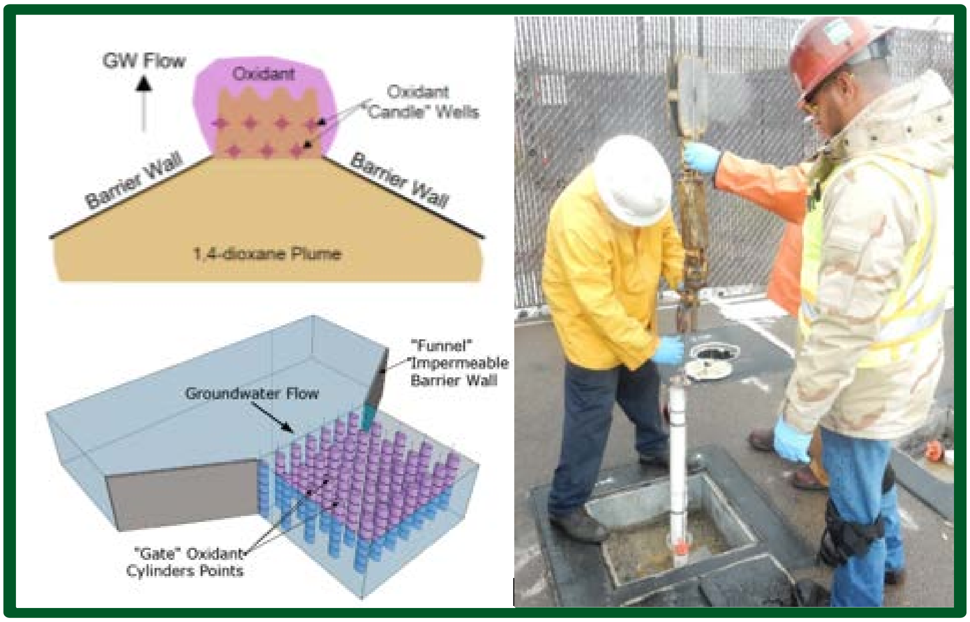
ESTCP
Cost and Performance Report

(ER-201324)



Sustained In situ Chemical Oxidation (ISCO) of 1,4-Dioxane and Chlorinated VOCs Using Slow-release Chemical Oxidant Cylinders

July 2018

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14. ABSTRACT

This study demonstrated the use of slow-release chemical oxidant cylinders to treat a plume containing dioxane and chlorinated volatile organic compounds. The objectives were to demonstrate/evaluate the technology effectiveness, sustainability/longevity, oxidant transport and destruction, implementability/secondary water quality impacts, and technology reproducibility. Unactivated persulfate embedded in a slow-release paraffin wax formulation was emplaced in two 4-inch wells which were housed inside 18-inch diameter boreholes. The majority of the performance objectives were met.

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In situ treatment, remediation, chemical oxidation, ISCO, persulfate, permanganate, groundwater treatment, 1,4-dioxane, permeable reactive barrier, funnel and gate

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ACRONYMS AND ABBREVIATIONS

AOP	advanced oxidation process
bgs	below ground surface
CCL3	Third Contaminant Candidate List
CCL4	Fourth Contaminant Candidate List
cis-1,2-DCE	cis-1,2-dichloroethene
cm/d	centimeters per day
cm/s	centimeters per second
CPT	cone penetrometer tool
CVOC	chlorinated volatile organic compound
1,1-DCA	1,1-dichloroethane
1,1-DCE	1,1-dichloroethene
1-D	one-dimensional
2-D	two-dimensional
DI	de-ionized
DoD	Department of Defense
DOT	Department of Transportation
ER	Environmental Restoration
ESTCP	Environmental Security Technology Certification Program
ft	feet
ft/d	feet per day
ft/ft	foot/foot
F&G	funnel and gate
gpm	gallons per minute
IATA	International Air Transport Association
IDW	investigation-derived waste
ID	identification number
ISCO	*in situ* chemical oxidation
M	molar
MCL	maximum contaminant level
MEC	munitions and explosives of concern
mg	milligrams
µg/L	micrograms per liter
mg d^{-1} cm^{-2}	milligrams per day per square centimeter
mg/L	milligrams per liter
mg L^{-1} d^{-1}	milligrams per liter per day
mL/min	milliliters per minute

$M^{-1}\ s^{-1}$	per molar per second
MTBE	methyl tertiary-butyl ether
mV	millivolts
NAS NI	Naval Air Station North Island
NOD	natural oxidant demand
NOM	natural organic matter
O&M	operations and maintenance
ORP	oxidation-reduction potential
OU11	Operable Unit 11
P&T	pump and treat
PRB	permeable reactive barrier
PVC	polyvinyl chloride
QA/QC	quality assurance/quality control
RPD	relative percent difference
SDWA	Safe Drinking Water Act
SR	slow release
SVOC	semivolatile organic compound
1,1,1-TCA	1,1,1-trichloroethane
TCE	trichloroethene
US	United States
USEPA	US Environmental Protection Agency
VC	vinyl chloride
W	watts

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EXECUTIVE SUMMARY

OBJECTIVES OF THE DEMONSTRATION

The Department of Defense (DoD) has hundreds of sites contaminated with chlorinated solvents, which represents a large remediation liability. Dioxane is increasingly recognized as a challenging contaminant at sites where 1,1,1-trichlorethane (1,1,1-TCA) was released to soil and groundwater. Dioxane can form persistent plumes that require ongoing treatment. While these large plumes may contain relatively low concentrations of dioxane (e.g., less than 100 µg/L), sites with concentrations greater than the health-based drinking water standards continue to involve active remediation. Although no federal drinking water standards have been established to date, the US Environmental Protection Agency has established an "action level" of 3 µg/L for dioxane. State drinking water guidance limits have been put in place by various states which include values as low as 0.25 µg/L in New Hampshire.

Dioxane is not easily treated. *Ex situ* advanced oxidation processes (AOPs) are the most developed approach for dioxane treatment. Because of high operation and maintenance (O&M) costs associated with AOPs, successful deployment of *in situ* approaches would grant remedial project managers a far more flexible and cost-effective remedial approach. Traditional *in situ* chemical oxidation (ISCO) is not a solution to persistent plumes because the reactants are relatively short-lived.

The overall objective of this project was to demonstrate the use of slow-release chemical oxidants to destroy dioxane and chlorinated volatile organic compounds (CVOCs) in groundwater *in situ*. Specific quantitative performance objectives concerned effectiveness; sustainability/longevity; and oxidant transport which were met.

TECHNOLOGY DESCRIPTION

Slow-release chemical oxidant cylinders match the contaminant destruction rate to the contaminant transport rate with a sustainable, simple, and low O&M approach. Chemical oxidant (i.e., sodium persulfate or potassium permanganate or mixtures thereof) embedded in a slow-release wax formulation "cylinder" can be emplaced in groundwater wells, using a funnel and gate (F&G) configuration, permeable reactive barrier (PRB), or directly installed into boreholes. The oxidant/paraffin mixtures have been designed to allow oxidant to gradually diffuse into the groundwater and slowly oxidize dioxane and CVOCs. They are slowly consumed and persist sufficiently to result in dioxane destruction as a dilute plume migrates through the treatment zone created by these cylinders.

The demonstration was conducted at Naval Air Station North Island Operable Unit 11. The system consisted of two boreholes containing sodium persulfate cylinders without any activators. A pump was used to extract groundwater and to promote a controlled hydraulic aquifer because of the low ambient gradient at the site. The extracted water was then injected into a downgradient reinjection well. Samples upgradient and downgradient of the oxidant cylinders were collected and analyzed to evaluate technology performance. A treatability study was also conducted prior to the field demonstration.

DEMONSTRATION RESULTS

Maximum contaminant destructions (99.3% and 99.0% for dioxane and total CVOCs, respectively) exceeded the performance objective of 90%. The upgradient dioxane and total CVOC concentrations were 20,000 µg/L each. The downgradient dioxane concentration was 140 µg/L. 1,1-DCE was reduced from 7,600 to < 33 µg/L; 1,1-DCA was reduced from 2,200 to 110 µg/L; cis-1,2-DCE was reduced from 7,900 to 75 µg/L; and TCE was reduced from 2,700 to 15 µg/L. Sodium persulfate concentrations decreased in an exponential pattern over time with 31% and 9% predicted to be remaining after 6 and 12 months, respectively. Dioxane and CVOC removals were ≥ 99% after 119 days corroborating high contaminant destruction for extended time periods even when oxidant concentrations may be variable or declining. Thus, the criterion of contaminant destruction effectiveness being maintained for greater than 4 weeks was exceeded.

Capital and operating costs were estimated for a hypothetical site approximately 400 ft in length and 100 ft in width, with a treatment thickness of 20 ft ranging between 20 and 40 ft below ground surface (bgs), a 1,4-dioxane concentration in groundwater of approximately 10,000 µg/L, and a groundwater velocity of approximately 5 feet per day (ft/day). Various remediation scenarios were evaluated. A PRB with persulfate cylinders had a total project cost of $2.9 million, which is less than an F&G $3.7 million. It was also less than AOP at $4.3 million and a PRB with periodic manual injection of the same mass of aqueous sodium persulfate at $6.2 million. The results indicate that persulfate cylinders in a passive PRB configuration may potentially result in significant cost saving over traditional approaches.

IMPLEMENTATION ISSUES

Technology selection should keep in mind the intended use of slow-release oxidant cylinders – passive and long-term treatment of contaminated groundwater. Applicable contaminants include those that are capable of being oxidized by chemical oxidants that are released by the oxidant cylinders. At this site dioxane was demonstrated to be oxidized by unactivated persulfate. It may or may not be oxidized at sufficient rates at other sites and engineering, treatability, or pilot studies should be conducted. Other contaminants including CVOCs and petroleum hydrocarbons, such as benzene and methyl tertiary butyl ether (MTBE), are also potentially applicable.

Other technologies that should be considered are pump and treat and *in situ* bioremediation. The technology selection process conducted as part of a feasibility study will consider effectiveness, implementability and cost. The most common applications include passive PRBs or F&G systems as alternates to pump and treat. The ultimate goal of utilizing the slow-release oxidant cylinders should be to treat the aquifer rather than water in monitoring wells. Therefore, consideration should be made prior to deploying the oxidant cylinders in monitoring wells.

Design of a remediation system using slow-release oxidant cylinders must consider cylinder spacing; changeout frequency; groundwater velocity; contaminant plume width, depth, and length; reaction kinetics of the released oxidant with target contaminants as well as natural oxidant demand in the aquifer; the potential for density driven flow; and the optimal configuration (e.g., PRB vs. F&G). The oxidant cylinders are commercially available off the shelf from Carus Corporation. Equipment for suspending cylinders in wells or reactive gates are not standardized and will require engineering design and possible custom fabrication.

1.0 INTRODUCTION

Environmental Security Technology Certification Program (ESTCP) Project Number Environmental Restoration (ER)-201324 involves demonstration and validation of sustained *in situ* chemical oxidation (ISCO) of 1,4-dioxane (dioxane) using slow-release oxidant cylinders. This Cost and Performance Report summarizes the demonstration. Detailed information on the demonstration is available in the ESTCP Final Report (Evans et al. 2018).

1.1 BACKGROUND

The Department of Defense (DoD) has hundreds of sites contaminated with chlorinated solvents, which represents a large remediation liability (Parsons 2004). Dioxane can form persistent plumes that require ongoing treatment. While these large plumes may contain relatively low concentrations of dioxane (e.g., less than 100 micrograms per liter (µg/L)), sites with concentrations greater than the health-based drinking water standards continue to involve active remediation. These plumes present significant challenges to the DoD as they can be costly to contain and clean up (Steffan 2007).

Dioxane is increasingly recognized as a challenging contaminant at sites where 1,1,1-trichlorethane (1,1,1-TCA) was released to soil and groundwater. Once released into groundwater, dioxane can migrate more rapidly than chlorinated volatile organic compounds (CVOCs) due to its miscibility with water, low affinity for sorption to soil organic matter, and resistance to biodegradation and abiotic breakdown (Mohr et al. 2010). Dioxane is not easily treated. *Ex situ* AOPs are the most developed approach for dioxane treatment (USEPA 2006). Because of high operation and maintenance (O&M) costs associated with AOPs, successful deployment of *in situ* approaches would grant remedial project managers a far more flexible and cost effective remedial approach. Traditional *in situ* chemical oxidation is not a solution to persistent plumes because the reactants are relatively short-lived (Siegrist et al. 2011).

Slow-release chemical oxidant cylinders match the contaminant destruction rate to the contaminant transport rate with a sustainable, simple, and low O&M approach. Chemical oxidant (i.e., sodium persulfate or potassium permanganate or mixtures thereof) embedded in a slow-release wax formulation “cylinder” can be emplaced in groundwater wells, using a funnel and gate (F&G) configuration, permeable reactive barrier (PRB), or directly installed into boreholes. The oxidant/paraffin mixtures have been designed to allow oxidant to gradually diffuse into the groundwater and slowly oxidize dioxane and CVOCs. They are slowly consumed and persist sufficiently to result in dioxane destruction as a dilute plume migrates through the treatment zone created by these cylinders.

Slow-release oxidant cylinders used in this demonstration were comprised of unactivated sodium persulfate (i.e., no activator was added either via incorporation in the slow-release oxidant cylinder formation or by direct injection into groundwater) embedded in paraffin wax. These cylinders were placed in groundwater wells where sodium persulfate was released passively into groundwater and oxidized dioxane and CVOC co-contaminants. Groundwater samples were collected up- and down-gradient of the oxidant cylinders to assess destruction of dioxane and CVOCs.

1.2 OBJECTIVE OF THE DEMONSTRATION

The overall objective of this project was to demonstrate the use of slow-release chemical oxidants to destroy dioxane and CVOCs in groundwater *in situ*. Specific performance objectives concerned technology effectiveness, sustainability/longevity, oxidant transport and destruction, technology implementability/secondary impacts, and technology reproducibility.

Technology Effectiveness

This objective focused on demonstrating the ability to destroy dioxane and CVOCs in the reactive zone. The success criterion was established at a minimum of 90% reduction in concentration. The maximum destructions observed were 99.3% and 99.0% for dioxane and total CVOCs, respectively. Thus, the 90% minimum destruction criteria were exceeded.

Sustainability/Longevity

This objective focused on demonstrating the ability to consistently distribute the oxidant in the reactive zone and to meet the above Technology Effectiveness objective for a minimum time of four weeks. Sodium persulfate concentrations decreased in an exponential pattern over time with 42% remaining at the final sampling event (134 days) and 31% and 9% predicted to be remaining after 6 and 12 months, respectively. Dioxane and CVOC removal was ≥ 99% after 119 days corroborating high contaminant destruction for extended time periods even when oxidant concentrations may be variable or declining. Thus, the criterion of contaminant destruction effectiveness being maintained for greater than 4 weeks was exceeded.

Oxidant Transport and Destruction

This objective focused on demonstrating that oxidants will not be transported significantly past the reactive zone. Sodium persulfate decreased from a maximum concentration of 2100 milligrams per liter (mg/L) in a boring located 14 feet (ft) downgradient of the cylinders to 21 mg/L in a boring located 26 ft downgradient. Additional data trends suggest that persulfate concentrations would be reduced to non-detectable levels further downgradient.

Technology Implementability/Secondary Impacts

This objective focused on demonstrating that secondary groundwater quality impacts are either acceptable or transient. Potential secondary impacts include elevated dissolved metals including hexavalent chromium and generation of bromate as a product of bromide oxidation. A treatability study conducted prior to the field demonstration indicated the potential for hexavalent chromium generation in the presence of sodium persulfate. Success criteria during the field demonstration were initially based on filtered metals and bromate concentrations, but these analyses were not conducted because of project constraints. Rather, the potential impacts were evaluated considering secondary parameters including pH and oxidation-reduction potential (ORP) trends downgradient of the oxidant cylinders. pH decreased and ORP increased in response to the presence of sodium persulfate. Downgradient of the maximum sodium persulfate concentration, pH increased and ORP decreased to background values. Hexavalent chromium and bromate can be chemically or biologically reduced. Thus, elevated dissolved metal concentrations could be expected to decline to background levels as background pH and ORP values were re-established.

Technology Reproducibility

Two replicate cylinder installations were used to characterize reproducibility in this qualitative performance objective. Two methods of comparison were used including: 1) the relative percent difference of oxidant concentrations within the two boreholes, and 2) comparison of the sodium persulfate flux from the cylinders in the field demonstration and in the treatability study. The relative percent difference of the sodium persulfate concentrations in the cylinder borehole monitoring wells was 66±50% and represented three sampling events where the concentration in one oxidant cylinder monitoring well was consistently greater than that in the other. The estimated sodium persulfate flux from the cylinders ranged from 4 to 17 milligrams per day per square centimeter (mg d^{-1} cm^{-2}) from which is reasonable when compared to the maximum flux of 22 mg d^{-1} cm^{-2} measured during the treatability test.

1.3 REGULATORY DRIVERS

In September 2013, United States Environmental Protection Agency (USEPA) published the *Toxicological Review of 1,4-Dioxane* (USEPA 2013). In this review, USEPA revised the 1×10^{-6} cancer risk assessment level for dioxane to 0.35 µg/L from 3.0 µg/L. Although there is no federal maximum contaminant level (MCL) in drinking water established for 1,4-dioxane to date, there have been federal screening levels determined based on a 1 in 10^{-6} lifetime excess cancer risk (USEPA 2017). In 2017, USEPA calculated a screening level for tap water of 0.46 µg/L. Although no federal drinking water standards have been established to date, USEPA has established an “action level” of 3 µg/L for dioxane and it was listed on the third Contaminant Candidate List (CCL3) (Federal Register 2014). In November 2016, the EPA published the Fourth Contaminant Candidate List (CCL4) including 1,4-dioxane (Federal Register 2016). Contaminants on the CCL4 are currently not held to any national primary drinking water regulations, but may require future regulation under the Safe Drinking Water Act (SDWA) (USEPA 2016). State drinking water guidance limits have been put in place by various states which include values as low as 0.25 µg/L in New Hampshire (USEPA 2014).

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2.0 TECHNOLOGY

This section provides an overview of the technology that was demonstrated.

2.1 TECHNOLOGY DESCRIPTION

The technology concept involves use of slow-release chemical oxidant cylinders shown in **Figure 2.1** to treat persistent plumes of dioxane and CVOCs. Chemical oxidant (i.e., sodium persulfate or potassium permanganate or mixtures thereof) embedded in a slow-release wax formulation "cylinder" can be emplaced in groundwater wells or directly installed in boreholes. The cylinders can be used in grids, PRB, or F&G configurations (**Figure 2.2).** The oxidant/paraffin mixtures have been designed to allow oxidant to gradually diffuse into the groundwater and slowly oxidize dioxane and CVOCs. They are slowly consumed and persist sufficiently to result in dioxane destruction as a dilute plume migrates through the treatment zone created by these cylinders. Dioxane and CVOCs can be oxidized by permanganate or unactivated persulfate as described below. Because of the flexibility in distribution methods, this technology can be used in a permeable reactive barrier or in a grid configuration, and can be used in multiple hydrogeologic environments. For large and dilute dioxane plumes or sites with access restrictions, a PRB or F&G configuration may be the best remediation approach. In general, applications of the technology include long-term, passive treatment of groundwater contaminants that are capable of being oxidized by permanganate and/or persulfate. Thus, in addition to dioxane and CVOCs, the technology is potentially applicable to treatment of petroleum hydrocarbons, fuel oxygenates such as methyl tertiary butyl ether (MTBE), phenols, semivolatile organic compounds (SVOC), and potentially munitions and explosives of concern (MEC).

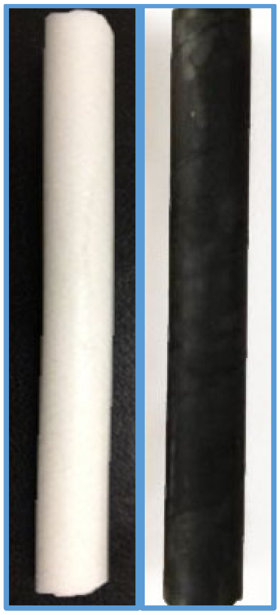

Figure 2.1. Persulfate (left) and Permanganate (right) Slow-release Oxidant Cylinders.

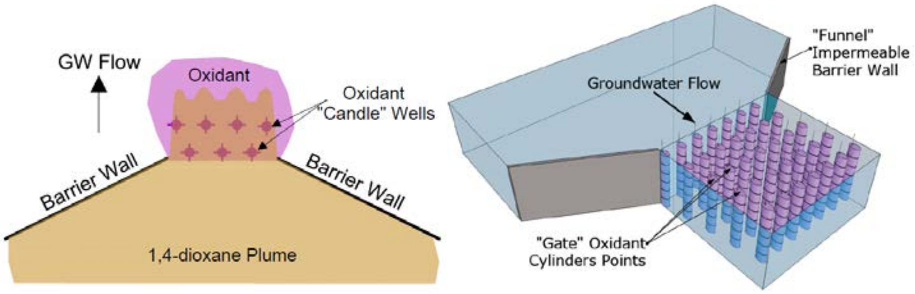

Figure 2.2. Funnel and Gate Concept.

A detailed product development timeline for the Carus slow-release (SR) technology product lines is provided below.

- April 2009 – Development work begins on the RemOx SR technology;
- October 2011 – Pilot-scale manufacturing begins;
- October 2011 – First RemOx SR field implementation;
- August 2012 – Persulfate SR and RemOx SR+ Technology Development work begins (1-D columns and 2-D tanks);
- August 2014 – ESTCP Persulfate SR field implementation; and
- September 2015 – First RemOx SR+ Technology Field implementation.

2.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

<u>Advantages</u> of sustained ISCO of dioxane and CVOCs using slow-release chemical oxidant cylinders include:

- This technology provides an *in situ* application to treat persistent plumes of dioxane.
- This technology is also applicable to a multitude of co-contaminants such as CVOCs and benzene.
- Sustained ISCO is implementable in a variety of configurations with different oxidants.
- This flexible and adjustable technology can be configured to match the rate of oxidant release to the mass flux of dioxane and solvents and control cylinder replacement frequency.
- It can be used in heterogeneous aquifers.
- The technology mitigates rebound problems with ISCO.
- *In situ* application is a sustainable application, which significantly reduces energy usage and overall costs.
- It offers an excellent health and safety profile.

- Can be deployed at active sites with minimal infrastructure required for deployment and monitoring.
- The technology does not depend on biodegradation which may require cometabolism to be successful (Hatzinger et al. 2017).
- It does not require injection of gases for cometabolic biodegradation.

Limitations of sustained ISCO of dioxane and CVOCs using slow-release chemical oxidant cylinders currently include:

- Technology applicability for a given site will depend on several factors including but not limited to: 1) reaction rate(s) of the released oxidant with the contaminant(s) of concern, 2) groundwater velocity, 3) available flow path length for the contaminant(s) to be destroyed, and 4) the remediation goal that must be achieved for the contaminant(s) by the end of the available flow path length. The technology is only applicable to sites where these four factors are such that adequate contaminant removal is achieved within an acceptable distance. For example, if the reaction rate of a released oxidant with a given contaminant is too slow to result in attainment of the remediation goal in the required treatment flow path, then the technology may not be applicable. Installation of more cylinders can potentially overcome this limitation but economics must also be considered. Engineering calculations along with treatability and/or pilot tests can be conducted to make this determination. Published rate constants (Waldemer and Tratnyek 2006, Waldemer et al. 2007) can also be useful in this regard.
- Secondary environmental effects can occur including mobilization of metals, low pH resulting from persulfate decomposition (Crimi and Siegrist 2003, Tsitonaki et al. 2010), and oxidation of chromium and bromide to hexavalent chromium or bromate. These risks are minimized in the cylinder configuration because of the lower concentration of oxidant involved in the reactions. Note that potential adverse effects associated with metal mobilization as a result of oxidation and/or pH depression are generally transient and limited to the target treatment area only.
- Potential for low transverse dispersion of oxidants may require close spacing between cylinders perpendicular to migration direction. The use of a F&G-style system could be used to overcome this limitation.
- Generation of oxidation byproduct such as manganese dioxide (in the case of permanganate) or iron hydroxides may lead to decrease in oxidant release rate or, possibly, preferential flow due to plugging within the reactive zones.
- Density-driven flow and non-uniform oxidant transport may be exacerbated at sites with low horizontal groundwater gradient. However, this can be mitigated by proper site investigation, modeling, and engineered measures to induce an artificial gradient or facilitate vertical mixing.
- Depending on site-specific mineralogy, persulfate may be activated to varying extents resulting in variable natural organic matter (NOM) oxidation thereby impacting the effectiveness towards contaminants of concern.

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3.0 PERFORMANCE OBJECTIVES

Performance objectives and results for the demonstration are presented in **Table 3.1**. See Section 6 for a discussion of the basis for the conclusions presented.

Table 3.1. Performance Objectives.

Performance Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives			
Technology Effectiveness	Dioxane and chlorinated ethene concentrations	90% reduction in 1,4-dioxane concentration or concentration reduced to < 3 µg/L	**Exceeded.** 99.3% reduction.
		90% reduction of chlorinated ethene co-contaminants	**Exceeded.** 99.0% reduction in sum of 1,2-dichlorethene (DCE), 1,1-dichloroethane (DCA), cis-1,2-DCE, and trichloroethene (TCE).
Sustainability / Longevity	Oxidant and contaminant concentrations along flow path	Rate of oxidant concentration change at any given location ≥ 0 miligrams per liter per day (mg L^{-1} d^{-1}) over 1 year	**Not met.** Observed exponentially decreasing persulfate concentrations over time in cylinder wells with 9% predicted to be remaining after one year.
		90% contaminant removal is sustained for at least 4 weeks	**Exceeded.** Dioxane and CVOCs destruction ≥99% observed in deep groundwater 119 days after cylinder deployment.
Oxidant Transport and Destruction	Oxidant concentrations along flow path	Oxidant consumed to below detection at final downgradient monitoring point or trends support its destruction along the flow path	**Met.** 21 mg/L in deep sample from boring B21 26 ft downgradient compared to 2,100 mg/L in deep sample from boring B14 14 ft downgradient. Trends also support further attenuation. See text for explanation.
Technology Implementability / Secondary Impacts	pH, ORP, persulfate, filtered metals (As, Ba, Be, Cd, Cr, Cu, Hg, Pb, Se, Tl, and U), and bromate.	Filtered metals and bromate below background (upgradient well concentration) in the final downgradient monitoring point or demonstrated decrease in concentration along flow path. pH, ORP, and persulfate concentrations will be used to evaluate attenuation trends.	**Met** for pH, ORP, and persulfate. Not analyzed for bromate and metals. See text for discussion as well as treatability study results.
Qualitative Performance Objective			
Technology Reproducibility	Oxidant concentrations in cylinder boreholes and seepage velocity estimated using a chloride tracer test	Oxidant concentrations over time will be compared and relative percent difference will be calculated to characterize reproducibility. Persulfate flux will be calculated and compared to treatability test results.	The relative percent deviation of persulfate concentrations in the two cylinder borehole monitoring wells was 66%±50%. Estimated sodium persulfate flux from the cylinders ranged from 4 to 17 mg d^{-1} cm^{-2} which compares well to the maximum treatability flux of 22 mg d^{-1} cm^{-2}.

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4.0 SITE DESCRIPTION

4.1 SITE LOCATION

Operable Unit 11 (OU11) of Naval Air Station North Island (NAS NI) (**Figure 4.1**) was selected for this demonstration.

Figure 4.1. NAS North Island Location Map.

4.2 SITE GEOLOGY/HYDROGEOLOGY

Groundwater flow direction in the proposed demonstration area is to the northwest with a seepage velocity about flow rate about 0.1 foot per day (ft/d) and a hydraulic gradient of approximately 0.00037 foot per foot (ft/ft) (Accord Mactec 2013). Lithology at OU11 includes a thick sequence of fine to very fine sand and silty sand to a depth of approximately 40 ft bgs. Below these layers are several fine-grained layers of silt and clay. Because the gradient is generally flat and groundwater flow directions can vary, an induced gradient was created by pumping for the purposes of this demonstration.

4.3 CONTAMINANT DISTRIBUTION

Based on OU11 groundwater quality data collected in 2012 (Accord Mactec 2013), dioxane concentrations are as high as 6,500 µg/L upgradient of the demonstration area (OU11-SMW05A). Similarly, the dioxane concentration was 6,000 µg/L in OU11-SMW07A on the downgradient portion of the demonstration area. TCE, cis-1,2-DCE, 1,1-DCE, 1,1-DCA, vinyl chloride, and hexavalent chromium are co-contaminants at the site. 2012 TCE concentrations within the proposed demonstration area were 9,200 µg/L in OU11-SMW05A and 3,500 µg/L in OU11-SMW07A. Other VOC concentrations (cis-1,2-DCE, 1,1-DCE, 1,1-DCA, and vinyl chloride were generally similar to TCE (350-6,400 µg/L) except vinyl chloride, which was detected at 39 µg/L in OU11-SMW07A.

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5.0 TEST DESIGN

This section presents the design and results of the demonstration tasks.

5.1 CONCEPTUAL EXPERIMENTAL DESIGN

The detailed design layout of the technology demonstration is illustrated in **Figure 5.1**. Upgradient cylinder wells containing the oxidant cylinders were installed to simulate a small-scale F&G design. Due to the flat gradient observed at the site, a recirculation system consisting of a downgradient extraction well and a further-downgradient reinjection well was constructed to facilitate better hydraulic control. A series of upgradient and downgradient monitoring wells were used to aid performance monitoring, evaluation, and optimization. A cross-sectional view of the demonstration well network is provided in **Figure 5.2**. As shown in this cross section, the demonstration was performed in the 15-ft saturated thickness above a semi-confining unit located approximately 40 ft bgs. This treatment thickness is within the depth interval where dioxane and other contaminants were observed.

5.2 BASELINE CHARACTERIZATION

Snap Samplers® were deployed at 29-31, 33-35, and 37-39 ft bgs to determine the relative distribution of contaminants over different stratigraphic units. Concentrations are reported in **Table 5.1**, indicating that contaminant concentrations were generally lowest in the shallowest groundwater horizon. Dioxane in particular had the greatest concentration in the deepest groundwater horizon.

Table 5.1. Groundwater Concentrations of Select Analytes.

Analyte	Concentration (µg/L)		
	29-31 ft bgs	33-35 ft bgs	37-39 ft bgs
1,1-Dichloroethane (1,1-DCA)	35	85	80
1,1-Dichloroethene (1,1-DCE)	560 D	1,600 D	1,000 D
cis-1,2-Dichloroethene (cis-1,2 DCE)	18	38	34
Trichloroethene (TCE)	570 D	1,600 D	850 D
1,4-Dioxane	53 J	90	250

Notes: µg/L – microgram per liter D – Diluted sample J – Estimated value

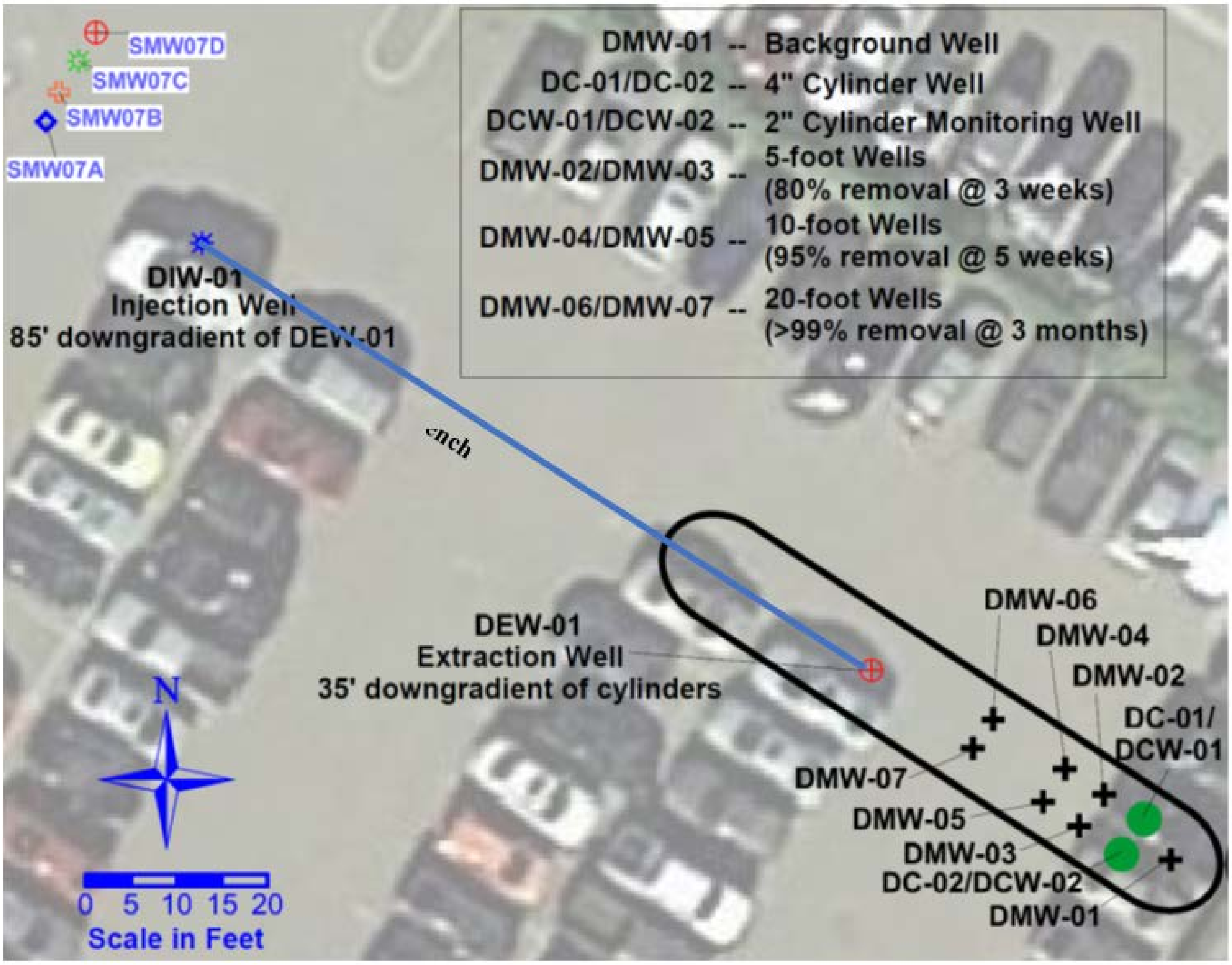


Figure 5.1. Detailed Demonstration Layout w/ Tool-estimated Removal Distances and Times.

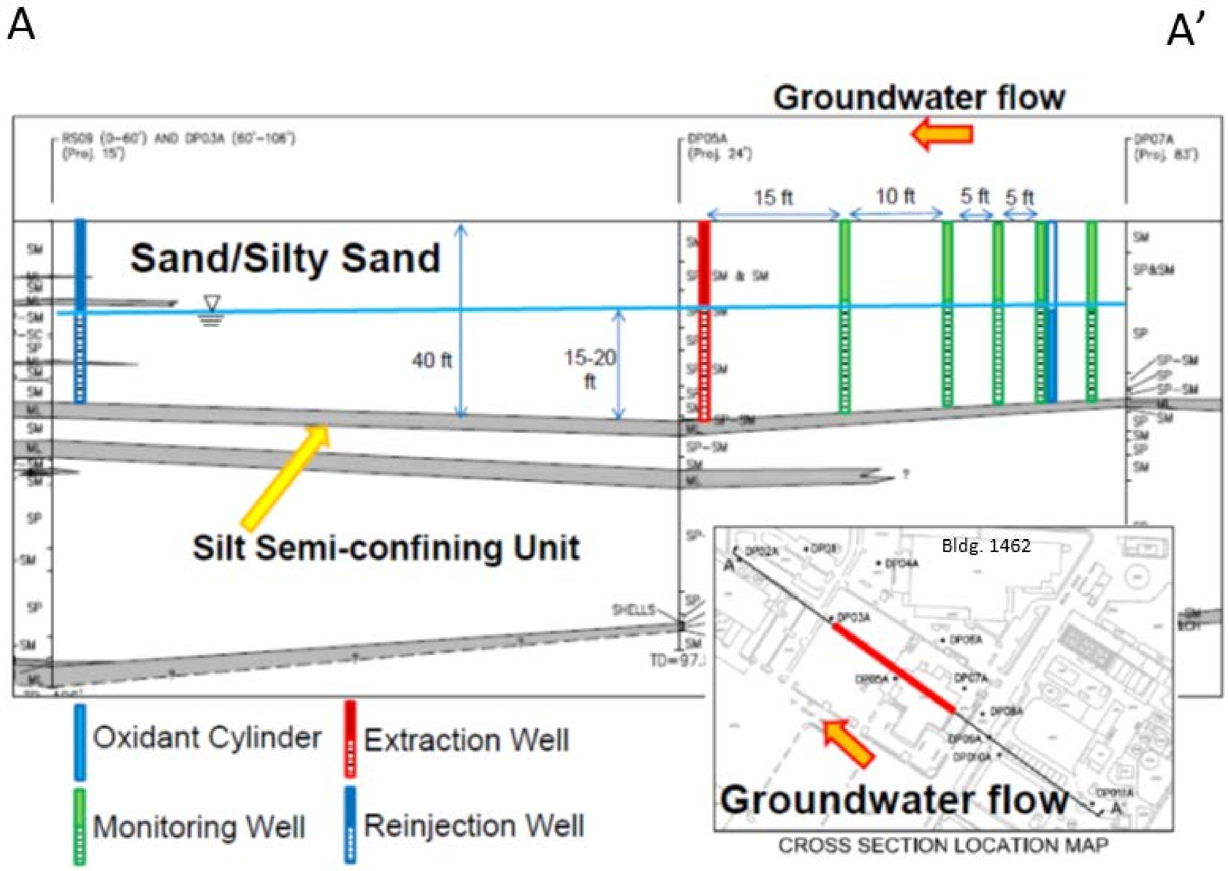


Figure 5.2. Cross-sectional View of the Demonstration Well Network.

5.3 TREATABILITY OR LABORATORY STUDY RESULTS

Treatability studies were conducted using soil and groundwater collected from the site. The purpose of these studies was to determine whether activated or unactivated persulfate were capable of destroying dioxane and the CVOCs. In addition, data were collected to facilitate design of the field demonstration.

Figure 5.3 shows the removals of individual contaminants in the permanganate column study. Dioxane was not appreciably removed by permanganate even though removal was observed in the batch kinetics study. The chlorinated ethenes TCE, cis-1,2-DCE and 1,1-DCE were removed to non-detectable concentrations. 1,1-DCA was not removed, which is consistent with the batch kinetic study results.

Figure 5.4 shows the removals of individual contaminants in the persulfate column study. Initially, dioxane was not appreciably removed. The flow rate was decreased from 0.15 to 0.05 milliliters per minute (mL/min) on day 40 to determine if dioxane removal could be increased. Dioxane removal did increase however the increase appears to have started about two days earlier. Nevertheless, dioxane removal continued to increase and effluent concentration decreased to less than 100 µg/L on day 74 (> 99% removal).

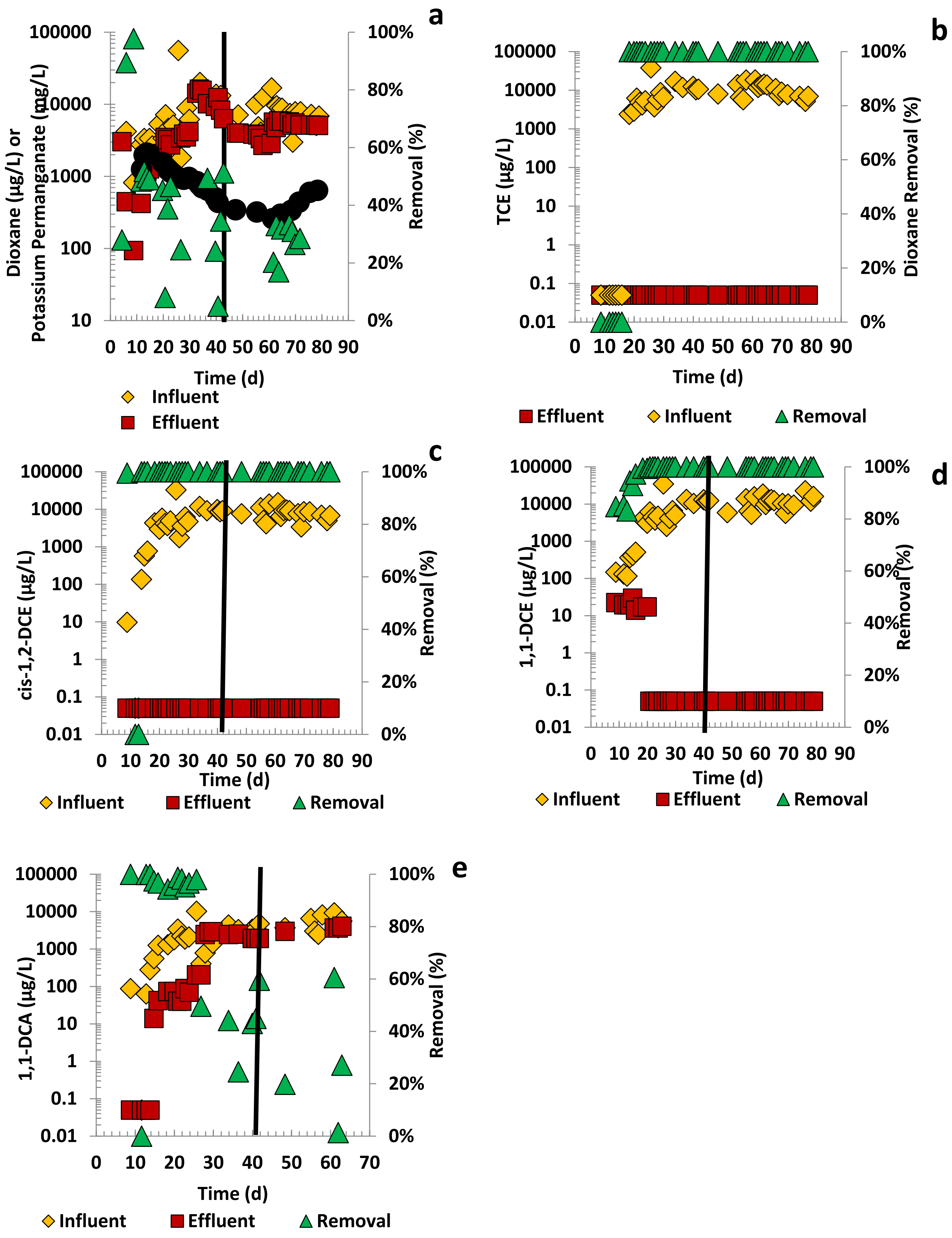


Figure 5.3. **Removal of Dioxane (a), TCE (b), cis-1,2-DCE (c), 1,1-DCE (d), and 1,1-DCA (e) by Potassium Permanganate ($KMnO_4$) in the Column Study.**

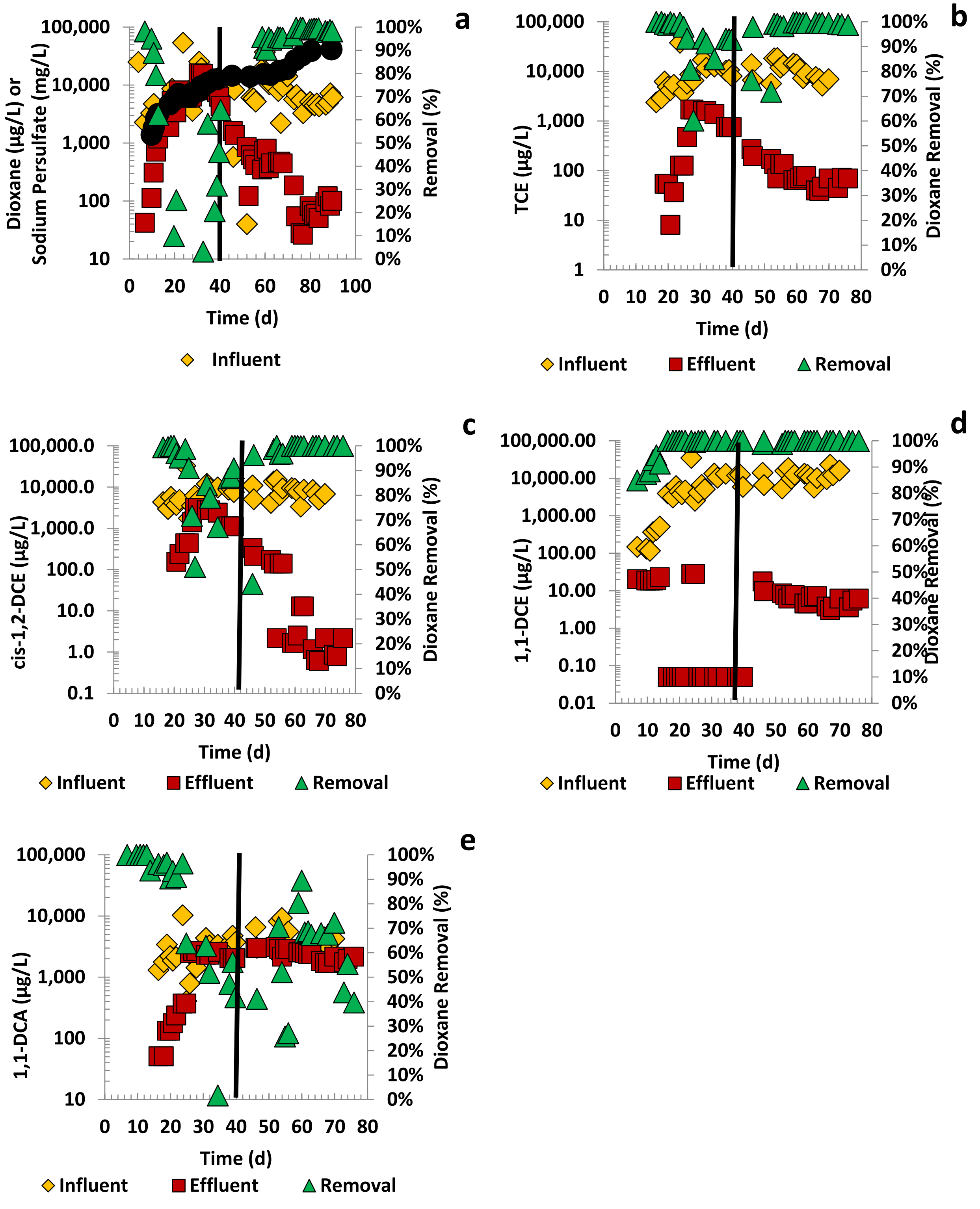


Figure 5.4. Removal of Dioxane (a), TCE (b), cis-1,2-DCE (c), 1,1-DCE (d), and 1,1-DCA (e) by Sodium Persulfate ($Na_2S_2O_8$) in the Column Study.

Figure 5.5 shows photographs of the cylinders at the conclusion of column operation. A rind, possibly manganese dioxide (MnO$_2$), is evident around the circumference of the permanganate cylinder. This rind appears to have inhibited oxidant release from the cylinder, which resulted in the relatively low permanganate concentrations and in turn lower than expected dioxane removal. The photographs of the persulfate cylinders show some staining but no clear evidence of a coating as was observed on the permanganate cylinder.

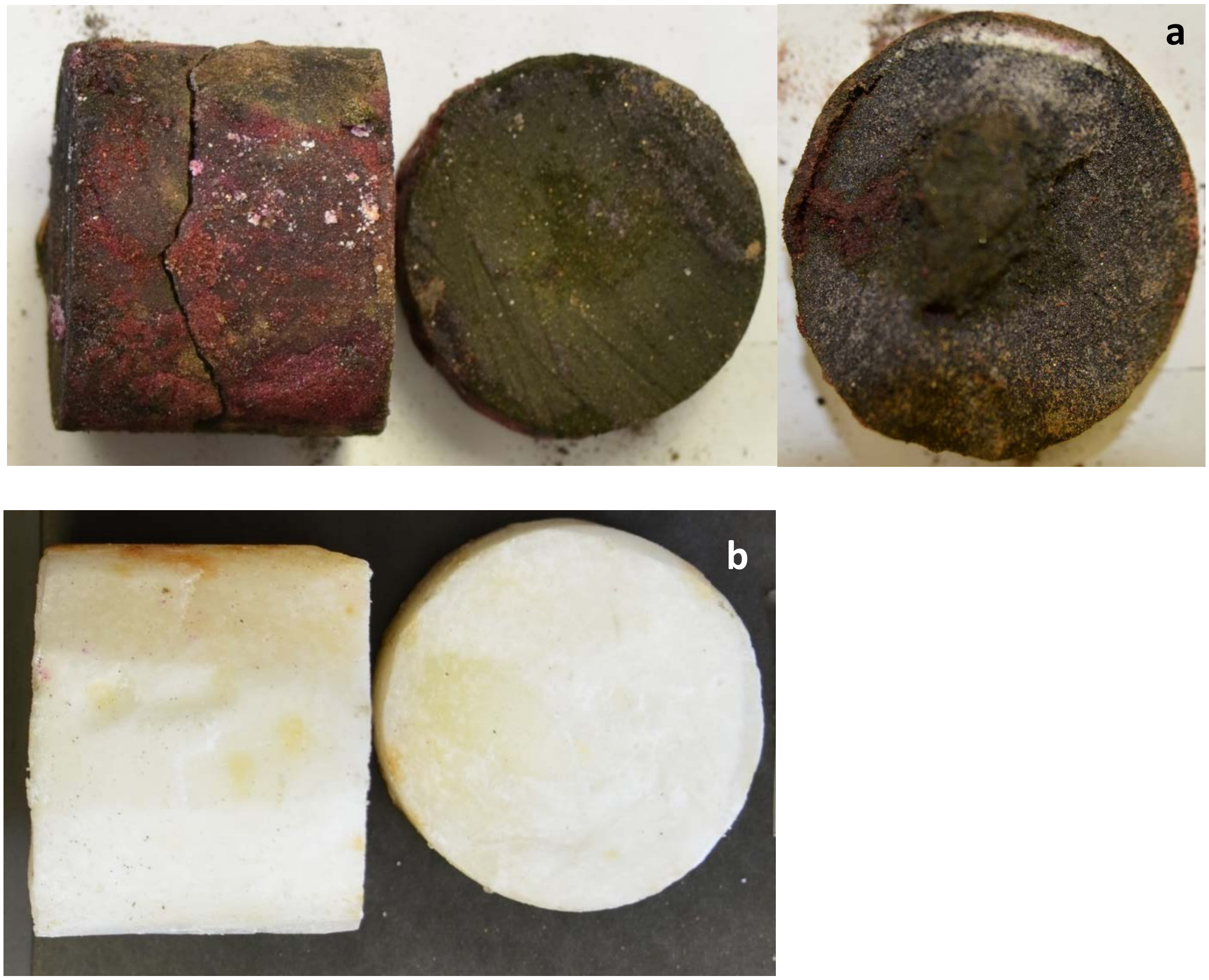
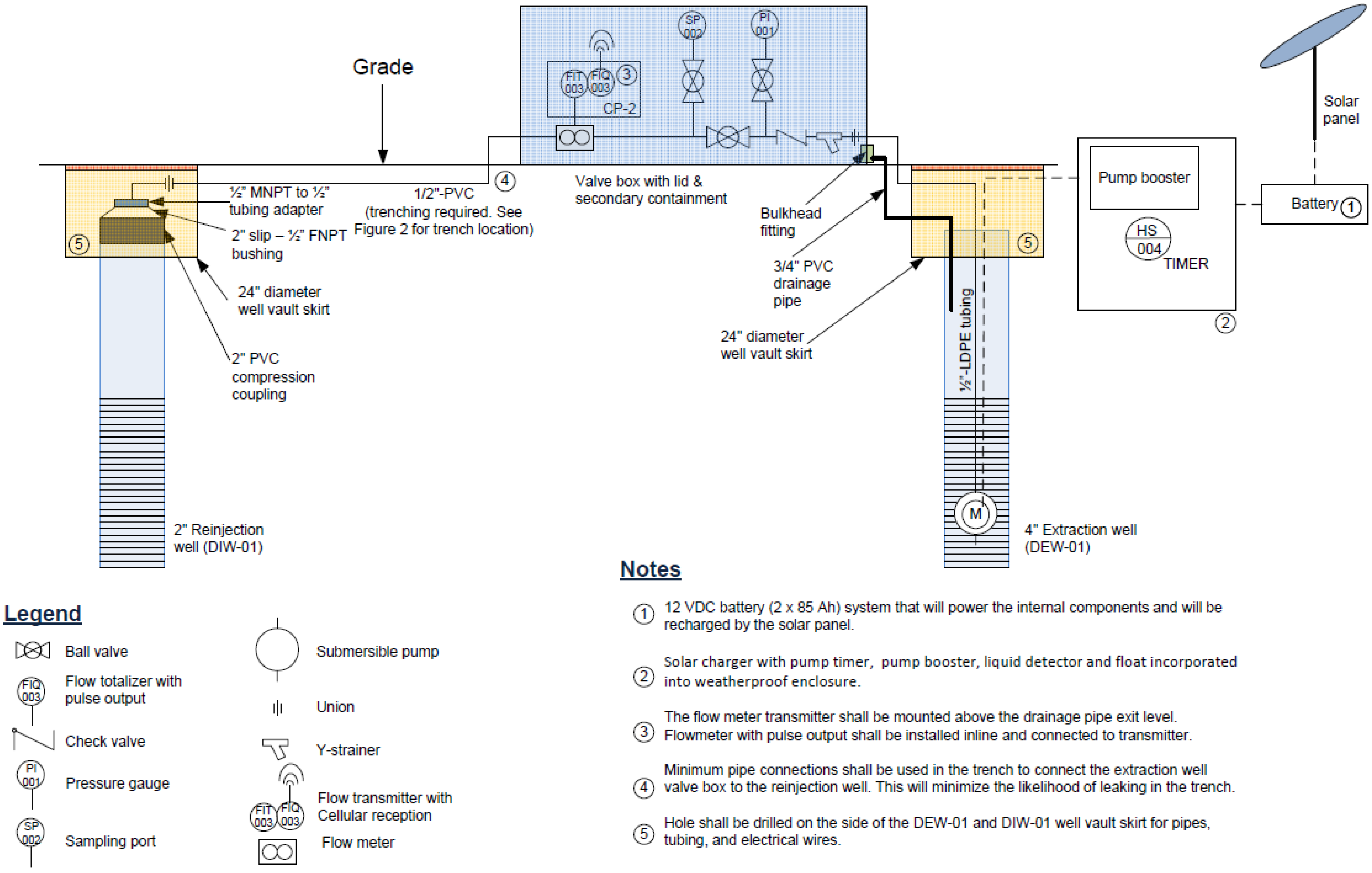


Figure 5.5. Photographs of Permanganate (a) and Persulfate (b) Column Cylinders at the Conclusion of the Study.

Unactivated persulfate was successfully demonstrated to oxidize dioxane and chlorinated ethenes (TCE, cis-1,2-DCE, and 1,1-DCE) in the presence of site soil and groundwater. Over 99% removal was observed in the column study, which exceeded the project go/no-go criterion of 90%. The pseudo second-order rate constant for dioxane removal in site soil and groundwater (4.6×10^{-5} per molar per second (M^{-1} s^{-1})) was less than that measured in deionized (DI) water (1.1×10^{-3} M^{-1} s^{-1}). These data suggest some form of partial inhibition by site soil and groundwater. Dioxane removal did not follow first-order kinetics (i.e., the slope of the semi-logarithmic plot of concentration versus time was not linear, and the absolute value of the slope increased over time), suggesting some type of activation. Dioxane oxidation by persulfate in the absence of an activator has been previously observed (Felix-Navarro et al. 2007). Permanganate was capable of oxidizing dioxane and chlorinated ethenes in batch reactor studies. 1,1-DCA was not oxidized as expected. The column study demonstrated greater than 99% removal of chlorinated ethenes but little to no removal of dioxane because of precipitation of manganese dioxide which limited persulfate release from the cylinder. Based on the treatability study results, a field demonstration using slow-release persulfate cylinders was conducted as the next step in the demonstration and validation of this technology.

5.4 FIELD TESTING

As discussed in **Section 5.1**, the demonstration system was designed to simulate the use of persulfate to treat groundwater contaminated with dioxane and CVOCs in an induced groundwater gradient. The system consisted of two boreholes/wells containing the persulfate cylinders, one upgradient and eight downgradient monitoring wells, an extraction well, and a reinjection well as shown previously in **Figure 5.1**. A submersible pump housed inside a 4-inch diameter extraction well was used to extract groundwater and promote a controlled hydraulic system at flow rate of 0.35 gallons per minute (gpm). The extracted water was then injected into the downgradient reinjection well. A simplified process and instrumentation diagram for the pilot system is presented in **Figure 5.6**. Construction was completed on December 17, 2015 and the system was then operated for 15 days from December 22, 2015 to January 5, 2016 to identify and resolve any issues. Cylinder deployment was then conducted. A series of oxidant cylinders (12 per well) housed in cylinder holders illustrated in **Figure 5.7** was assembled and lowered into the cylinder wells. A cable was tied to each set of holders and secured inside the cylinder well vaults to allow for easy retrieval, inspection, and replacement. In addition, 1-inch polyvinyl chloride (PVC) pipe was connected between the top of the cylinder setup and the top of the well. The 1-inch PVC pipe was used to restrict the cylinders from floating as the density decreases during oxidant release.



Notes

① 12 VDC battery (2 x 85 Ah) system that will power the internal components and will be recharged by the solar panel.

② Solar charger with pump timer, pump booster, liquid detector and float incorporated into weatherproof enclosure.

③ The flow meter transmitter shall be mounted above the drainage pipe exit level. Flowmeter with pulse output shall be installed inline and connected to transmitter.

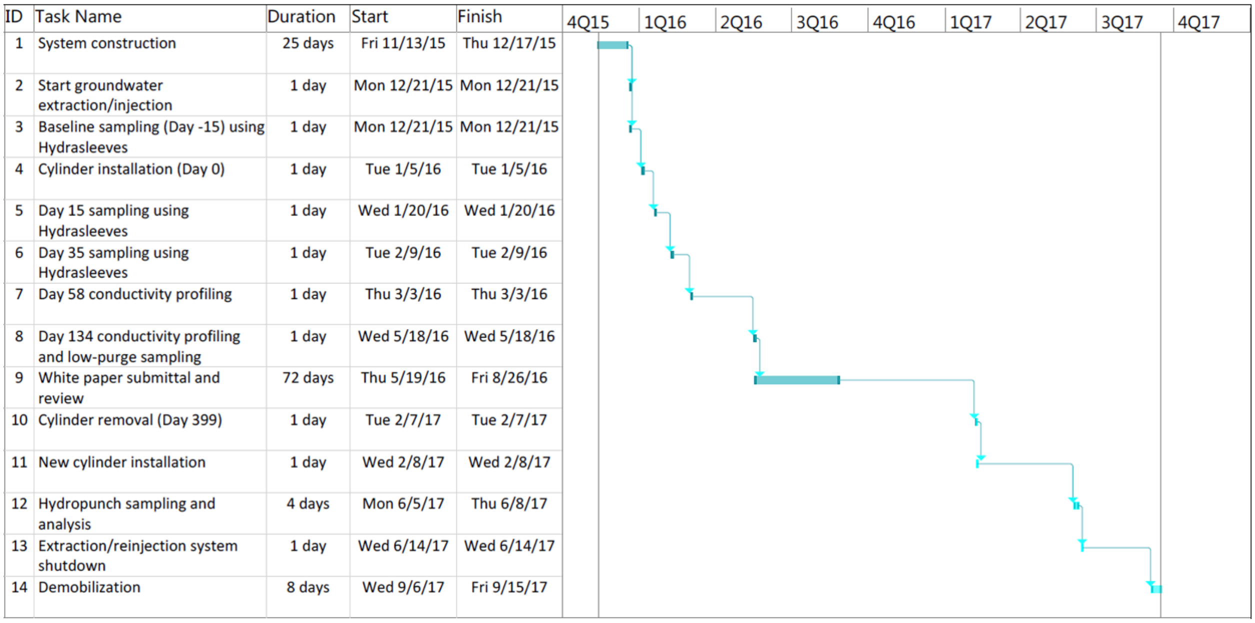
④ Minimum pipe connections shall be used in the trench to connect the extraction well valve box to the reinjection well. This will minimize the likelihood of leaking in the trench.

⑤ Hole shall be drilled on the side of the DEW-01 and DIW-01 well vault skirt for pipes, tubing, and electrical wires.

Figure 5.6. Process and Instrumentation Diagram.

Figure 5.7. Cylinder Holder Design and Installation Showing 12 Cylinders Assembled in Holder (a), Close-up of Top of Holder Showing Stainless Steel Cables, Stainless Steel Alignment Disk, Wax Separator Block, and Plastic Cable Ties for Stainless Steel Securement (b), Interconnection Between Two Cylinders (c), raising the Holder Using a Drill Rig (d, e, f), Lowering into Well (g, h), Attachment of PVC Pipe with slit to Support Cable to Prevent Cylinder Floating (i, j), and Attachment of Well Cap (k).

The major field activities are depicted in a Gantt chart in **Figure 5.8**. Upon completion of system construction and startup testing, groundwater extraction/injection commenced and baseline groundwater sampling was conducted using HydraSleeves. Cylinder deployment and a tracer study were conducted two weeks later and then periodic sampling events were conducted using HydraSleeves or low-flow sampling. Following the initial investigation indicating density-driven flow and lack of apparent persulfate transport, these results as well as recommendations for a second oxidant cylinder deployment and revised sampling approach were summarized in a white paper that was submitted to and accepted by ESTCP. Cylinder changeout and was subsequently conducted and Hydropunch^{TM} sampling then completed 119 days after cylinder installation.



ID	Task Name	Duration	Start	Finish
1	System construction	25 days	Fri 11/13/15	Thu 12/17/15
2	Start groundwater extraction/injection	1 day	Mon 12/21/15	Mon 12/21/15
3	Baseline sampling (Day -15) using Hydrasleeves	1 day	Mon 12/21/15	Mon 12/21/15
4	Cylinder installation (Day 0)	1 day	Tue 1/5/16	Tue 1/5/16
5	Day 15 sampling using Hydrasleeves	1 day	Wed 1/20/16	Wed 1/20/16
6	Day 35 sampling using Hydrasleeves	1 day	Tue 2/9/16	Tue 2/9/16
7	Day 58 conductivity profiling	1 day	Thu 3/3/16	Thu 3/3/16
8	Day 134 conductivity profiling and low-purge sampling	1 day	Wed 5/18/16	Wed 5/18/16
9	White paper submittal and review	72 days	Thu 5/19/16	Fri 8/26/16
10	Cylinder removal (Day 399)	1 day	Tue 2/7/17	Tue 2/7/17
11	New cylinder installation	1 day	Wed 2/8/17	Wed 2/8/17
12	Hydropunch sampling and analysis	4 days	Mon 6/5/17	Thu 6/8/17
13	Extraction/reinjection system shutdown	1 day	Wed 6/14/17	Wed 6/14/17
14	Demobilization	8 days	Wed 9/6/17	Fri 9/15/17

Figure 5.8. Field Demonstration Schedule.

5.5 SAMPLING METHODS

HydraSleeves or low-flow sampling was initially used to facilitate collection of formation-representative groundwater samples. Based on results of the initial rounds of sampling, density driven flow was determined to be occurring. Therefore, these data were only used for evaluation of oxidation chemistry in the cylinder borehole monitoring wells. A second-set of oxidant cylinders was then deployed and Hydropunch groundwater sampling was performed 119 days later to obtain representative groundwater samples as shown in **Figure 5.9.** These locations can be compared to the general site layout shown on **Figure 5.1**. Methods for sampling and analysis are presented in **Table 5.2** and **Table 5.3**.

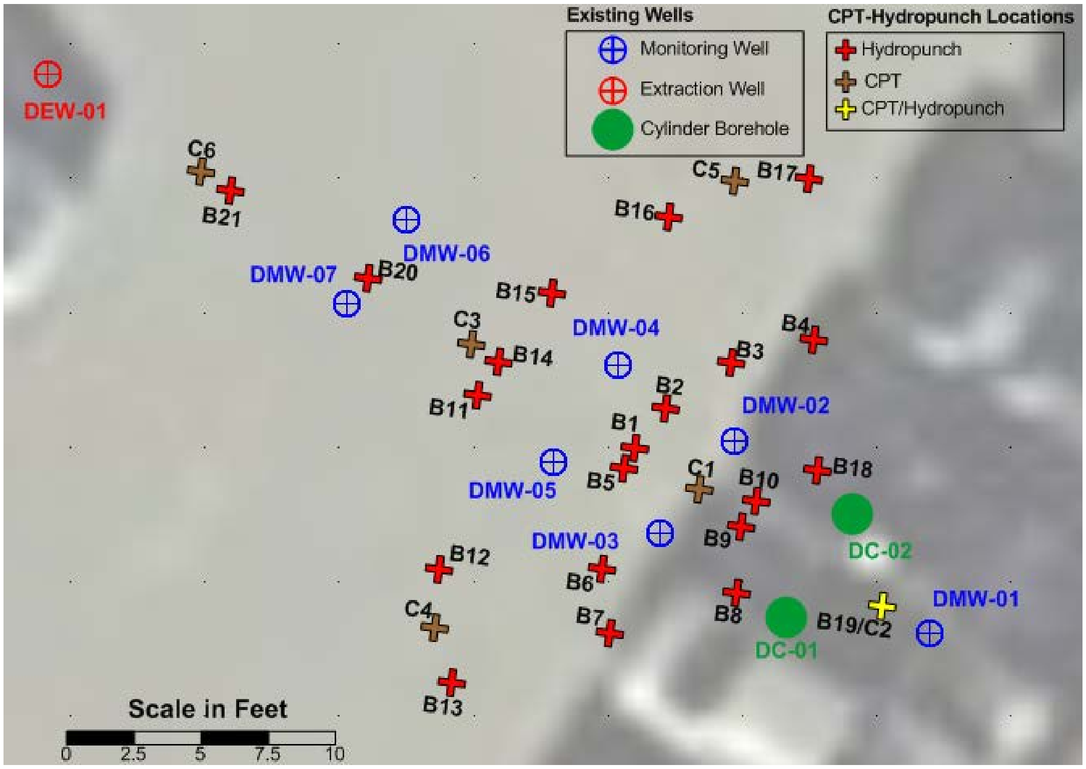


Figure 5.9a. Cone Penetrometer Tool (CPT) Boring and Sample Locations.

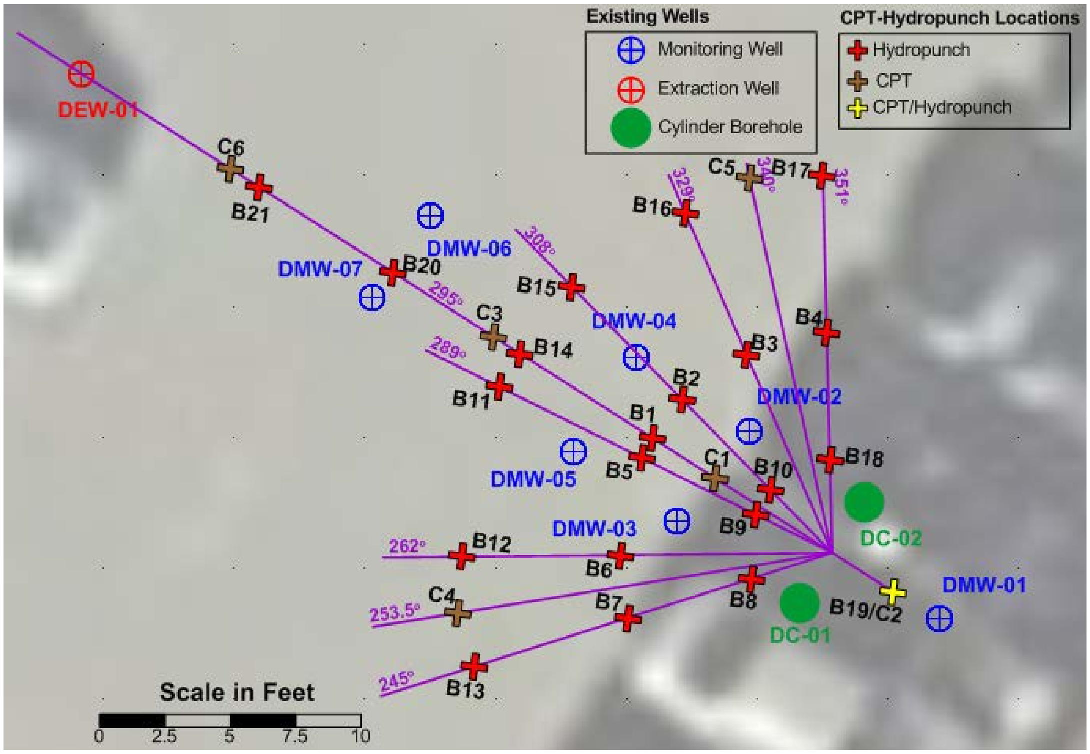


Figure 5.9b. CPT Boring and Sample Locations with Transects Based on Field Compass Readings.

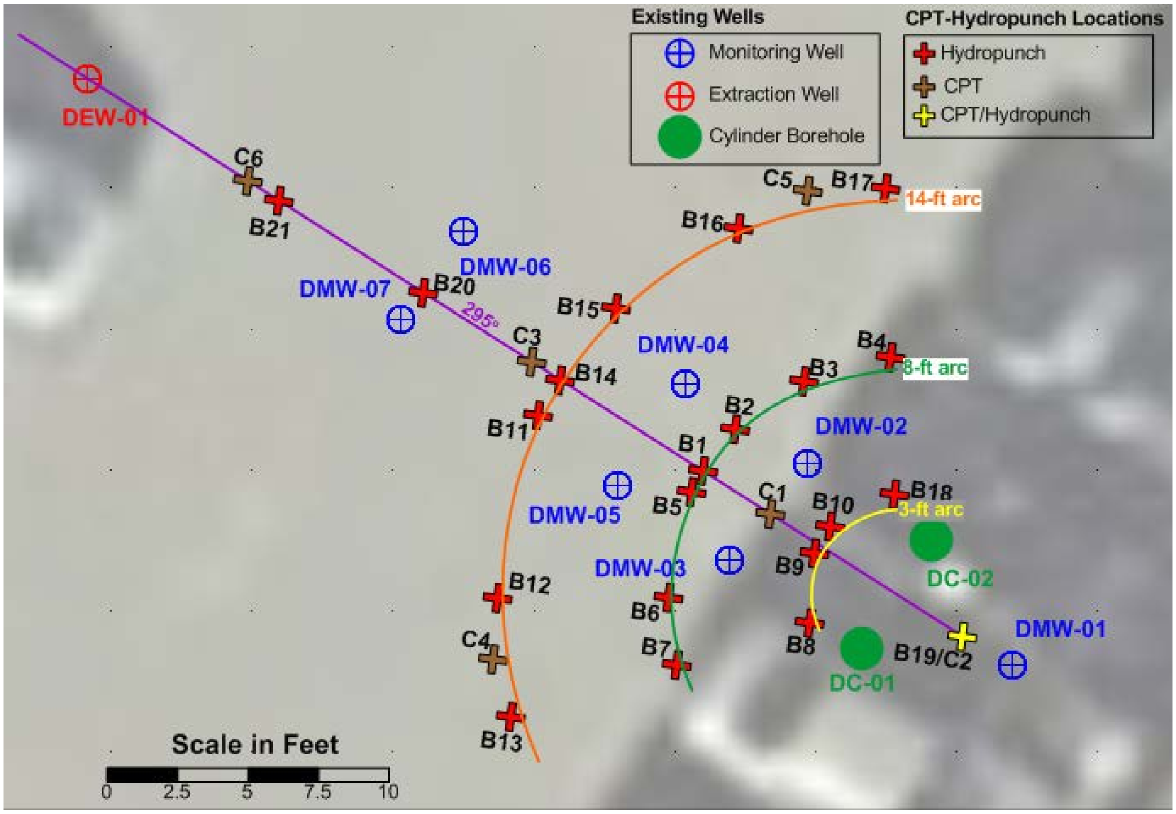


Figure 5.9c. CPT Boring and Sample Locations 3-ft, 8-ft, and 14-ft Arcs from Cylinder Locations. The 295° Design Flow Path is Shown.

Table 5.2. Performance Monitoring Schedule.

Component	Matrix	Collection method	# of Field Samples	Analyte	Location
Pre-demonstration sampling	Soil	Hollow-stem auger	1	Bench-scale testing	B1 and B2 boring locations; homogenized upon receipt at the laboratory
	Groundwater	Low-flow	1	Bench-scale testing	S11-MW-12
	Groundwater	HydraSleeves®	3	VOCs and dioxane	S11-MW-12
Technology performance sampling - Day -15	Groundwater	HydraSleeves®	9	VOCs and dioxane Field parameters	All cylinder and monitoring wells except DEW-01 and SMW-07A at 40 ft bgs
	Groundwater	Low-flow with extraction pump	2	VOCs and dioxane Field parameters	DEW-01 and SMW-07A at 40 ft bgs
	Groundwater	HydraSleeves®	4	VOCs and dioxane Field parameters	DCW-01, DMW-03, DMW-05, and DMW-07 at 32.5 ft bgs
Technology performance sampling - Day 15	Groundwater	HydraSleeves®	6	VOCs and dioxane Field parameters	DCW-01, DCW-02, and DMW-01 through -05
Technology performance sampling - Day 35	Groundwater	HydraSleeves®	9	VOCs and dioxane Field parameters	DCW-01, DCW-02, and DMW-01 through -07
Technology performance sampling - Day 134	Groundwater	Low-flow with bladder pump	9	VOCs and dioxane Field parameters	All cylinder and monitoring wells except DEW-01 and SMW-07A at 27 ft bgs
	Groundwater	Low-flow with bladder pump	9	VOCs and dioxane Field parameters	All cylinder and monitoring wells except DEW-01 and SMW-07A at 32 ft bgs
	Groundwater	Low-flow with extraction pump	2	VOCs and dioxane Field parameters	DEW-01 and SMW-07A
Post-demonstration sampling - Day 400	Groundwater	Hydropunch™	16	VOCs and dioxane Field parameters	B1 through B11, B15, B17, B18, B19, B20 at 28 ft bgs
	Groundwater	Hydropunch™	1	VOCs and dioxane Field parameters	B20 at 33 ft bgs
	Groundwater	Hydropunch™	20	VOCs and dioxane Field parameters	B1 though B20 at 38 ft bgs

Table 5.3. Analytical Methods for Sample Analysis.

Analyte	Analytical Methods	Minimum Sample Volume	Container (number, size, and type)	Preservative	Holding Time
VOCs	SW 846 EPA 8260B	120 mL	4 x 40-mL vials with Teflon-lined septum	Preserve with HCl to pH <2; Cool to 4ºC; No headspace.	14 days
1,4-dioxane	SW 846 EPA 8260 SIM			Preserve with ascorbic acid; Cool to 4ºC; No headspace.	
Sulfate	EPA 300.1	100 mL	1-250-mL polyethylene bottle	Cool to 4ºC	28 days
Chloride					
pH	Multiparameter water quality meter	50 mL	NA	Analyzed immediately	NA
Conductivity			NA	Analyzed immediately	NA
Temperature			NA	Analyzed immediately	NA
ORP			NA	Analyzed immediately	NA
Ferrous iron	HACH ferrous iron AccuVac® Ampoules		NA	Analyzed immediately	NA
Persulfate	Chemetrics kit K-7870		NA	Analyzed immediately	NA

5.6 SAMPLING RESULTS

5.6.1 Groundwater Well Sampling

Dioxane, chlorinated ethenes, and 1,1-DCA concentrations were reduced in the cylinder monitoring well deep samples one foot downgradient of the cylinders; these reductions corresponded to the elevated sodium persulfate concentrations (**Figure 5.10**). No reductions were observed in these wells prior to cylinder installation (a). The reductions were sustained through the last sampling event 134 days after cylinder installation. No contaminant destruction at greater downgradient distances was evident during any sampling event even though sodium persulfate was detected at 134 days in downgradient wells. The observed persulfate concentration may have been too low to promote detectable dioxane and CVOC destruction in downgradient sampling locations.

Reactivity of sodium persulfate with dioxane in the cylinder wells was evaluated. **Figure 5.11** presents the observed and predicted reductions in dioxane concentrations based on a second-order kinetic model. The rate constant determined in the treatability study (4.6×10^{-5} M^{-1} s^{-1}) was used in combination with the measured sodium persulfate concentrations to estimate first-order rate constants for dioxane destruction. These rate constants in combination with the observed dioxane concentrations at each time point were used to predict the reduction in dioxane concentration at the subsequent time point. The results demonstrate the observed decline in dioxane concentrations over time and the predicted declines are similar with the predicted declines being slightly greater.

Based on this analysis it can be concluded that reaction chemistry was occurring in a manner similar to that observed in the treatability test.

Sodium persulfate in the deep cylinder monitoring well samples decreased over time and an exponential model was used to fit the data (**Figure 5.12**). Even though sodium persulfate concentrations decreased over time, dioxane and total CVOCs also decreased over time indicating sustainability of contaminant destruction. Based on the exponential model, 42% of the sodium persulfate remained at the 134-day sampling point and 8% remained when the cylinders were removed after 399 days (**Figure 5.13**). Thus, the design assumption that the cylinders have a lifetime at least 0.5 years was reasonable. A lifetime up to about 1 year may be possible.

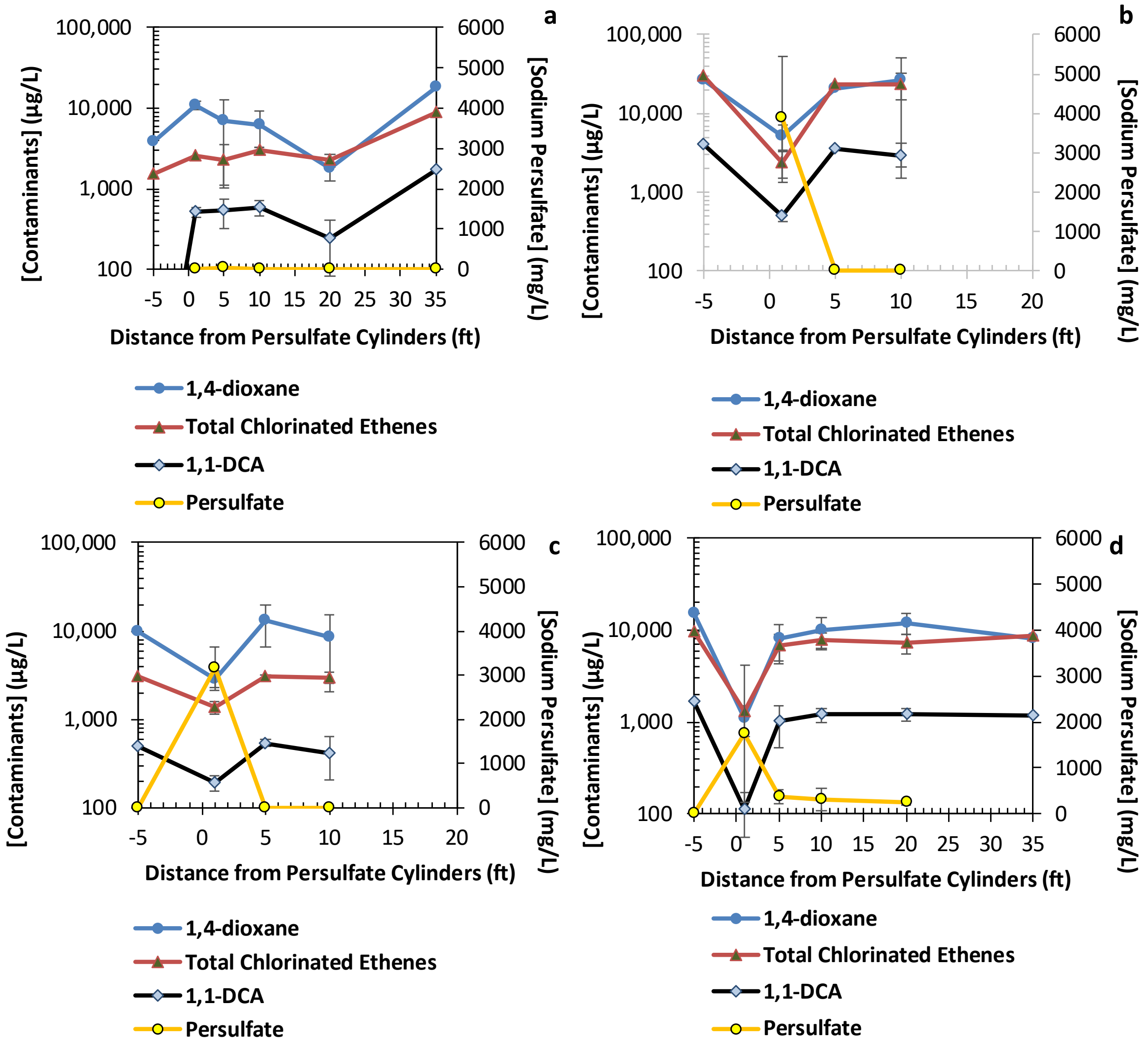


Figure 5.10. Average Sodium Persulfate, Dioxane, 1,1-DCA, and Total Chlorinated Ethenes (1,1-DCE, TCE, cis-1,2-DCE and vinyl chloride [VC]) in Deep Monitoring Well Samples Collected -15 (a), 15 (b), 35 (c) and 134 (d) Days After Persulfate Cylinder Installation.

VC was not analyzed on day 134 and is not included in total chlorinated ethenes. Error bars are ± 1 standard deviation.

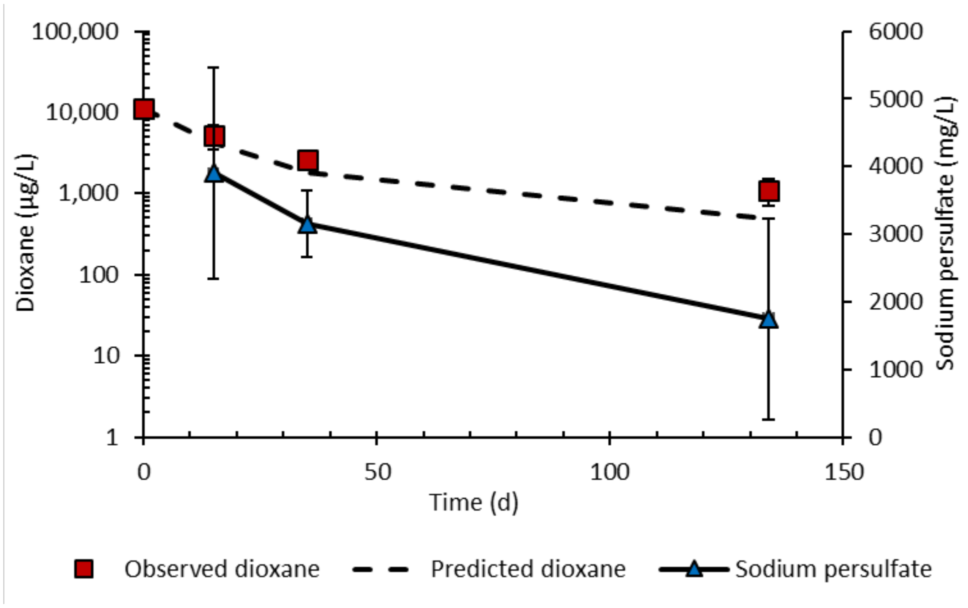


Figure 5.11. Observed and Predicted Average Deep Dioxane Concentrations in Cylinder Monitoring Wells DCW-01 and DCW-02.

Predicted values based on observed deep persulfate concentrations and a second-order rate constant of 4.6 × 10-^{5} *M-*^{1} *s-*^{1}*. Error bars are ± 1 standard deviation.*

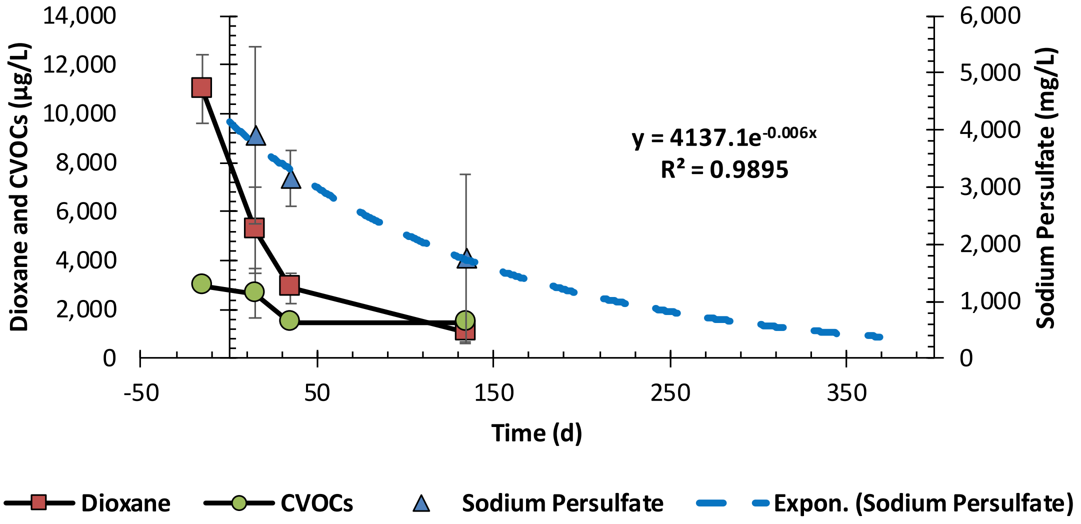


Figure 5.12. Average Sodium Persulfate, Dioxane, and Total CVOCs (1,1-DCA, 1,1-DCE, TCE and cis-1,2-DCE) in Deep Samples from Cylinder Monitoring Wells (DCW-01 and DCW-02).

Dashed line is an exponential fit plus extrapolation. Error bars are ± 1 standard deviation.

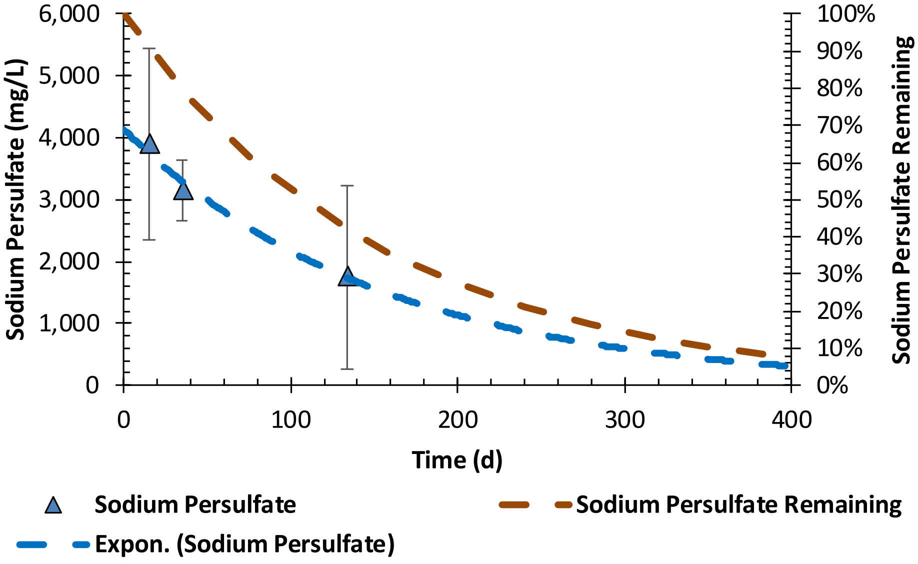


Figure 5.13. Sodium Persulfate Concentration in Deep Cylinder Monitoring Wells and Estimated Sodium Persulfate Remaining in Cylinders.

Error bars are ± 1 standard deviation.

Figure 5.14 indicates that most of the persulfate was located in deep samples. While the shallow concentrations were 45 to 67% of the deep concentration in the deep cylinder monitoring wells (1 ft downgradient), the shallow concentrations were 15 to 22% of the deep concentrations in the 5-ft downgradient monitoring wells. These data suggest density driven persulfate transport.

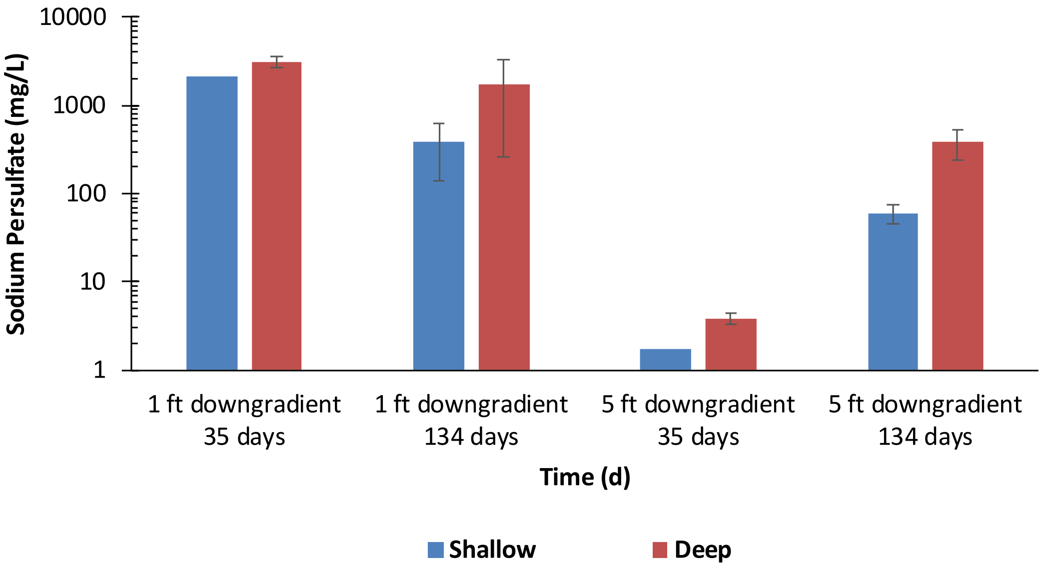


Figure 5.14. Comparison of Shallow and Deep Average Sodium Persulfate Concentrations in Cylinder and Downgradient Monitoring Wells.

Error bars are ± 1 standard deviation.

Density effects have previously been demonstrated to induce a relatively stronger vertical flow component in aquifers with low horizontal hydraulic gradients (Schillig et al. 2014). The natural gradient (non-pumping conditions) at the site has been reported to be 0.00037 ft/ft (Accord Mactec 2013). The observed horizontal gradients were 0.00022 ± 0.00039 ft/ft and 0.00062 ± 0.00073 ft/ft along the DC-01 and DC-02 flow paths, respectively. These values are not significantly different from the natural gradient and less than the gradient of 0.00145 ft/ft expected to be induced by pumping. This apparent lack of induced gradient may have been because the actual hydraulic conductivity was greater than the reported hydraulic conductivity for the site of 17.24 ft/d or 6 × 10^{-3} centimeters per second (cm/s) (Accord Mactec 2013) which was used in the model for design of the hydraulic control system. For a sodium persulfate concentration of 1,000 mg/L and an average hydraulic gradient of 4 × 10^{-4} ft/ft, previously developed correlations (Schillig et al. 2014) suggest that the vertical flow component would be greater than 70% of the overall seepage velocity (**Figure 5.15**). These data further support the existence of sodium persulfate-induced density driven flow during the demonstration.

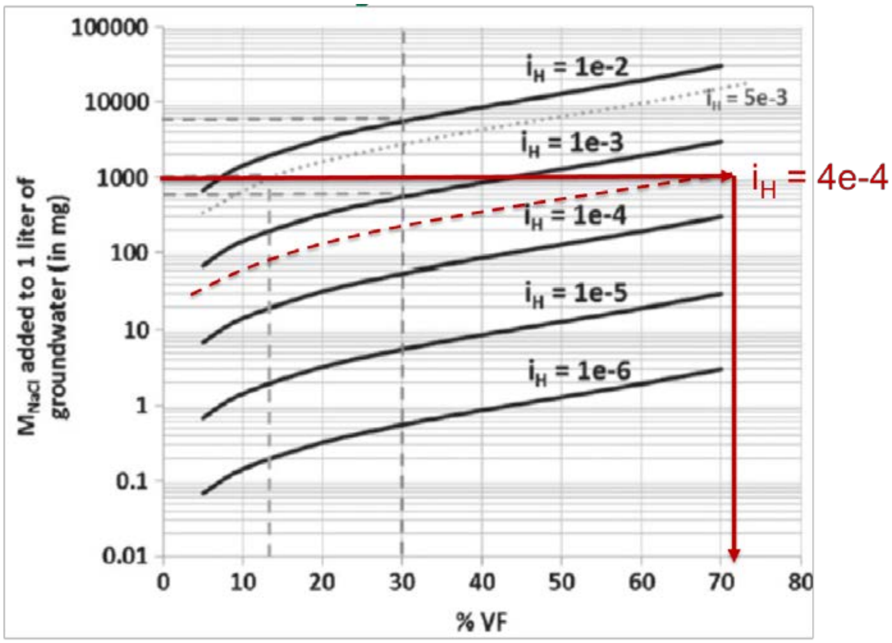


Figure 5.15. Predicted Vertical Flow Component (%VF) in Relation to Salt Concentration Based on Previously Published Data (Schillig et al. 2014).

The overlain red lines indicate the approximate vertical flow component that could result from 1,000 mg/L sodium persulfate in an aquifer with a horizontal hydraulic gradient of 4 × 10^{-4} ft/ft.

5.6.2 Discrete Interval Groundwater Sampling

Groundwater samples were collected using Hydropunch technology from a deep interval (37 to 39 ft bgs), a middle interval (32 to 34 ft bgs), and a shallow interval (27-29 ft bgs). The deep interval was located 1-3 feet above the silt aquitard to obtain samples that were representative of groundwater flowing along its surface because of density driven flow. The shallow interval was located 2.5-4.5 ft below the water table. Samples were collected in arc-shaped transects located 3, 8, and 14 ft downgradient of the cylinders and spanning 245 to 351° to identify the true flow path (**Figures 5.9 b and c**).

Figure 5.16 presents the results for transect concentrations of sodium persulfate, dioxane, and CVOCs along with percent removals of the contaminants. Large differences in sodium persulfate concentrations and contaminant percent removals were observed between the borings located 6.1 and 7.0 ft east of 245° along the 8-ft transect; dioxane removal decreased from 99 to 38% and CVOC removal decreased from 99 to 13%. The decreases were less along the 14-ft transect; dioxane removal decreased from 96% in the boring 11 ft east of 245° to 67% 12 ft east and CVOC removal decreased from 93 to 76%. These data suggest that while the lateral (i.e., orthogonal to the flow path) influence is small, a short distance from the oxidant cylinders, the lateral influence increases as the distance from the cylinders increase likely because of dispersion.

High contaminant removal (i.e., > 90%) appears to have been limited to a small lateral influence (**Figure 5.16f**). On the other hand, contaminant removals exceeding 50% were observed across a 10-ft lateral zone ranging from 11 to 21 ft east of 245° (**Figure 5.16f).** The distance between the cylinder boreholes was only 5 ft. Therefore, greater lateral influence may be possible. Greater contaminant removals may have been limited by diffusion of contaminants from groundwater cross-gradient to the induced flow path. Use of a reactive barrier consisting of more than two-cylinder boreholes may promote greater contaminant removal because cross-gradient effects would be minimized.

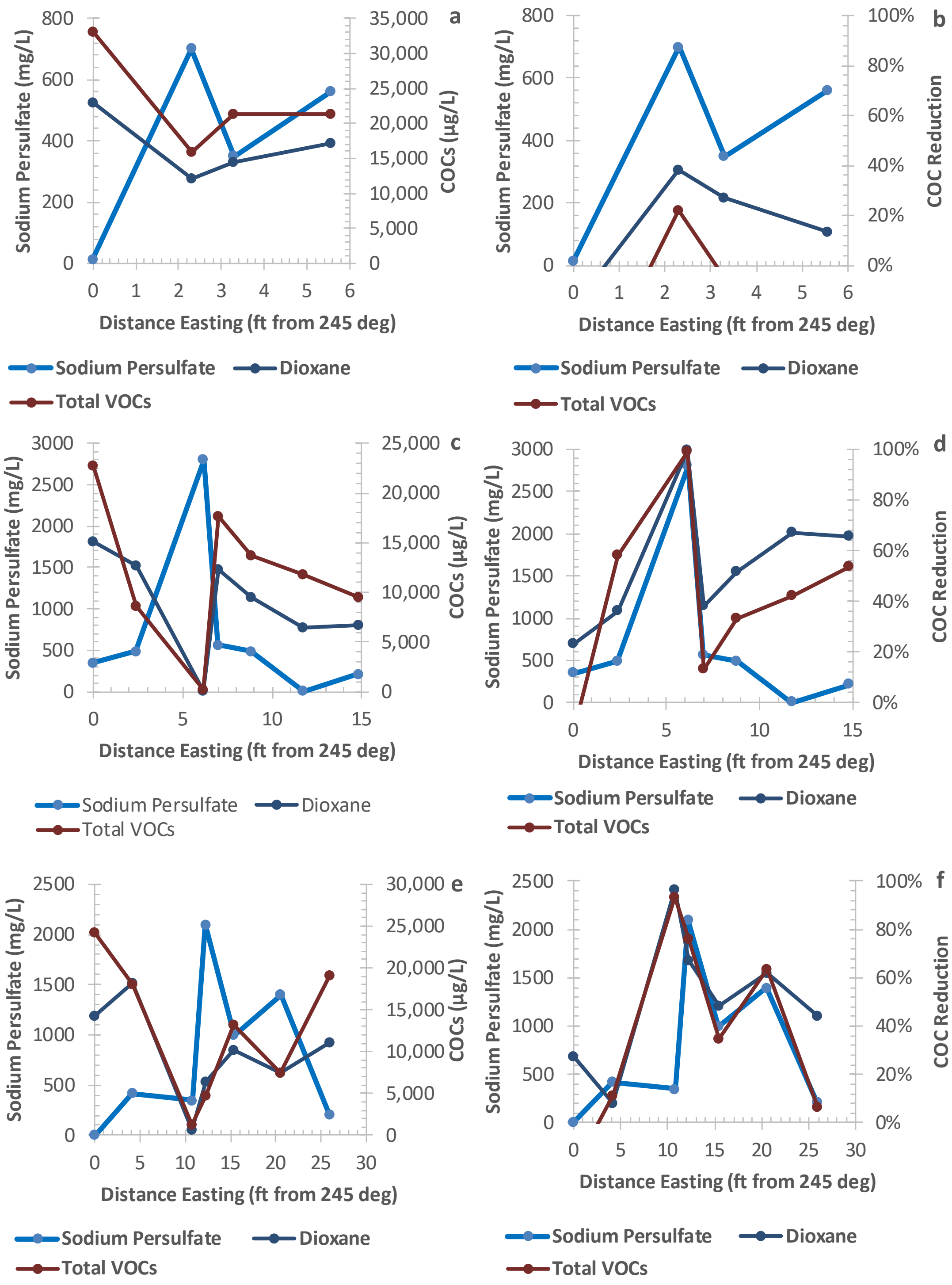


Figure 5.16. Hydropunch Boring Groundwater Sample Results for Sodium Persulfate, Dioxane and Total VOCs (1,1-DCE, 1,1-DCA, cis-1,2-DCE and TCE) Collected from the Deep Interval 12.5-14.5 ft Below the Water Table 119 Days After the Second Persulfate Cylinder Installation Event.

Results are plotted as transects along arc easting distances located 3 ft (a,b), 8 ft (c,d) and 14 ft (e,f) downgradient of the cylinders.

Concentrations trends of sodium persulfate and contaminants in deep boring samples along the observed 289° flow path were evaluated (**Figure 5.17**). Dioxane and CVOCs concentrations were reduced by 99% 8 ft downgradient of the oxidant cylinders which translates to 20-d travel time based on an estimated seepage velocity of 12.2 centimeters per day (cm/d) (0.40 ft/d). This result compares well to the predicted removal of >99% at 20 ft downgradient (**Figure 5.1**) and exceeds the performance objective of 90% removal. The percent removal was >90% 14 ft downgradient of the cylinders even though the sodium persulfate concentration decreased from 2,800 to 350 mg/L. This result is consistent with the design concept of the oxidant cylinders performing as a permeable reactive barrier. Maximum sodium persulfate concentrations were observed at 8 ft downgradient and were lower in samples collected at 1 and 3 ft downgradient. Based on the exponential model used to describe sodium persulfate concentration release from the oxidant cylinders (**Figure 5.12**), sodium persulfate concentration released from the cylinders after 119 days (i.e., the time of sampling) was predicted to be 46% of that at the time of cylinder installation. The observed sodium persulfate concentration in the cylinder monitoring wells was 30% of the maximum concentration compared to the predicted 46%. Considering experimental uncertainties, the observed profile of sodium persulfate concentrations is reasonable.

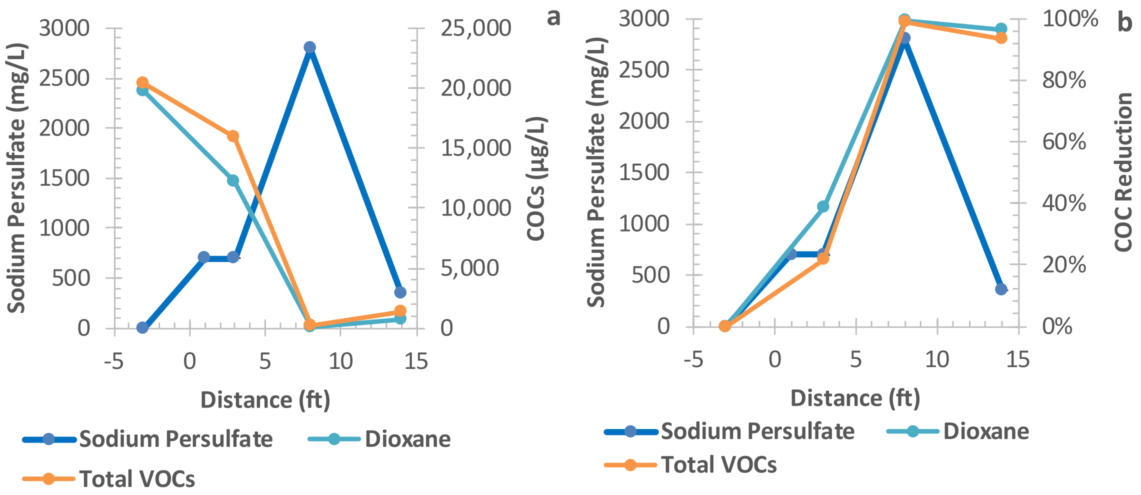


Figure 5.17. Total VOC (1,1-DCE, 1,1-DCA, cis-1,2-DCE and TCE) Concentrations (a) and Percent Removals (b) and Persulfate Concentrations (a,b) from Hydropunch Groundwater Samples Along the 289° Flow Path Downgradient of the Persulfate Cylinders and from the Deep Interval 12.5-14.5 ft below the Water Table 119 Days After the Second Persulfate Cylinder Installation Event.

Sodium persulfate concentrations 1 ft downgradient were grab samples collected from cylinder monitoring wells DCW-01 and DCW-02 using bailers.

Individual CVOCs were all reduced and the greatest reduction correlated to the maximum sodium persulfate concentration (**Figure 5.18**). Some rebound of TCE was observed 14 ft downgradient possibly because of back diffusion from the aquifer. 1,1-DCA was oxidized here, however it was poorly removed in the column study (**Figure 5.4**). The reason for this difference is uncertain but may be associated with natural activation by soil minerals (Ahmad 2008, Ahmad et al. 2010, Liu et al. 2014, Teel et al. 2011) and differences between the mineral composition of discrete sample used for the treatability study and those present in the subsurface flow path during the field demonstration.

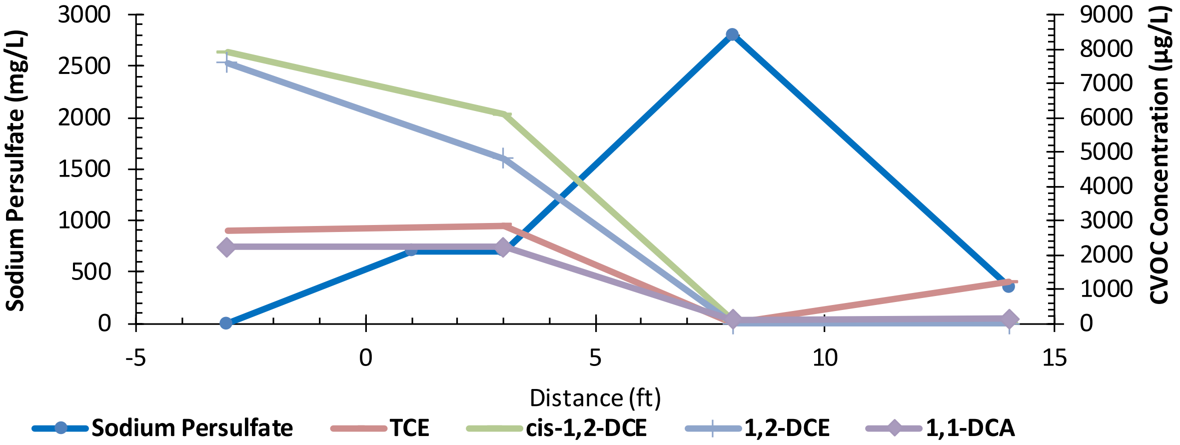


Figure 5.18. Individual CVOC Concentrations from the 12.5-14.5 ft Interval Along the 289° Flow Path Downgradient of the Persulfate Cylinders.

Geochemical data were consistent with sodium persulfate decomposition (**Figure 5.19**). Sulfate and oxidation-reduction potential increased and pH decreased in response to increased sodium persulfate concentrations. These geochemical parameters returned to their background values further downgradient suggesting that adverse secondary effects such as metals mobilization associated with depressed pH would likely be attenuated.

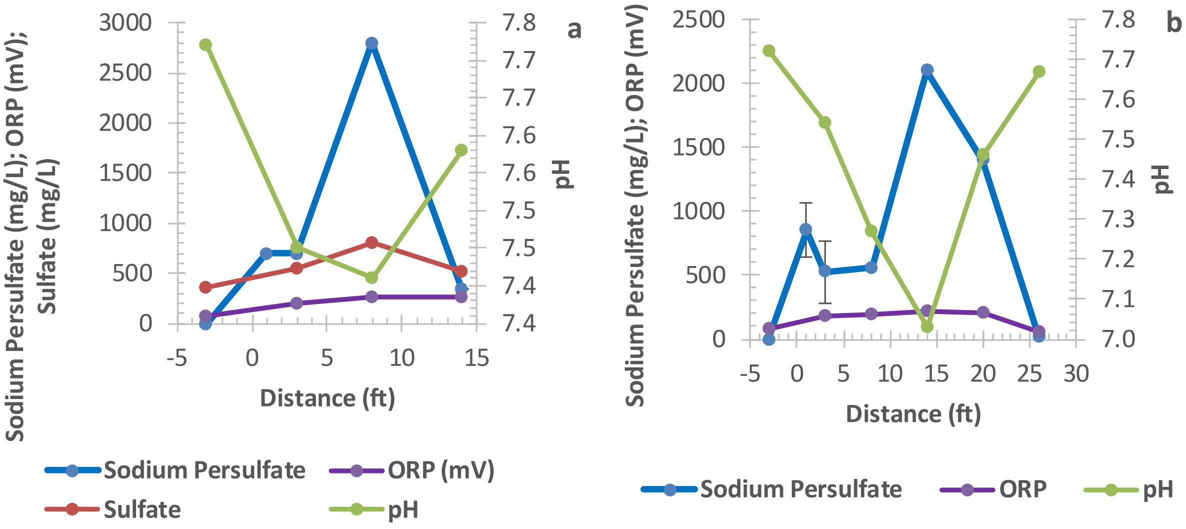


Figure 5.19. Geochemical Parameters from the 12.5-14.5 ft Interval Along the 289° (a) and 295° (b) Flow Paths Downgradient of the Persulfate Cylinders.

Samples collected from shallow borings along the 289° flow path also demonstrated CVOC removal even though sodium persulfate concentrations were substantially lower than in deep boring samples (**Figure 5.20**). Commensurately, the degree of CVOC reduction was less. Dioxane reduction was not quantifiable because upgradient concentrations in the shallow zone were low.

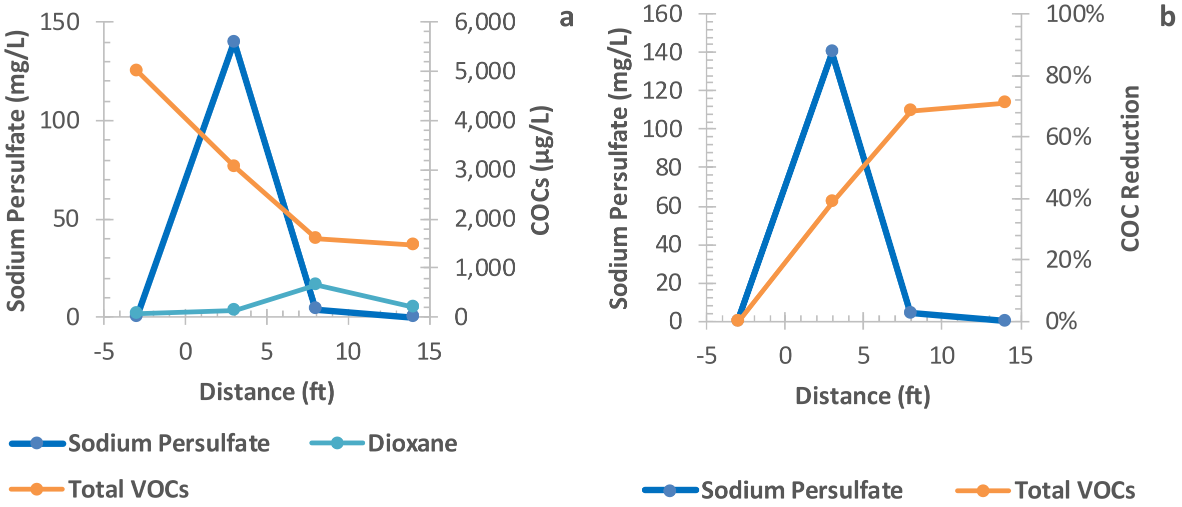


Figure 5.20. Total VOC (1,1-DCE, 1,1-DCA, cis-1,2-DCE and TCE) Concentrations (a), Percent Removals (b) and Persulfate Concentrations (a,b) from Hydropunch Groundwater Samples Along the 289° Flow Path Downgradient of the Persulfate Cylinders and from the Shallow Interval 2.5-4.5 ft Below the Water Table 119 Days after the Second Persulfate Cylinder Installation Event.

Percent removal for dioxane is not shown because upgradient concentrations were negligible and calculated percent removals were negative.

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6.0 PERFORMANCE ASSESSMENT

6.1 QUANTITATIVE PERFORMANCE OBJECTIVE: TECHNOLOGY EFFECTIVENESS

The maximum dioxane and total CVOC destructions along the flow path were used to assess performance. The maximum destructions (99.3% and 99.0% for dioxane and total CVOCs, respectively) were observed in the deep sample located 8 ft downgradient along the main hydraulic flow path (**Figure 5.17**). The upgradient dioxane and total CVOC concentrations were approximately 20,000 µg/L each. The downgradient dioxane concentration was 140 µg/L. Thus, the 90% minimum destruction criterion for dioxane was exceeded. Individual CVOCs were also reduced in concentration along the flow path (**Figure 5.18**). 1,1-DCE was reduced from 7,600 to < 33 µg/L (> 99.5% reduction; MCL = 7 µg/L); 1,1-DCA was reduced from 2,200 to 110 µg/L (95% reduction); cis-1,2-DCE was reduced from 7,900 to 75 µg/L (99.1% reduction; Federal MCL = 70 µg/L); and TCE was reduced from 2,700 to 15 µg/L (99.4% reduction; MCL = 5 µg/L).

The reductions in contaminant concentrations reported above were observed in deep aquifer samples. These samples are considered to be representative of the primary contaminant flow path at 40 ft bgs running along the top a silt aquitard (**Figure 5.2**). This path appears to have been density driven and induced by: 1) the density of sodium persulfate and 2) the low horizontal hydraulic gradient (**Figure 5.15**).

While sodium persulfate appears to have promoted density-driven flow, contaminant reductions were also observed in shallower portions of the aquifer (**Figure 5.20**). Total CVOCs were reduced by 71% 14 ft downgradient of the oxidant cylinders. The upgradient concentration of dioxane was 67 µg/L in the shallow sample compared to 20,000 µg/L in the deep sample and downgradient concentrations of dioxane in the shallow sample were greater than the upgradient concentration. Therefore, evaluation of dioxane removal in the shallow aquifer was not possible. The shallow aquifer would not be anticipated to be a major contributor to overall contaminant flux in the case of density driven flow. In this case, high contaminant destruction in the shallow aquifer would not be necessary for a remedial performance objective of contaminant mass flux reduction.

A permeable reactive barrier comprised of oxidant cylinders must be capable of contaminant destruction along the length of the barrier as well as between individual oxidant cylinders. The above results indicate that a simulated barrier comprised of two-cylinder boreholes was capable of exceeding the performance objective at a distance 8 ft downgradient. Contaminant removal was maintained at a level > 90% also at a distance 14 ft downgradient (**Figure 5.17**). However, the zone of contaminant destruction > 90% was narrow and less than the cylinder borehole spacing of 5 ft (**Figure 5.16**). This narrow lateral zone of influence may be attributable to diffusive influx of contaminants from groundwater cross-gradient to the main hydraulic flow path. Installation of a barrier containing more than two-cylinder boreholes and wider than 5 feet would minimize diffusive influx. Nevertheless, contaminant bypass via advective transport through a “gap” between cylinder boreholes where the oxidant does not come into contact with the contaminant is an issue that must be considered during design. Modeling can be used to address this issue.

6.2 QUANTITATIVE PERFORMANCE OBJECTIVE: SUSTAINABILITY/ LONGEVITY

Sodium persulfate concentrations decreased in an exponential pattern over time with 42% remaining at the final sampling event (134 days) and 31% and 9% predicted to be remaining after 6 and 12 months, respectively (**Figure 5.13**). Contaminant concentrations in the borehole monitoring wells continued to decline throughout the 134-day sampling period resulting from oxidation by the released sodium persulfate (**Figure 5.12**). Dioxane removal steadily increased to 90% in the oxidant cylinder borehole monitoring wells by the time of the final sampling event thus meeting the performance objective (**Figure 5.11)**. Therefore, the decreasing oxidant concentrations did not adversely affect dioxane removal. CVOC removal increased only to 51% over the same time period. Previous treatability studies demonstrated the reaction rate of sodium persulfate with CVOCs was greater than that with dioxane. Thus, the 51% value may be an underestimate.

During the second oxidant cylinder deployment, dioxane and CVOC removals were ≥ 99% after 119 days further corroborating high contaminant destruction for extended time periods even when oxidant concentrations may be variable or declining (**Figure 5.17**). Thus, the criterion of contaminant destruction effectiveness being maintained for greater than 4 weeks was exceeded.

6.3 QUANTITATIVE PERFORMANCE OBJECTIVE: OXIDANT TRANSPORT AND DESTRUCTION

Initial investigations into sodium persulfate transport were complicated by density driven flow. HydraSleeve sampling techniques in monitoring wells were not capable of discretely sampling the deeper groundwater horizon overlaying the silt aquitard. HydroPunch sampling provided better contrast and demonstrated that sodium persulfate was transported at least 20 ft downgradient of the oxidant cylinders (**Figure 5.19**). Concentrations were variable but ultimately decreased along the flow path from a maximum concentration of 2,100 mg/L 14 ft downgradient to 21 mg/L 26 ft downgradient. This represents a 99% reduction in oxidant concentration. pH and ORP trends also indicate that groundwater downgradient of the oxidant returned to natural conditions (**Figure 5.19**).

6.4 QUANTITATIVE PERFORMANCE OBJECTIVE: TECHNOLOGY IMPLEMENTABILITY/ SECONDARY IMPACTS

pH decreased and ORP increased in response to the presence of sodium persulfate (**Figure 5.19**). Downgradient of the maximum sodium persulfate concentration, pH increased and ORP decreased to background values. Dissolved chromium (presumed to be hexavalent chromium) concentrations increased in the treatability column study to concentrations ranging from 200 to 300 µg/L (Evans et al. 2018). Lead may have also been elevated but conflicting results from two different laboratories make this result uncertain. Concentrations of other hazardous metals were not elevated during the treatability study. Hexavalent chromium can be chemically or biologically reduced. If hexavalent chromium concentrations in groundwater were observed during the field demonstration, it is possible that chemical or biological reduction could have occurred downgradient. The basis for this assertion is: 1) pH increased the baseline values and increased pH decreases metal solubility, and 2) ORP decreased to naturally reducing aquifer conditions that could reduce hexavalent chromium to less soluble trivalent chromium hydroxide.

6.5 QUALITATATIVE PERFORMANCE OBJECTIVE: TECHNOLOGY REPRODUCIBILITY

The relative percent deviation (RPD) of the sodium persulfate concentrations in the cylinder borehole monitoring wells was 66±50% (**Table 3.1**). The RPD ranged from 22 to 56% during the first 35 days of operation and then increased to 120% on day 134. The increase was associated with the sodium persulfate concentration in one of the cylinder wells decreasing to 700 mg/L while the concentration in the other well was 2,800 mg/L. Sodium persulfate concentrations also varied along flow paths that were adjacent to the main flow path (**Figure 5.16**). These variations may have been associated with variability of persulfate concentrations released from the cylinders and/or a narrow plume of persulfate-containing groundwater resulting from low dispersion. The sodium persulfate flux from the cylinders was reasonable when compared to treatability study results (**Table 3.1**). The observed variability may be inherent to the technology and can be exacerbated by aquifer heterogeneity. This variability will need to be addressed during design through use of multiple oxidant cylinders and careful specification of cylinder spacing.

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7.0 COST ASSESSMENT

The cost assessment includes presentation of the different cost components used in the cost model, an analysis of primary drivers for the technology, and a comparison of full-scale implementation of the technology at one theoretical site. Cost analysis was completed for one theoretical site under five different remedial scenarios. Details are provided in the subsequent sections.

7.1 COST MODEL

Various cost elements for implementation of the demonstrated technology are presented in **Table 7.1**. The major cost elements include bench-scale treatability/field pilot testing, drilling services, (IDW disposal, and costs for contractor oversight of the fieldwork. The presented costs are project-specific and may vary from site to site depending on physical (e.g., location), hydrogeological (e.g., hydraulic conductivity), and stratigraphic (e.g., lithology) characteristics. Costs presented include those required or recommended for implementing the demonstrated technology, on-site costs for monitoring well installation, groundwater sampling, and system O&M. Travel costs are not included, as they are site-specific. Overall, the cost model presented herein is intended to provide a representation of the primary cost elements to be considered, as well as the required time to implement the technologies at actual sites.

Table 7.1. Cost Model.

Cost element	Basis
Bench-scale treatability/field pilot testing	Previous projects
Drilling services	Previous projects
IDW disposal	Previous projects
Contractor oversight	Previous projects
O&M	Based on estimated project duration and discount factor
Treatment reagent	This project or previous projects
Project management	10% of all costs
Procurement, health and safety, coordination, quality assurance/quality control (QA/QC), auditing, and other miscellaneous activities	15% of all costs
Contingency	20% of all costs

7.2 COST DRIVERS

Several important cost drivers must be considered for implementing the demonstrated technology including target lithology and depth and site-specific hydrogeological characteristics, plume width, contaminant concentration, and O&M. Both site lithology and target treatment depth influence how the drilling will be performed at a given site. Although direct push may be appropriate for installing monitoring wells in select overburden materials in a cost-effective manner, it may not be suited for drilling cylinder wells. In addition, direct push is not applicable for sites with more consolidated materials and thus the use of more cost- and labor-intensive drilling technologies including hollow-stem auger, sonic or rotary techniques must be considered for installing both cylinder and monitoring wells. Lithology may also drive material costs as carbon-rich soils will exert a higher oxidant demand, rendering more frequent changing and resulting in higher material as well as O&M costs. Similar to site-specific lithology, the target treatment depth interval affects the selection of the appropriate drilling technique.

In addition, vertical depth interval targeted for treatment influences the number of cylinder wells and oxidant cylinders required. Site-specific hydrogeological characteristics and contaminant profile may also affect implementation cost. Specifically, sites with high groundwater velocities and contaminant concentrations and therefore, high contaminant flux, may lead to greater numbers of oxidant cylinders resulting in potentially higher capital and O&M costs. On the other hand, sites with flat groundwater gradients may require pumping and reinjection to induce the necessary groundwater flow velocity and direction, resulting in higher capital and O&M costs. The plume width will directly impact the number of cylinders required to create a passive barrier to intercept the plume and therefore represents a direct cost driver of field implementation of the subject technology.

7.3 COST ANALYSIS

This section compares the capital, O&M, and overall project costs for implementing different remedial techniques for treating 1,4-dioxane and CVOCs at a theoretical site in a full-scale setting. Pertinent design parameters for the theoretical site are presented in **Table 7.2**. For simplicity, it is assumed that site lithology is primarily fine to coarse sand with a relatively high hydraulic conductivity and a low degree of heterogeneity. Hollow-stem auger drilling is assumed to be amenable to all cost scenarios and all IDW generated was assumed to be non-hazardous.

Table 7.2. Assumptions for Theoretical Site.

Parameters	Value
Lithology	Fine to coarse sand
Groundwater velocity	5 ft/day
Drilling technology	Hollow-stem auger
Plume length	400 ft
Plume width	100 ft
Treatment depth	20-40 ft bgs
1,4-Dioxane concentration	10,000 µg/L
CVOCs	5,000 µg/L

The plume is assumed to be persistent and thus will require ongoing treatment for a period of 30 years. A discount factor of 7% was used for estimating lifecycle costs over the 30-year duration. Cost data used for this analysis were based on this or recently completed projects (e.g., drilling and persulfate cylinder costs), industry-standard estimates (e.g., trenching and installation of bentonite slurry walls) or vendor-provided estimates (e.g., capital and O&M costs of an AOP system). Remedial technologies being evaluated in this exercise include the following:

1. PRB with persulfate cylinders as demonstrated with cylinder changeouts being performed every 6 months for 30 years at different cylinder spacings of 1, 2.5, 5, and 10 feet.
2. PRB with persulfate cylinders as demonstrated with a cylinder spacing of 5 feet for 30 years with cylinder changeouts being performed every 3, 6, 12 or 18 months.
3. PRB using aqueous sodium persulfate injection with an injection spacing of 5 feet and reinjection performed every 30, 45, 60 or 90 days for 30 years.
4. F&G with persulfate cylinders as demonstrated with cylinder changeouts being performed every 6 months.
5. Pump and treat (P&T) using pump and treat using AOP and discharge to surface water for 30 years.

A side-by-side comparison of the different scenarios being evaluated is presented in **Table 7.3**. Note the annual mass of sodium persulfate delivered varies in Scenarios 1 and 2 depending on the spacing (Scenario 1) or the changeout frequency (Scenario 2). In Scenario 3, the annual mass of sodium persulfate is intentionally kept constant to allow comparability to Scenarios 1c and 2b (which in fact are identical). This mass is also equal to the mass delivered in Scenario 4.

Table 7.3. Comparisons of Different Remedial Scenarios.

Scenario	Sub-scenario	Technology	Cylinder spacing/Radius of Influence	Changeout frequency/Reinjection frequency	Annual Mass $Na_2S_2O_8$ (pounds)
1	1a	PRB with cylinders	1 ft	Every 6 months	13,000
	1b		2.5 ft	Every 6 months	5,300
	1c		5 ft	Every 6 months	2,700
	1d		10 ft	Every 6 months	1,300
2	2a	PRB with cylinders	5 ft	Every 3 months	5,300
	2b		5 ft	Every 6 months	2,700
	2c		5 ft	Every 12 months	1,300
	2d		5 ft	Every 18 months	890
3	3a	Traditional ISCO	5 ft	Every 30 days	2,700
	3b		5 ft	Every 45 days	2,700
	3c		5 ft	Every 60 days	2,700
	3d		5 ft	Every 90 days	2,700
4	-	F&G with cylinders	NA	Every 6 months	2,700
5	-	AOP	10 ft	Constant	-

Injection or cylinder spacing and changeout/injection frequency are strong cost-drivers. As shown in **Figure 7.1**, installing persulfate cylinder in a passive PRB configuration may potentially result in significant cost saving over manual ISCO application over the duration of the remedy.

Even at a cylinder spacing of 2.5 ft, the overall project cost utilizing PRB with persulfate cylinder is still less than that associated with manual ISCO injections at a reinjection frequency of 90 days. Use of slow-release oxidant cylinders provide a consistent flux of oxidant rather than a pulsed dose and is more cost-effective.

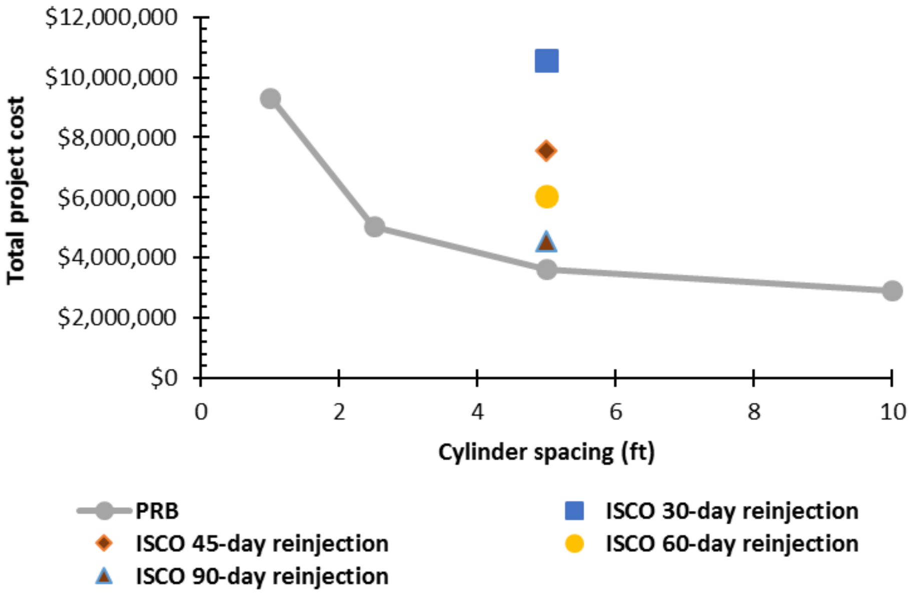

Figure 7.1. Overall Project Cost as a Function of Cylinder Spacing (PRB) and Reinjection Frequency (ISCO).

Similar to **Figure 7.1**, **Figure 7.2** showed the cost competitiveness of implementing the persulfate cylinder technology in a PRB configuring over manual ISCO injections. The overall project cost of PRB at the most aggressive changeout frequency of every 90 days is similar to that utilizing traditional ISCO at a reinjection frequency of every 90 days.

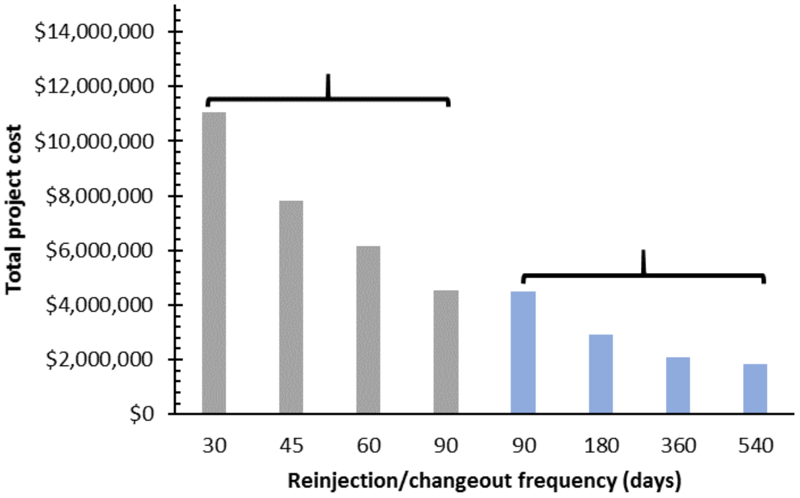

Figure 7.2. Overall Project Cost for Periodic Manual Oxidant Injections (ISCO) and Slow-release Oxidant Cylinders (PRB).

A comparison of the remedial scenarios 1c/2b, 3c, 4, and 5 was conducted. This comparison was based on demonstration results showing that a 5-ft spacing and a 6-month changeout frequency is reasonable for the sodium persulfate cylinders. Note that Scenarios 1c and 2b are the same. Scenario 3c involves manual injection of the same mass of sodium persulfate as Scenario 1c/2b as a comparative alternative to use of slow-release oxidant cylinders. Scenario 4 was simulated to provide a side-by-side comparison of F&G with PRB implementation of the cylinders. Scenario 5 was developed to compare P&T with AOP. A side-by-side cost comparison among these four scenarios is presented below in **Table 7.4**.

Table 7.4. Cost Comparisons Among Four Remedial Scenarios.

Cost category	Cost element	1c PRB with cylinders at 5-ft spacing	3c Traditional ISCO at 5-ft spacing; same persulfate mass per year	4 F&G with cylinders (same # as 1c)	5 AOP
Capital	Bench-scale treatability/field pilot testing	$200,000	$200,000	$200,000	$200,000
	Drilling	$113,000	$107,000	$113,000	$38,000
	IDW disposal	$47,000	$30,000	$47,000	$17,000
	ISCO reagent & injection system or other infrastructure	$34,000	$19,000	$544,000	$320,000
	Field oversight	$50,000	$31,000	$50,000	$31,000
	Project Management	$44,000	$42,000	$99,000	$61,000
	Project Procurement, Health and Safety, Coordination, QA/QC, Auditing, and Other Misc. Activities	$67,000	$63,000	$148,000	$91,000
	Contingency	$89,000	$77,000	$191,000	$121,000
	Total capital cost	**$644,000**	**$569,000**	**$1,392,000**	**$879,000**
O&M	Annual monitoring	$60,000	$60,000	$60,000	$60,000
	Annual changeout or reinjection or overall O&M	$125,000	$279,000	$125,000	$172,000
	Project Management	$19,000	$34,000	$19,000	$23,000
	Contingency	$37,000	$68,000	$37,000	$46,000
	Total annual O&M cost - First Year	$241,000	$412,000	$241,000	$282,000
	Total annual O&M cost - Remaining Year	$2,763,000	$5,056,000	$2,763,000	$3,458,000
	Total O&M	**$3,004,000**	**$5,468,000**	**$3,004,000**	**$3,740,000**
Overall cost		**$3,648,000**	**$6,037,000**	**$4,396,000**	**$4,619,000**

As shown in **Table 7.4**, highest capital costs are associated with Scenarios 4 and 5 (approximately $1.4 million and $880,000, respectively) where, while sharing the majority of the capital expenditures, additional costs are incurred for installation of a F&G system and an AOP system, respectively. Because of the same cylinder well/injection well spacing, the capital costs associated with Scenario 1b and 3c are very similar (between approximately $570,000 and $640,000), with the difference in cost primarily attributable to the drilling of 2-inch ID injection well versus 4-inch cylinder wells and corresponding IDW cost disposal. Because 2-inch ID injection wells were assumed to be sufficient for ISCO injection applications instead of the 4-inch ID cylinder wells used to deploy the persulfate cylinder, significant less IDW waste is generated in the former. While monitoring cost is the same among the four scenarios of interest, the difference in annual costs associated with cylinder changeout, reinjection, and labor/material results in the widely varied overall O&M cost. The total O&M cost over the 30-year duration of the project is the same for Scenarios 1c and 4 (approximately $3 million) because the same number of cylinders and changeout frequency are assumed. The highest overall O&M cost is associated with the traditional ISCO approach at approximately $5.5 million because of the frequent and material- and labor-intensive reinjection requirements. AOP has the second highest overall O&M cost of approximately $3.7 million. The overall project cost is lowest with Scenario 1c utilizing persulfate cylinders in a passive PRB configuration ($3.7 million) followed by Scenario 4 utilizing persulfate cylinders in a F&G configuration ($4.4 million), Scenario 5 with AOP ($4.6 million), and Scenario 3c with traditional ISCO ($6 million).

Comparison of the overall project cost associated with the four scenarios of interest in this discussion is graphically depicted in **Figure 7.3**.

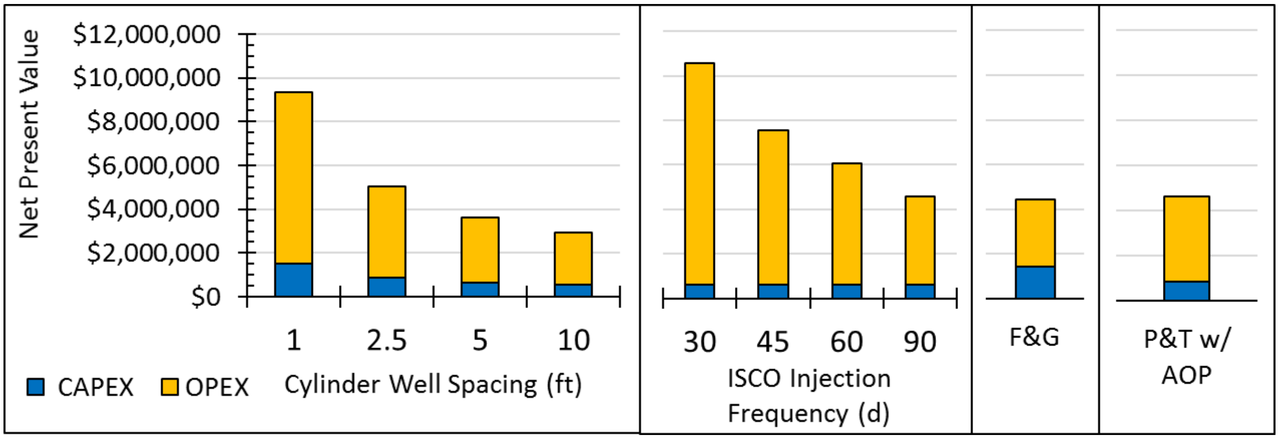

Figure 7.3. Comparison of the Overall Project Cost Among Scenario 1 with Slow-release Oxidant Cylinder PRB Changed Out Every 6 months (a), Scenario 3 with Manual ISCO Injections on a 5-ft Spacing in a PRB (b), Scenario 4 with a Slow-release Oxidant Cylinder F&G System Changed Out Every 6 Months (c), and Scenario 5 with P&T plus AOP (d). CAPEX = Capital Expenditures and OPEX = Operating Expenditures.

A slow-release oxidant cylinder PRB changed out every 6 months (a) and a well spacing of ≥2.5 ft is more cost effective than manual ISCO injections (b). Note the same annual mass of sodium persulfate is released/injected in Scenarios 1c (**Figure 7.3a** with a 5-ft spacing) as in Scenario 3 (**Figure 7.3b**). Demonstration results indicated that a spacing of 5 ft is reasonable. The cylinder PRB with spacing of 5 ft is lower cost than an F&G having the same number of cylinders (**Figure 7.3c**). Depending on specific site characteristics, a F&G system could potentially be the lowest cost option. P&T with AOP (**Figure 7.3d**) has a greater cost than a cylinder PRB with 5-ft spacing **Figure 7.3a**) and also has the disadvantage of being an active remediation system compared to the passive slow-release oxidant PRB system. These results are specific to the hypothetical cost evaluation conducted but provide an example of how slow-release oxidant cylinder technology has good potential to be cost-competitive with alternative technologies used for long-term treatment of persistent groundwater plumes.

The above scenarios are hypothetical and were developed to illustrate the sensitivity of costs to cylinder spacing and changeout frequency. Several other site-specific factors must also be considered when developing cost estimates. These include: 1) the reaction rate(s) of the contaminant(s) of concern with the released oxidant, 2) the groundwater velocity, 3) the remedial action goal, and 4) the maximum distance along the flow path in which the remedial action goal must be met. In general, lower reaction rates, higher groundwater velocities, lower remedial action goals, and shorter flow path distances will require greater numbers of oxidant cylinders leading to greater costs. Greater natural oxidant demands will also lead to greater costs.

Various engineering approaches can be envisioned to enhance lateral distribution of the released oxidant and in turn increase the spacing between oxidant cylinders. An example is groundwater mixing via constant or intermittent pumping at nearby locations. Depending on the site, installation of a mixing system and use of 5-ft cylinder spacing may be more cost effective than use of 2.5-ft cylinder spacing without mixing. However, the mass-based release rate of the oxidant must be sufficient to achieve the desired degree of contaminant destruction within the available flow path distance. Increasing the cylinder spacing from 2.5 to 5 ft will decrease the oxidant release rate by 50%. The engineer must determine whether this reduction in oxidant release rate is acceptable. Clearly there are several factors that must be considered when designing a system using slow-release oxidant cylinders and subsequently estimating lifecycle costs.

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8.0 IMPLEMENTATION ISSUES

A variety of end-use considerations are relevant when considering and implementing the persulfate cylinder technology for *in situ* treatment of 1,4-dioxane, CVOCs, and other contaminants as follows:

- Technology selection:
    - The intended use of slow-release oxidant cylinders is passive and long-term treatment of contaminated groundwater. This technology can be implemented in remediation wells or via direct push, used as a permeable reactive barrier or a grid, or in a reactive gate in an F&G system. Other technologies that should be considered are pump and treat and in situ bioremediation. The technology selection process conducted as part of a feasibility study will consider effectiveness, implementability, cost, and other factors.
    - The subject technology, because of its sustained and slow-release nature, can be very competitive compared to conventional ISCO applications via permanent injection wells. However, the most common applications are envisioned to be implementation of passive PRBs or funnel and gate systems for treatment of long, dilute plumes as an alternate to pump and treat.
    - Applicable contaminants include those that are capable of being oxidized by chemical oxidants that are released by the oxidant cylinders. Dioxane was demonstrated to be oxidized by unactivated persulfate at this site. It may or may not be oxidized at sufficient rates at other sites and engineering, treatability, or pilot studies should be conducted. Bench-scale treatability/field pilot testing should be conducted using site soil and groundwater.
    - The oxidant selection (i.e., persulfate, permanganate, or a mixture of persulfate and permanganate) should be based on the specific contaminants that are to be oxidized, the oxidant release rate, hydrogeological parameters such as groundwater velocity, and reaction rates. Formation of manganese dioxane crusts around permanganate-only cylinders will decrease the release rate and should be taken into account. In this study CVOCs were capable of being treated sufficiently in spite of the formation of a manganese dioxane crust.
    - Like other in situ techniques, the ultimate goal of utilizing the persulfate cylinders should be to treat the groundwater in an aquifer rather than groundwater in monitoring wells. Therefore, careful consideration should be made prior to deploying the oxidant cylinders in existing monitoring wells at a site because monitoring wells are designed and placed with the intent of monitoring and not remediation. The radius of influence of the cylinders has the potential to be small requiring close cylinder spacing. Existing monitoring wells are unlikely to be spaced appropriately with regard to slow-release oxidant cylinder technology. If oxidant cylinders are placed in monitoring wells, it is likely that groundwater in the monitoring well and only in the immediate vicinity of the monitoring wells will be treated. Groundwater that is not in the immediate vicinity of the monitoring wells is unlikely to be treated.
- Regulatory aspects:

  - Because of its reactive (i.e., oxidizing) nature, persulfate cylinders must be handled and shipped with care and in accordance with all local, state, and federal (i.e., Department of Transportation (DOT) and International Air Transport Association [IATA]) regulations.
  - Upon receipt, the cylinders must be handled and stored in compliant with manufacturer-provided recommendations. Specifically, the cylinders must be stored at a dry and cool environment as they may be subject to degradation via exposure to elevated temperature, moisture and/or light. The cylinders should not be cut under any circumstances because of risk of fire.
  - Similar to conventional ISCO implementation utilizing persulfate, transient pH reduction and metal mobilization may be occurring within the target treatment zone as a result of the persulfate degradation and subsequent generation of sulfuric acid. However, it is also equally important to emphasize the transient nature of these geochemical changes. Specifically, geochemical changes within the treatment zone will likely revert to baseline conditions downgradient of the treatment zone.
- Design:
  - Cylinder spacing and changeout frequency can represent the primary cost drivers for implementing the subject technology. These design parameters can be determined using site-specific hydrogeological characteristics and modeling of oxidant dispersion.
  - The depth of the contaminant plume requiring treatment must also be considered. Because the cylinders are manufactured in 18-inch lengths, a cylinder holder assembly is required to allow for deployment of multiple cylinders encompassing the entire target treatment depth interval.
  - Density driven flow can result in downward migration of the oxidant and associated downward migration of groundwater and dissolved contaminants, as observed in this study. At sites with a relatively flat gradient, an artificial gradient may be required to facilitate the appropriate groundwater transport as well as to prevent density-driven flow issues. Modeling and pilot-scale testing can be conducted to evaluate this potential issue.
  - Reaction rates of released oxidants with targeted contaminants as well as with natural oxidant demand (NOD) must be considered. Measurement of the second-order natural oxidant demand consumption rate using site soil and groundwater is recommended. Conducting a treatability study to determine reaction rates of the released oxidant with target contaminants in the presence of NOD is also recommended.
  - Cylinder deployment in a funnel and gate configuration may be appropriate for certain sites. The cylinders could be placed in wells in the gate or a customized cylinder holder could be used to lower multiple cylinders into a vault that comprises the gate.
- Procurement:
  - The oxidant cylinders can be purchased from Carus Corporation.

  - Equipment for suspending multiple cylinders in wells is not standardized and will engineering design and possible custom fabrication. The simplest approach is to use threaded hooks and eyes that are manually screwed into the ends of cylinders. In this way one or more cylinders can be linked together and suspended. The maximum number of cylinders that can be suspended without the hooks and eyes tearing out of the wax matrix must be evaluated. Other approaches were discussed in preceding sections in this report.

- Modeling and future work:
  - An Excel-based design tool was developed to support conceptual design of site remediation using slow-release oxidant cylinders. The tool simulates oxidant release and its distribution with groundwater flow, along with contaminant destruction based on rates of oxidant release, groundwater movement, natural oxidant demand, and contaminant reaction with oxidant. Based on oxidant distribution and the size of the treatment zone, the tool determines the number of cylinders needed for treatment and the associated costs for purchasing, installing, and changing out the cylinders.
  - A draft version of the tool was distributed to over 30 practitioners and site managers to solicit feedback on the form and function of the tool. The tool was then revised based on their feedback. Unfortunately, the tool, which was verified in the laboratory, could not be field-validated based on site data collected, therefore it has not and will not be publicly released; however, Carus Corporation does use the tool to support their customers in determining the number and spacing of cylinders necessary for managing their sites.
  - An advanced version of the tool is currently in progress that builds upon previous research (Yao et al. 2016). This tool uses numerical methods to solve and simulate oxidant release and reactive transport of oxidant and contaminant in 2-dimensions (in the direction of groundwater flow and lateral to groundwater flow). While the Excel-based tool simulates a single oxidant cylinder and presumes its behavior translates across the site uniformly (i.e., more cylinders behave exactly the same), the 2D tool can incorporate site heterogeneity and simulates multiple cylinders that can be spatially dispersed at user-defined points. Furthermore, the 2D tool calculates cylinder purchase, installation, and change-out costs similar to the Excel tool; however, the 2D tool will have additional functionality. The tool will have an optimization function to automatically spatially distribute cylinders to provide the least cost distribution that effectively treats the site. This work is currently in progress by Clarkson Mathematics Ph.D. candidate Jesse Clark-Stone. Completion is anticipated in 2018.

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