant (Figure 2B). For this reason, site-specific seepage velocities will be an important consideration in determining the spacing between oxidant drive points. Modeling by Kambhu et al. [26] also predicted the oxidant would move upgradient or against groundwater flow near the upper half of the screen. This upgradient flow pattern has been detected in our flow box experiments (Figure 2B,C) and as presented below, in some of our upgradient monitoring wells at the field sites. In the absence of aeration, our narrow flow box shows that much less coverage of the target zone occurred during advection due to density-driven flow of the permanganate (Figure 2C).

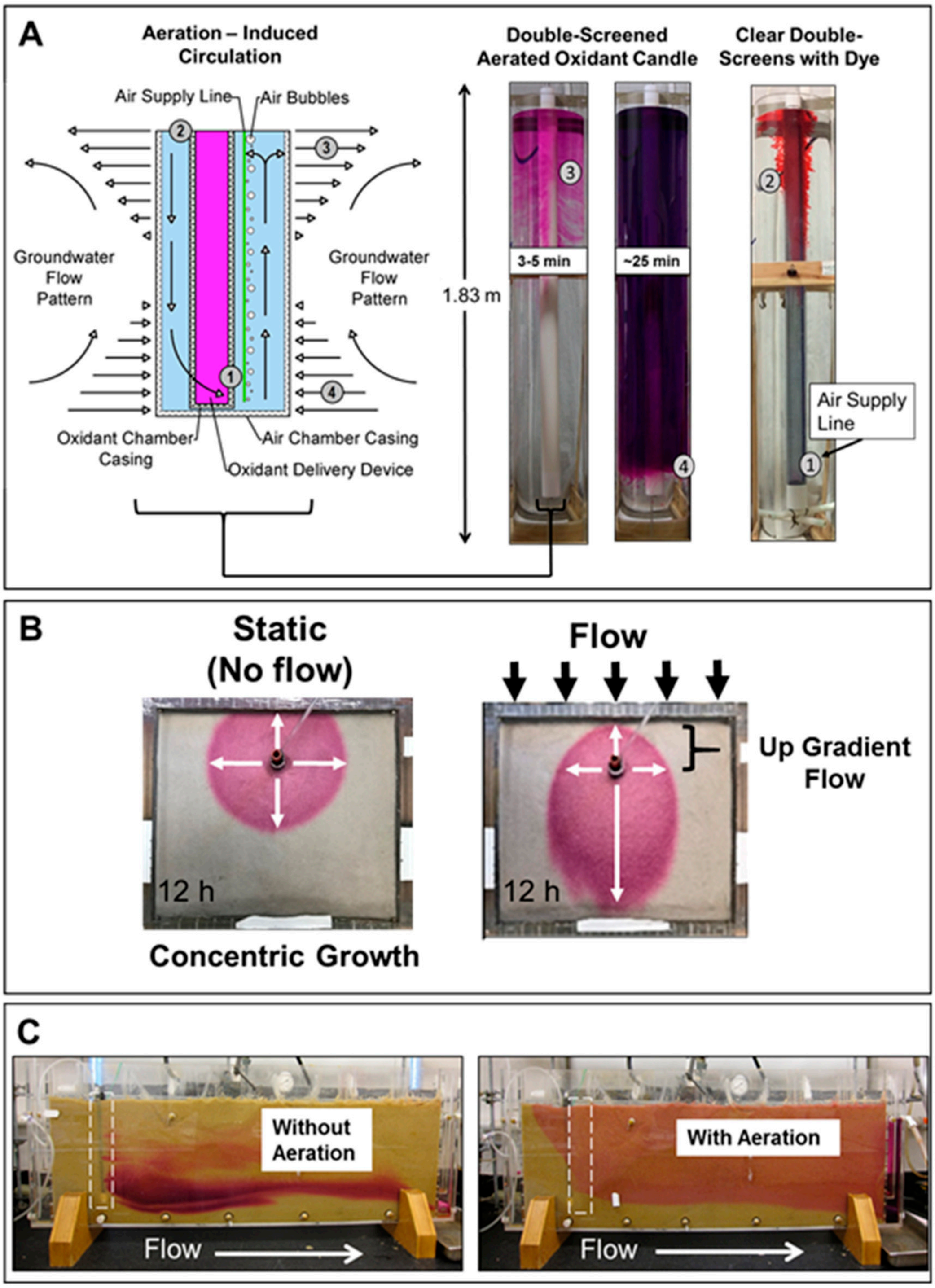

Figure 2. (**A**) Schematic illustrating observed flow patterns and temporal side-view photographs of oxidant dispersal patterns from field-scale, aerated oxidant candles; (**B**) top view of wide flow box (35.6 cm W × 30.5 cm L, see Figure S3) showing permanganate spreading from miniature double-screened candles after receiving similar aeration rates for 12 h, one with advection and one without (static) and (**C**) photographs of narrow flow box (122 cm W × 45 cm H) containing permanganate candle under advection, with and without aeration.

3.2. Field Testing of Aerated, Direct-Push, Oxidant Candles

Each field site was treated with multiple drive points containing permanganate or persulfate candles. Research that went into developing these field-scale oxidant candles has previously been reported [17,18,21,25,27]. These publications provide details on oxidant-wax ratios, oxidant candle compositions; oxidant release rates, pairing of persulfate candles with zerovalent iron candles and contaminant degradation rates via oxidant candle exposure. The chemistries of the two oxidants used in the slow-release candles (i.e., permanganate and persulfate) have also been extensively studied from both a kinetic and mechanistic perspective (e.g., [32–36]). In brief, permanganate is widely accepted as an efficient oxidant for ISCO applications and is extremely efficient in oxidizing chlorinated ethenes to CO_2 [37–40]. Likewise, several researchers have reported positive results in treating BTEX compounds with persulfate in contaminated soil and water [35,41–45].

When treating a contaminated plume, traditional ISCO injections using liquid oxidants must typically account for soil oxidant demand (SOD) of the aquifer solids. While soil oxidant demand is still a consideration when using aerated oxidant candles, the direct-push, aerated oxidant candles are stationary and continuously release oxidant to the same zone around the drive points. This means that the SOD within the radius of influence will eventually decrease with time. Thus, as oxidant candles are reloaded into the drive points, less oxidant would be consumed by the SOD and more would be available to treat the contaminants. For sites with high soil oxidant demands, using the aerated oxidant candles in a barrier design may be preferred because it would provide a stationary source of oxidant to the same treatment zone for months to years and avoid having to account for the soil oxidant demand of the entire plume.

3.3. Freeman Site

The Freeman site was a typical abandoned gas station that had experienced leaking petroleum from its underground storage tanks. This site was responsible for vapor intrusion in a resident's basement approximately 21 m downgradient (Figure 3). Following several years of investigation and remedial treatments, which included two ISCO injections, the Nebraska Department of Environment and Energy (NDEE) approved the use of aerated, direct-push, oxidant candles. Before the oxidant candles were installed at the site, a treatability study was first performed where miniature oxidant candles were allowed to react with the groundwater for 14 d prior to quenching and sending off for analysis. Based on this treatability test, the persulfate + zerovalent iron (ZVI) candles worked best followed by the permanganate candles (Table S1). For comparison, we placed the field-scale persulfate + ZVI candles upgradient of two monitoring wells (SG-10, SG-19, Figure 3) and permanganate candles upgradient of monitoring well SG-20 (Figure 3).

While the chemistries of permanganate and persulfate are effective in degrading various contaminants, the key to successful treatment has always been achieving adequate coverage of the target zone. By including aeration in the technology to induce a circulation pattern around each oxidant drive point (Figure 2), oxidant coverage was greatly enhanced.

Temporal samplings of Freeman monitoring wells showed significant reductions (>99%) in groundwater contaminants following oxidant candle installation. By plotting the historical xylene concentrations (which were in most abundance), results showed contaminant concentrations decreased following the two ISCO injections, but concentrations eventually rebounded (Figure 4). By contrast, all BTEX concentrations decreased after installation of the oxidant candles with no sustained rebound (Figure 4). The continued reduction in BTEX concentrations combined with the lack of vapor intrusion in the nearby resident's basement prompted NDEE regulators to close the site to further treatment. These results provided support for combining aeration with slow-release oxidants.

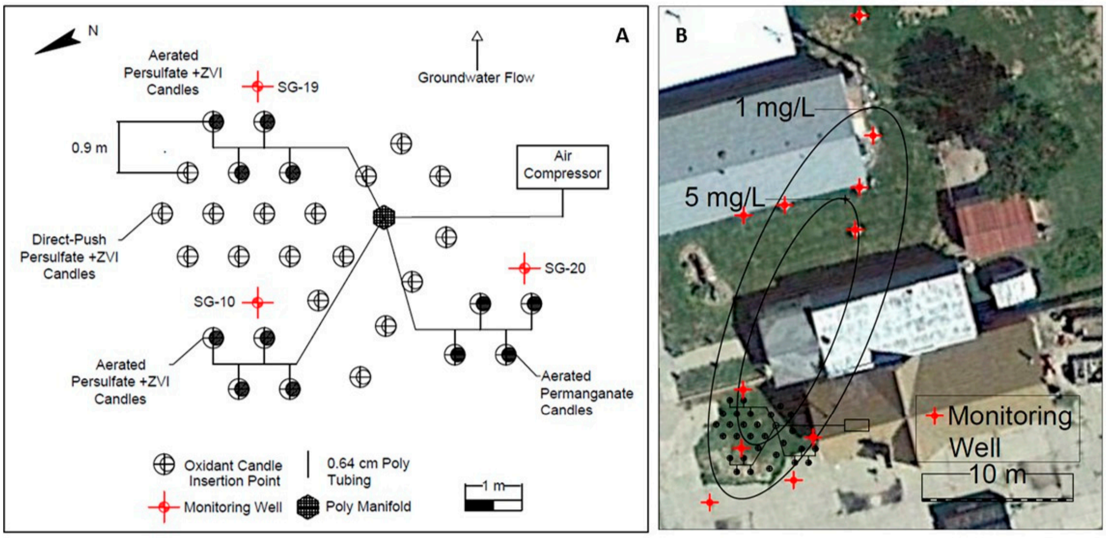

Figure 3. (**A**) Plot plan of Freeman site showing location of monitoring wells and direct-push oxidant candles, with and without aeration and (**B**) plan view of Freeman site showing locations of xylene plume and oxidant drive points (circled).

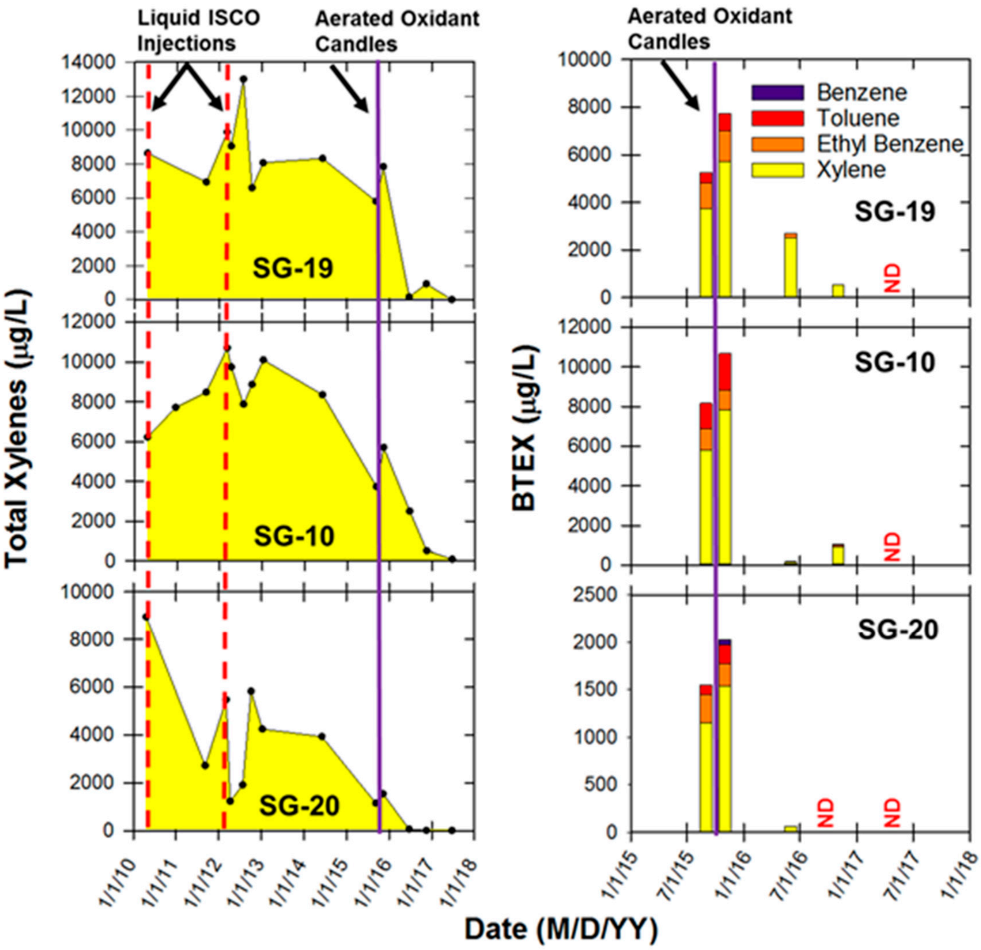

Figure 4. (**Left**) Historical changes in total xylene concentrations at the Freeman site following treatments with two liquid oxidant injections and aerated oxidant candles and (**Right**) temporal changes in BTEX concentrations following installation of aerated oxidant candles.

3.4. ISCO with the Liquid Oxidant versus Aerated Oxidant Candle

While traditional ISCO (i.e., injected liquid oxidants) and oxidant candles were both used on the Freeman site (Figure 4), these two field technologies were not set up to be directly compared due to differences in time (years) and space (injection points) and the mass of oxidant deployed. To provide a more objective comparison, a larger flow tank experiment was conducted where similar masses of oxidant were added (via liquid vs. oxidant candles) under the same advection rate. This series of transport experiments demonstrated the removal of the surrogate contaminant (i.e., phenol) from the flow tank by three means, namely: (i) physical displacement (control); (ii) physical displacement plus oxidation by liquid oxidant injection and (iii) physical displacement plus oxidation by aerated oxidant candles.

Differences in the mass of phenol recovered between the control and liquid injections were between 34 and 39% (for the two concentrations) whereas the difference between the control and aerated oxidant candles was 66% (Figure 5). Therefore, the aerated oxidant candles removed significantly more phenol than the liquid oxidant injections. Given that the mass of the oxidant added was similar between the liquid injections (12 and 15 g for the two concentrations) and oxidant candles (12.5 g via mass released), differences in the percent of phenol removed were due to differences in the spatial distribution of the permanganate throughout the flow box, which ultimately impacted contaminant contact. Although the liquid oxidant was added as 8% of the flow tank pore volume and injected at three locations and multiple depths, the density of the permanganate eventually caused it to sink to the bottom of the flow tank (Figure 5). By contrast the aerated oxidant candles produced a more even vertical distribution of the permanganate in the flow tank, with permanganate visibly present at the surface (Figure 5). The greater oxidant spreading produced by the aerated system resulted in a more efficient removal of the phenol during transport.

3.5. Textron Site

The Textron site is a targeted brownfield and previous environmental assessments have confirmed the presence of petroleum products in the groundwater, namely benzene, ethylbenzene, toluene and xylene (i.e., BTEX). Using the reloadable drive points at the Textron site (Figure 6), we observed that the aerated oxidant candles dramatically decreased BTEX concentrations (Figure 7). The highest initial BTEX concentrations were located in monitoring wells TX-1 (6909 µg BTEX/L) and TX-2 (7687 µg BTEX/L). Monitoring well TX-1 was located just upgradient from the first line of drive points and TX-2 was just downgradient of the drive points (Figure 6). Within 3 months, we observed significant BTEX decreases in all four monitoring wells (81–99%) and by 12 months, decreases ranged between 96% and below detection limits (Figure 7).

The decrease in BTEX concentrations in the upgradient well (TX-1) is perhaps curious but as mentioned above (Figure 2), the circulation pattern created around the drive point causes water and oxidant to be expelled and move out concentrically away from the drive point (Figure 2B). This can cause upgradient concentrations to decrease, as observed in well TX-1, where traces of persulfate were observed (<0.7 mg/L) and BTEX concentrations declined but at a slower rate than the downgradient wells where higher persulfate concentrations were recorded (TX-2, 2.1 mg/L; TX-3, >70 mg/L; TX-4, 21 mg/L). Supporting flow tank experiments verified that the oxidant can move upgradient (Figure S1) with the radius of influence around each drive point largely a function of the outward velocity of the oxidant exiting the screen. This outward velocity would be a function of the aeration rate and the depth of water above the aeration tube, with greater heads producing more velocity [21,26].

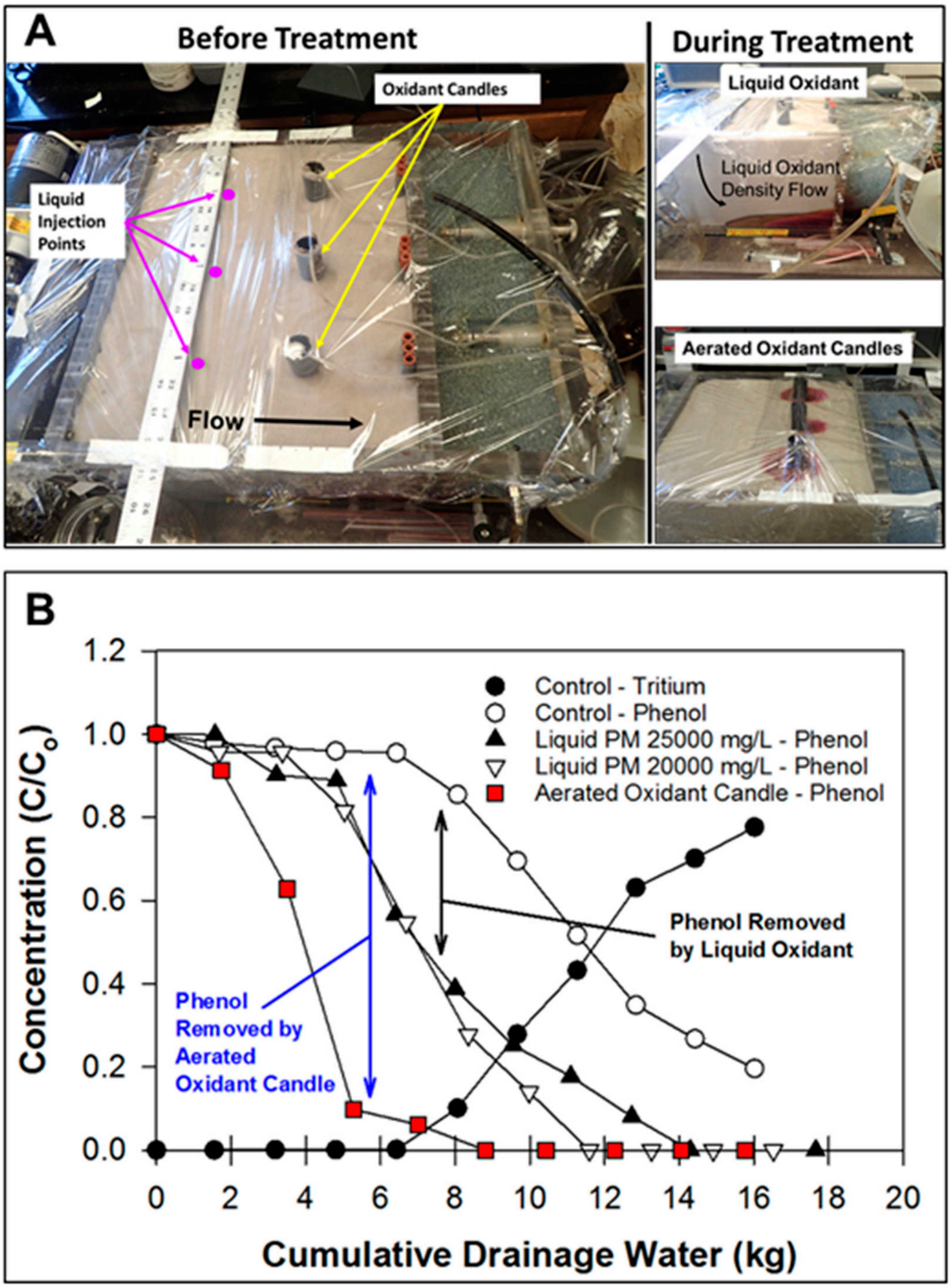

Figure 5. (**A**) Photographs of the flow box used to compare liquid oxidant versus aerated oxidant candles during transport and (**B**) breakthrough curves of ^{3}H2O and phenol removal during transport experiments. Transport experiments were repeated four times and included the following treatments: control (^{3}H20 only); liquid permanganate (PM) injection (20,000 mg/L); PM injection (25,000 mg/L) and aerated oxidant candles.

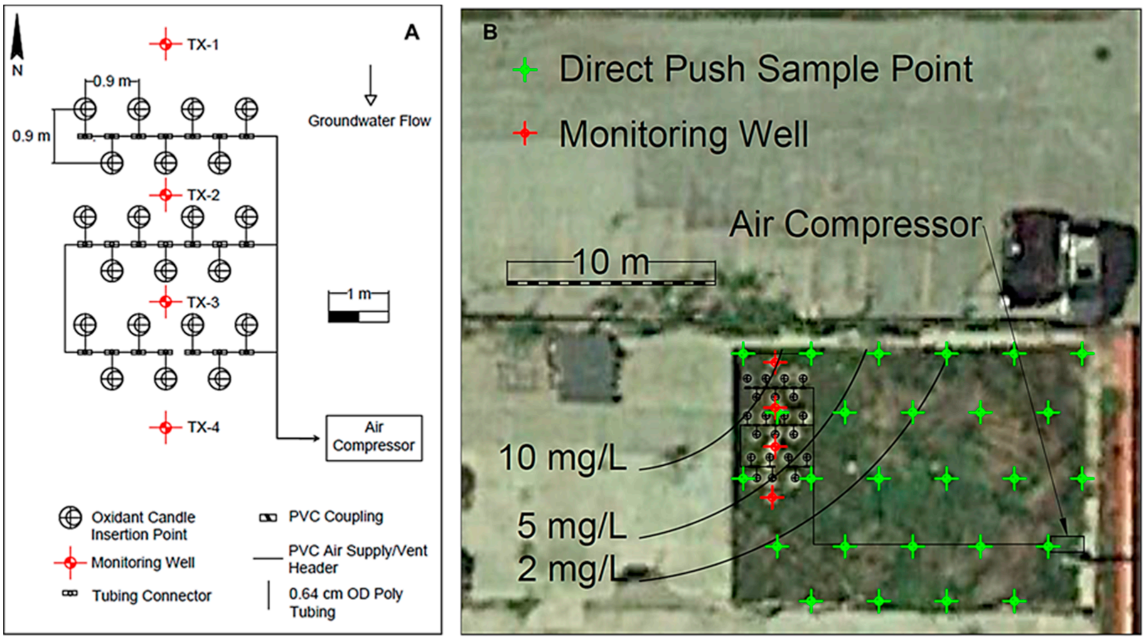

Figure 6. (**A**) Plot plan of the Textron site showing the location of monitoring wells and direct-push oxidant candles with aeration and (**B**) plan view of the Textron site showing BTEX contours and oxidant drive points (circled).

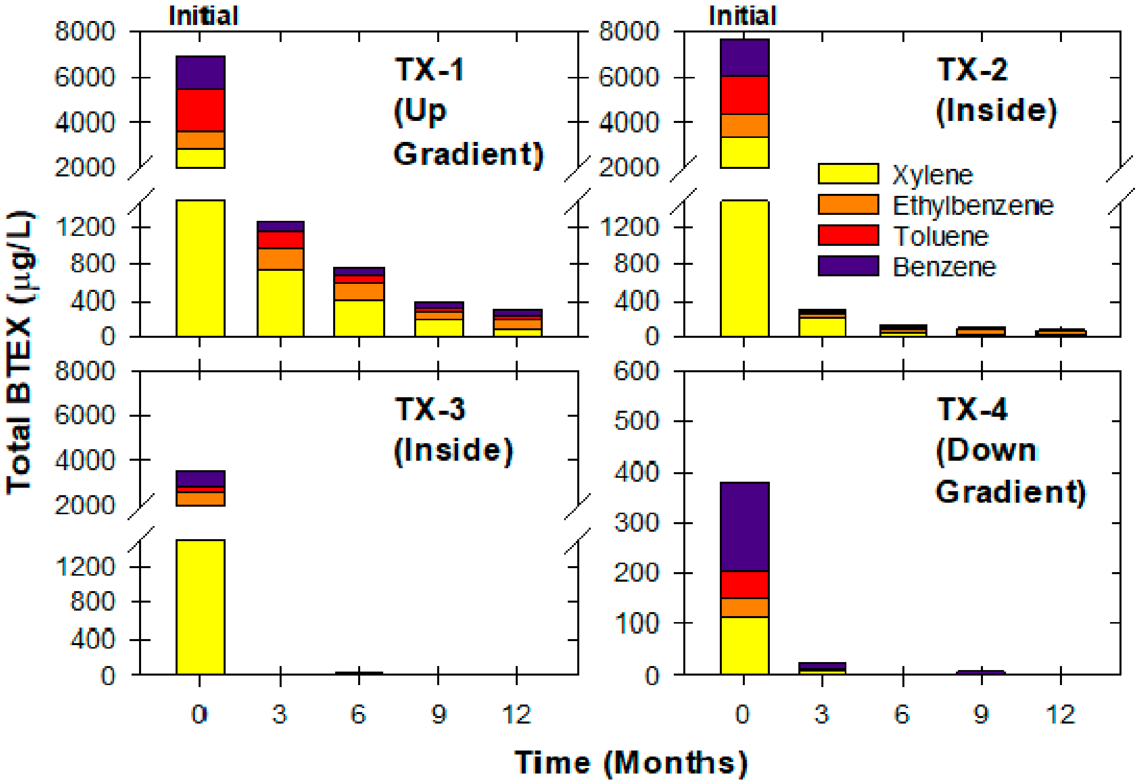

Figure 7. Changes in BTEX concentrations (µg L^{-1}) following treatment with reloadable direct-push aerated oxidant candles at the Textron site.

We also used this site to measure oxidant candle longevity in the field. Preweighed sodium persulfate candles were first installed (Figure 8). Specific candles placed in the drive points were marked and measured over time through sacrificial sampling. Results showed that under field conditions, the sodium persulfate candles would likely last 4–6 months. Once spent, we removed the sodium candles and replaced them with preweighed potassium persulfate candles. These results showed that the potassium persulfate candles would last approximately 8–9 months (Figure 8).

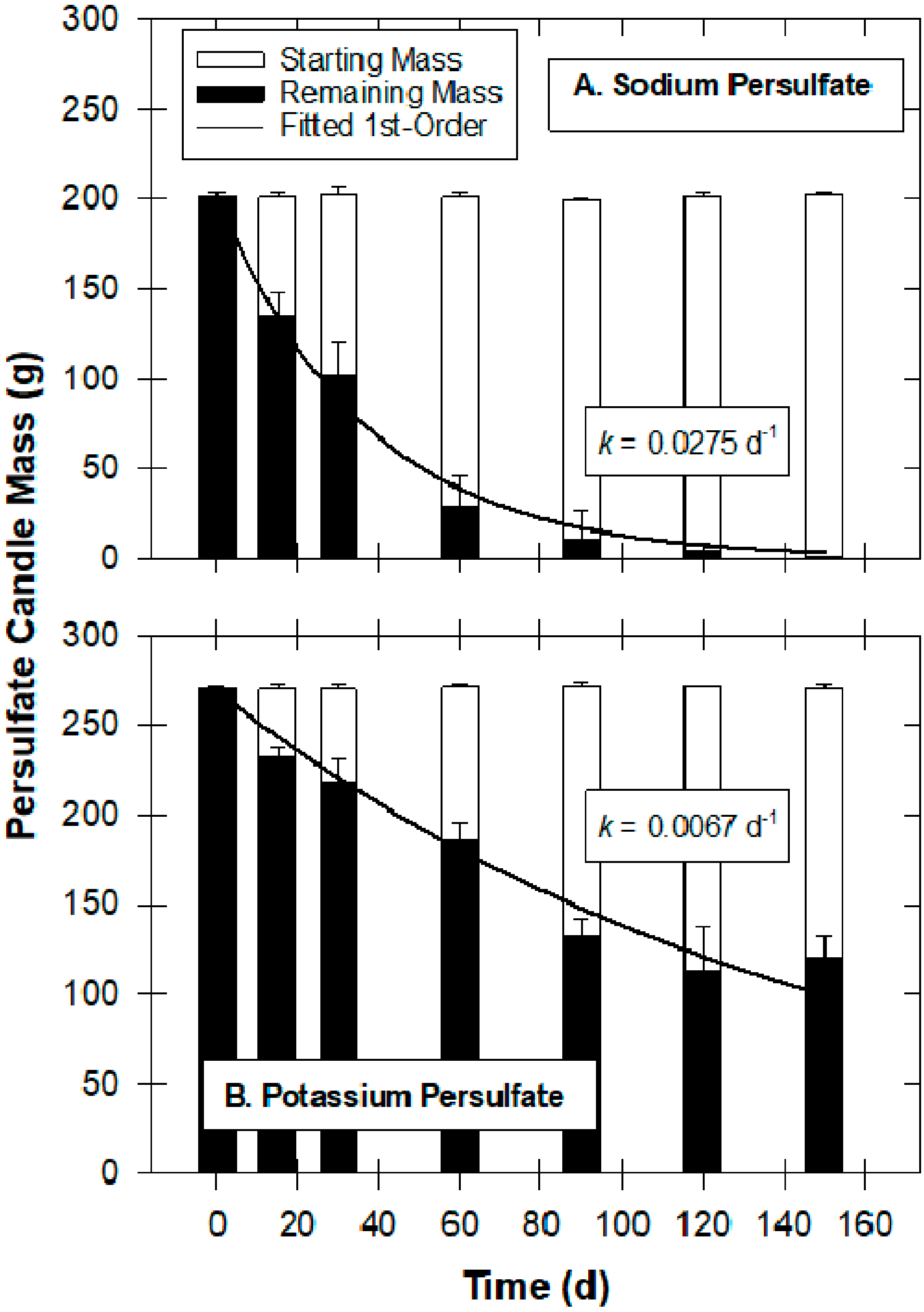

Figure 8. Temporal changes in persulfate mass in field-deployed oxidant candles at the Textron site; (**A**) sodium persulfate candles and (**B**) potassium persulfate candles. Open bars show candle weights at T = 0 d; solid bars show candle weights once removed from the aquifer and dried.

3.6. Hoover Site

Previous subsurface assessments of Hoover's property indicated detectable levels of metals, VOCs, SVOCs and hydrocarbons. The contaminant source areas include a former manufactured gas plant (MGP) site and two underground storage tanks, one containing gasoline and the other containing many different chemicals. Seepage from these source zones and the reducing conditions of the aquifer likely contributed to the suite of chlorinated degradation products present, including some reduced chlorinated degradation products (i.e., DCE and VC).

Initially, we performed a treatability test by incubating groundwater from the Hoover site with miniature permanganate candles (Table S2). Based on an initial treatability study, we installed permanganate candles into 14 reloadable drive points (Figure 9). One additional challenge this site posed was that groundwater was only 1 m deep above bedrock. The shallow depth reduced the strength of the airlift pump created in the drive points and thus likely provided less circulation. Moreover, a shallow water depth limits the number of candles that can be exposed, which results in less oxidant mass being released.

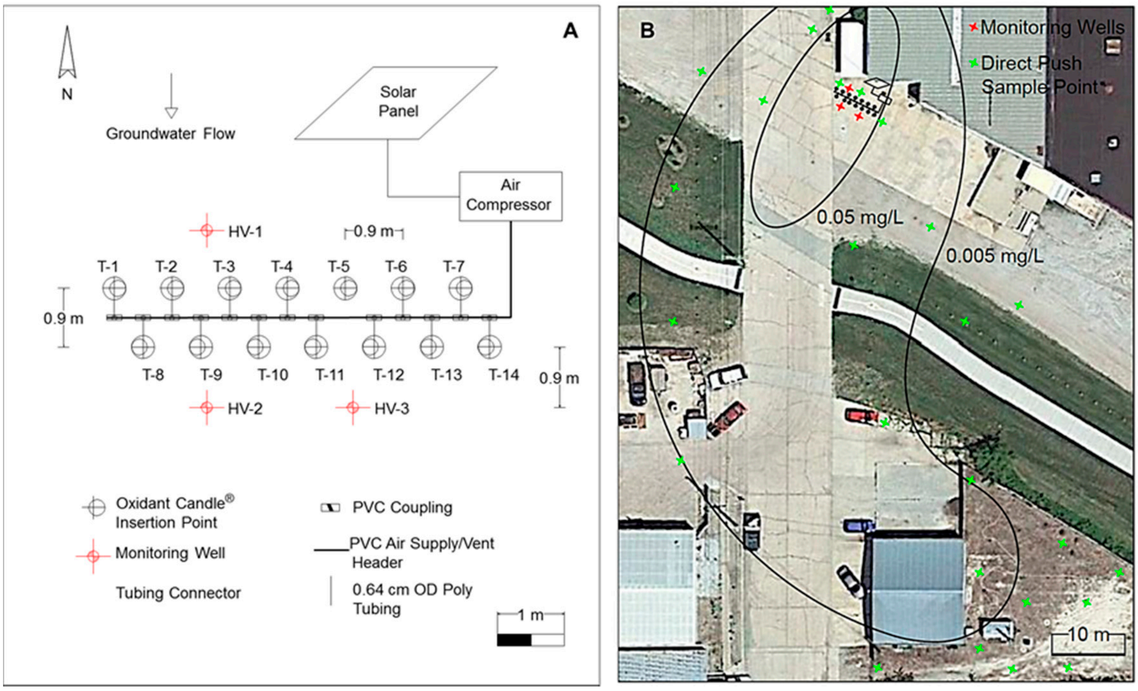

Figure 9. (**A**) Plot plan of the Hoover site showing the location of direct-push oxidant candles with aeration and (**B**) plan view of the Hoover site showing locations of TCE, BTEX and 1,4-dioxane plume and oxidant drive points (circled).

Monitoring the two downgradient wells after installation (HV-2 and HV-3, Figure 9) showed no consistent downward trends in contaminant concentrations (Figure 10). To verify that the permanganate candles were providing ample concentrations of permanganate to the treatment zone, we sampled inside the individual drive points (Figure 9) for permanganate and found concentrations in excess of 6000 mg/L. This proved the candle barrier was delivering adequate permanganate concentrations to the treatment zone.

We present two possible reasons for the initial lack of efficacy. The first is that this site was using a solar-powered compressor. Since aeration fluctuated diurnally, outlet ends of the aeration tubes became filled with permanganate when the aeration was off (nighttime hours) and some became coated with manganese dioxide (MnO_2), a product of permanganate oxidation. This likely clogged some of the aeration tubes and hindered oxidant spreading.

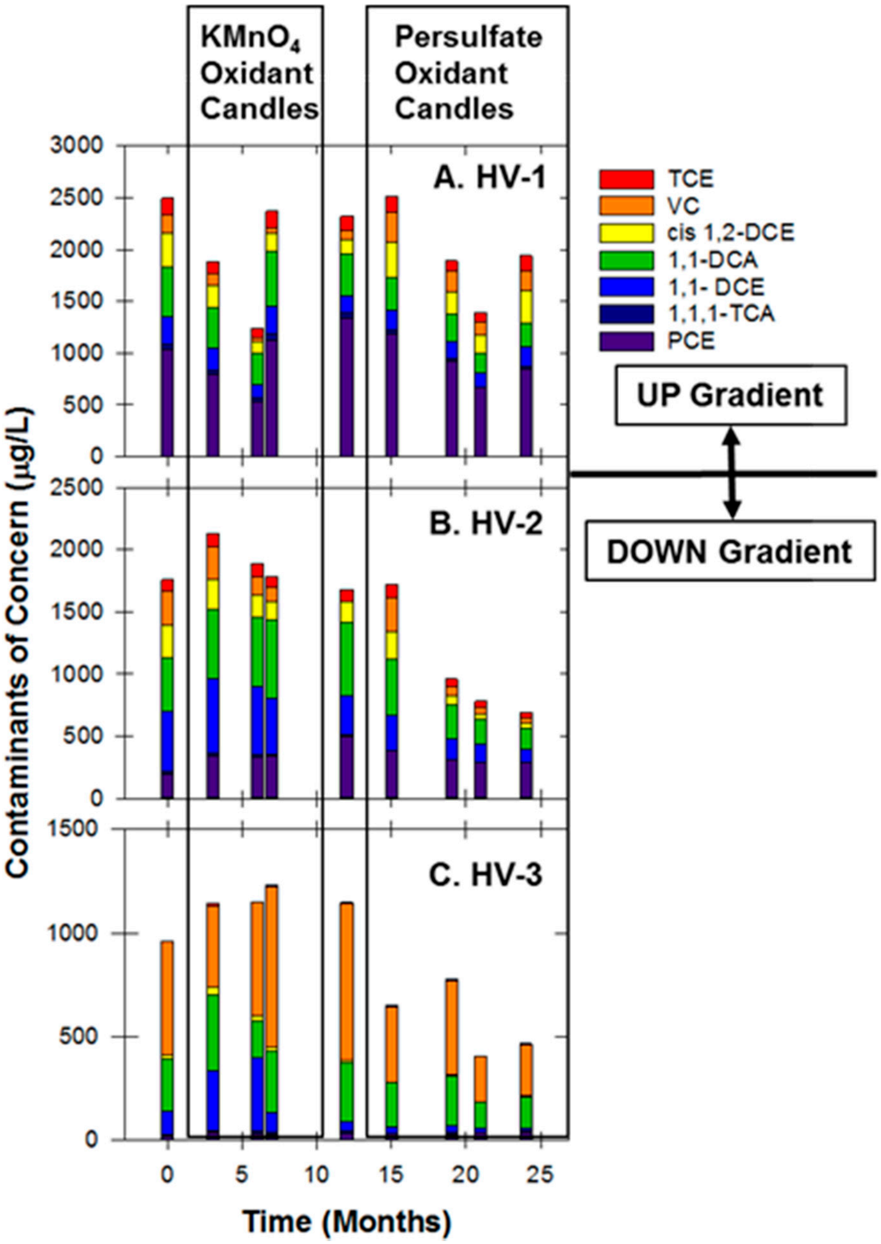

Figure 10. Temporal changes in contaminants of concern concentrations following installation of permanganate oxidant candles followed by persulfate oxidant candles at the Hoover site.

The second possible reason for the lack of efficacy by the permanganate candles was the observed production of acetone. Acetone and 2-butanone were not initially present in the Hoover groundwater but were observed in our treatability study (Table S2) and in the upgradient and downgradient wells after the permanganate candles were installed, with acetone concentrations ranging from 14 to 500 µg/L within the first 12 months. While acetone could have been an oxidation product of some of the other contaminants present, we performed additional testing and determined that both permanganate and persulfate could react with the wax and release acetone (Table S3). While the saturated paraffin structure would generally be inert to an oxidant attack, the presence of any unsaturated bonds near the end of a carbon chain could lead to formation of ketones (i.e., acetone and 2-butanone).

While acetone is known to biodegrade [46] and there currently is no federally enforceable maximum contaminant level (MCL) for acetone in drinking water, its production is problematic for other reasons. Treatment of acetone with permanganate can form oxalic acid [47] and oxalic acid treated with permanganate can form Mn(II) [48]. Manganese (II) is known to react with permanganate and cause autocatalysis [49]. These three reactions are summarized in Figure 11. Chokejaroenrat et al. [50] similarly found that small volumes of acetone in an aqueous matrix (1 mL/150 mL, *v*/*v*) caused permanganate reactions with the contaminant RDX to stall or plateau and correspondently showed that the loss of permanganate from solution (when acetone was present) was responsible for the stalled reaction. Chokejaroenrat [51] further showed that by keeping the pH acidic, the autocatalysis of permanganate induced by acetone could be avoided. Given that acetone was showing up in the downgradient wells without permanganate and that the contaminant concentrations were not decreasing, we believe that acetone was causing the permanganate to decrease and thus limiting permanganate effectiveness to degrade the contaminants.

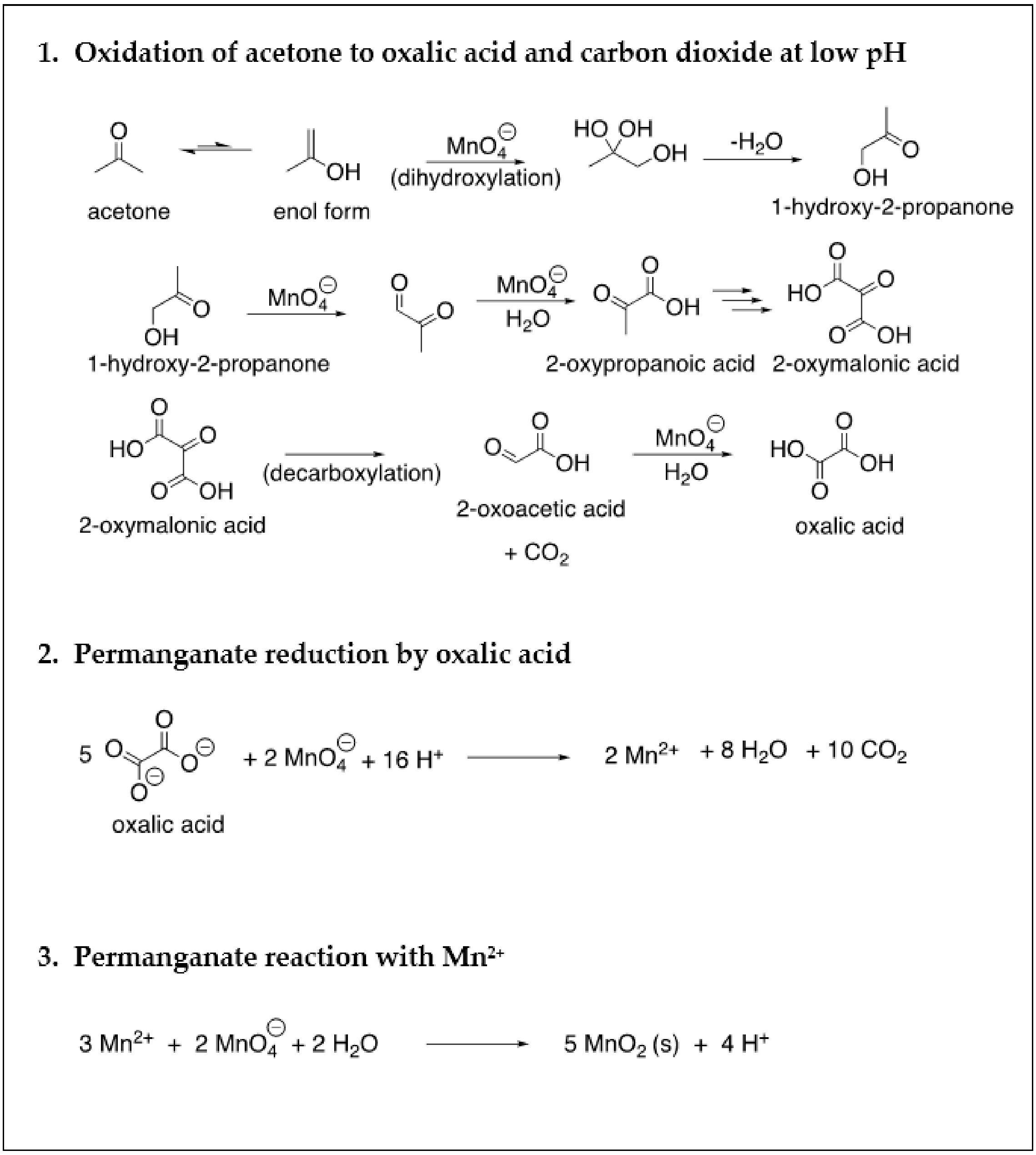

Figure 11. The reaction of acetone with permanganate leading to autocatalysis of permanganate.

To correct the situation, we performed a second treatability study, which included persulfate candles. The second treatability study showed that persulfate alone and persulfate + zerovalent iron combined [21] could both readily degrade the majority of contaminants present in the Hoover groundwater. The persulfate candles however, would provide the advantage of not being influenced by the production of acetone. For this reason, we removed the solid permanganate candles from the Hoover site and replaced them with persulfate and zerovalent iron candles. The flexibility of the reloadable design allowed for this change with minimal effort (i.e., the inside screen containing the oxidant was removed and replaced). In addition to changing the chemical oxidant, an electrically powered compressor replaced the solar-powered compressor.

Sampling results from the downgradient wells (HV-2 and HV-3, Figure 10) following installation of the persulfate candles showed that contaminant concentrations decreased by 52% (HV-3) and 61% (HV-2) from the initial concentrations with a clear downward trend observable in monitoring well HV-2 (Figure 10). As observed in the monitoring wells at the Textron site, persulfate was also observed in the upgradient well, HV-1 (<0.7–3.5 mg/L), and downgradient wells (HV-2, 0.7–2.1 mg/L and HV-3, 7–14 mg/L). This site is still being treated but sampling of monitoring wells has been infrequent since 2018. Still, the 2020 sampling showed continued marked decreases in contaminant concentrations, indicating the aerated, slow-release persulfate treatment is effective.

Finally, by isolating the effects of the oxidant candles on the contaminant 1,4-dioxane at the Hoover site, we similarly found the permanganate candles were not effective. However, decreases in 1,4-dioxane concentrations in the upgradient and downgradient wells were observed after the persulfate candles were installed (Figure S4). These field results corroborate Kambhu et al. [21] research, which showed that provided Fe^{2+} is not in excess, slow-release persulfate and zerovalent iron candles could effectively degrade 1,4-dioxane. Using unactivated persulfate, Evans et al. [52,53] also confirmed that slow release persulfate cylinders could degrade 1,4-dioxane under field conditions.

4. Conclusions

In O'Connor et al. [24] review of previously published papers on controlled-release remedial substances, they noted that in order for slow-release oxidants to become viable, it is imperative that new technologies be developed that increase the radius of influence under various geological settings. While the use of extraction wells to create gradients around oxidant cylinders has been proposed as one means of increasing oxidant coverage [13,14], Evans et al. [52,53] reported density-driven flow was still observed from persulfate-wax cylinders under an induced hydraulic gradient in the field.

We report herein, the design and installation of an aerated, modular oxidant delivery system that can be installed by direct-push equipment [28]. This technology avoids some of the burdens and inconveniences associated with liquid oxidant injections by eliminating the need for chemical mixing tanks, water source, pumps or pressurized injections. Likewise, the reloadable drive points allow for months to years of oxidant exposure to the treatment zone. Longer exposure times can facilitate oxidant penetration into lower permeable zones and reduce the potential for rebound [54]. By conducting various flow tank studies, we confirmed that a circulation pattern of oxidant and water is created around the aerated drive points and that this circulation pattern increases lateral dispersion, minimizes density-flow and thus eliminates the need to induce a gradient with extraction wells [26]. Field results confirm that the technology is effective in remediating contaminated groundwater either through the treatment of source zones or by creating a barrier.

5. Patents

Christenson M., Comfort S.D. Modular Oxidant Delivery System. United States Patent. Patent No. US 9,925,574 B2. 27 March 2018.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4441/12/12/3383/s1, Table S1. Laboratory results from treatability experiments using groundwater from SG-10 (Freeman site) and oxidant candles. Table S2. Treatability results showing changes in contaminant concentrations of Hoover Site groundwater following treatment with miniature permanganate oxidant candles for 14 d. Table S3. Acetone and 2-butanone analysis following wax-oxidant 14 d incubations. Figure S1. Examples of observed and simulated flow around aerated oxidant candles in narrow and wide flow boxes along with simulated oxidant flow. Figure S2. (A) Schematic of non-reloadable aerated, slow-release oxidant deployed by direct-push equipment for Freemont

Site; (C) Schematic of reloadable aerated, slow-release oxidant deployed by direct-push equipment for Textron and Hoover Sites. Figure S3. Schematic of wide flow box used to compare liquid oxidant versus aerated oxidant candles during transport. Figure S4. Temporal changes in 1,4-dioxane concentrations following installation of permanganate oxidant candles and persulfate oxidant candles at Hoover site.

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Conflicts of Interest: S.C. is a University of Nebraska-Lincoln faculty member who has financial interest in AirLift Environmental. In accordance with its Conflict of Interest Policy, the University of Nebraska-Lincoln's Conflict of Interest in Research Committee has determined that this must be disclosed.

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