Sites 2 and 12 In-Situ Chemical Oxidation Pilot Study Report Former Fort Ord, California

Prepared for

AHTNA Government Services Corporation (AGSC) 1115 Shore Street West Sacramento, California

Harding ESE Project No. 53900 00171

Damed J. Quing

(for)

Alfonso Ang Project Engineer

Buck King

Buck King, RG, CHG Senior Project Hydrogeologist

April 14, 2003



Engineering and Environmental Services 90 Digital Drive Novato, CA 94949 - (415) 883-0112

Sites 2 and 12 In-Situ Chemical Oxidation Pilot Study Report Former Fort Ord, California

Harding ESE Project No. 53900 00171

This document was prepared by Harding ESE, Inc. (Harding ESE) at the direction of AHTNA Government Services Corporation (AGSC) under the U.S. Army Corps of Engineers (USACE), Sacramento District, for the sole use of the Army, USACE, and the regulatory agencies, the only intended beneficiary of this work. No other party should rely on the information contained herein without the prior written consent of the USACE. This report and the interpretations, conclusions, and recommendations contained within are based in part on information presented in other documents that are cited in the text and listed in the references. Therefore, this report is subject to the limitations and qualifications presented in the referenced documents.

CONTENTS

ACRO	ONYMS	l	v	
1.0	INTRODUCTION			
	1.1 1.2 1.3 1.4	 Project Background. 1.1.1 Site History 1.1.2 Groundwater Remedy Description	1 2 3 3 3	
2.0	PILO	T STUDY METHODS	5	
	2.1 2.2	Pilot Study System Construction 2.1.1 Well Modifications 2.1.2 Pilot Study Chemical Addition System Pilot Study System Operation 2.2.1 Mechanical System Operation	5 5 6 6	
3.0	PILO	2.2.2 Chemical Monitoring T STUDY RESULTS		
5.0	3.1 3.2	Laboratory Water Chemistry Data Pilot Study Field Parameter Data		
4.0	DATA	A ANALYSIS AND INTERPRETATION		
	4.1 4.2 4.3 4.4 4.5	Relative Oxidation of VOCs in Groundwater Potassium Permanganate Concentration Effects Inorganic Chemistry Issues Horizontal Solution Transport and Reaction Vertical Solution Transport and Reaction	17 17 19	
5.0	CON	CONCLUSIONS AND RECOMMENDATIONS		
6.0	REFERENCES			

TABLES

1	Sites 2 and 12 Chemicals of Concern in Groundwater, Aquifer Cleanup Levels, a		
	Discharge Limits		
2	Analytical Methods, Target Analytes, and Practical Quantitation Limits		
3	Sample Collection Schedule		
4	Organic Chemicals Detected at EW-12-01-180U and EW-12-01-180M		
5	Inorganic Chemicals Detected at EW-12-01-180U and EW-12-01-180M		
6	Organic Chemicals Detected at PZ-12-04-180U and PZ-12-04-180M		
7	Inorganic Chemicals Detected at PZ-12-04-180U and PZ-12-04-180M		
8	Organic Chemicals Detected at EW-12-02-180U		
9	Chemical Mass Reduction at EW-12-01-180U		
10	Chemical Mass Reduction at PZ-12-04-180U		

PLATES

- 1 Sites 2 and 12 Site Map
- 2 Pilot Study Site Plan
- 3 Pilot Study Equipment Schematic
- 4 Vinyl Chloride vs. Time
- 5 Cis, Dichloroethene vs. Time
- 6 Tricheoroethene vs. Time
- 7 Tetrachloroethene vs. Time
- 8 Total Organic Carbon vs. Time
- 9 Manganese vs. Time
- 10 Chromium vs. Time
- 11 Hexavalent Chromium vs. Time
- 12 Chloride vs. Time
- 13 Total Dissolved Solids vs. Time
- 14 Total Suspended Solids vs. Time

APPENDIXES

- A Quality Control Summary Report
- B Field Parameter Data
- C Response to Agency Comments

DISTRIBUTION

ACRONYMS

DEFINITION

1,2-DCA 1,1-DCE	1,2-dichloroethane 1,1-dichloroethene
cis-1,2-DCE	cis-1,2-dichloroethene
1,3-DCP	1,3-dichloropropene
ACL	Aquifer Cleanup Levels
AGSC	AHTNA Government Services Corporation
ADR	Automated Data Review
CCA	
CCS	Comprehensive Certificate of Analysis
COC	Contract Compliance Screening Chain of Custody
COC	Chemicals of Concern
%D	Percent Difference
DO	
	Dissolved Oxygen Content Data Quality Objective
DQO EDD	Electronic Data Deliverables
GC/MS	
GAC	Gas Chromatography/Mass Spectrometry Granular Activated Carbon
GPM	
	Gallons per Minute
g/d	Grams per Day
g/min	Grams per Minute
g/L 2/12 CWTD	Grams per Liter Groundwater Treatment Plant – Sites 2 and 12
2/12 GWTP	
H&S	Health and Safety
LCS	Laboratory Control Sample
LDC	Laboratory Data Consultants
MDL MS/MSD	Method Detection Limit
MS/MSD	Matrix Spike and Matrix Spike Duplicate
OU2	Operable Unit 2
PQL	Practical Quantitation Limit
PCE	Tetrachlorethene
PVC	Polyvinyl Chloride
QA/QC	Qualitative Analysis/Quality Control
QCM	Quality Control Manager
QCSR	Quality Control Summary Report
Redox	Oxidation Reduction Potential
%RSD	Relative Standard Deviation
ROD	Record of Decision
RPD	Relative Percent Difference Values
SSHP	Site Safety and Health Safety Plan
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
TSS	Total Suspended Solids
TCE	Trichloroethene

μg/L	Microgram per Liter
mg/L	Milligram per Liter
USACE	U.S. Army Corps of Engineers
VOA	Volatile Organic Analysis
VOC	Volatile Organic Compounds

1.0 INTRODUCTION

On behalf of the U.S. Army Corps of Engineers (USACE) and AHTNA Government Services Corporation (AGSC), Harding ESE, Inc (Harding ESE) prepared this Sites 2 and 12 (Sites 2/12) In-Situ Chemical Oxidation Pilot Study Report (Report). Harding ESE prepared this report under subcontract to AGSC for USACE under Contract DCAA09-00-G-0015, DO No 15.

The pilot study methods and approach were presented in *Sites 2 and 12 In Situ Chemical Oxidation Pilot Study Work Plan* (Work Plan) dated January 4, 2002 (*Harding ESE, 2002a*). The Work Plan presented the technical scope of work and schedule for conducting the pilot study. The purpose of the pilot study was to determine if in-situ chemical oxidation is a feasible technology for reducing vinyl chloride concentrations to levels compatible with the Sites 2/12 system discharge limits (Table 1). The pilot study was conducted to evaluate site-specific conditions associated with in-situ chemical oxidation using potassium permanganate and to establish preliminary design and performance criteria for full-scale implementation.

The remaining portion of Section 1 presents a description of Sites 2/12 project background including site history, description of the Sites 2/12 remediation system, and description of the vinyl chloride plume. Section 1.2 describes purpose of the pilot study. Section 1.3 describes pilot study objectives. Section 1.4 describes the organization of this work plan.

1.1 Project Background

The following section describes Sites 2/12 historical background, existing Sites 2/12 groundwater remediation system, and the Sites 2/12 vinyl chloride plume.

The current status of the Sites 2 and 12 groundwater remediation system summarized in this report is described in further detail in *Revision 0, Sites 2 and 12 Groundwater remedy, Operating Properly and Successfully Evaluation Report, Former Fort Ord California (Harding ESE/IT, 2002b)* and *Annual Evaluation Report, Revision 0, October 2000 through December 2001, Sites 2 and 12 Groundwater Remedy, Former Fort Ord, California* (Harding ESE/IT, 2002c).

1.1.1 Site History

The Sites 2/12 groundwater contamination was first recognized in 1989 following the installation and sampling of monitoring wells during preliminary assessment/site investigation activities. Sites 2/12 groundwater investigation activities have resulted in the installation of 45 monitoring wells and piezometers of which 37 are installed in the Upper 180-foot aquifer and 8 are installed in the Lower 180-foot aquifer (Plate 1). Groundwater sampling and analysis for chemicals of concern (COC) and water level measurements from up to 45 Sites 2 or 12 monitoring wells has been occurring quarterly since 1992 as part of either RI/FS or groundwater monitoring activities.

Investigation and groundwater monitoring data indicate that the COC plume originates at Site 12 and has been transported by groundwater flow about 3000 feet to the southwest passing beneath Highway 1 and into the Site 2 area. The original source of the COC plume is assumed to be historical use and improper disposal of solvents in the Sites 12 area. The Upper 180-foot aquifer COC plume appears to have originated in the Site 12 Lower Meadow area.

The Sites 2/12 COCs are: chloroform, 1,2-dichloroethane (1,2-DCA), 1,1-dichloroethene (1,1-DCE), cis-1,2-dichloroethene (cis-1,2-DCE), total 1,3-dichloropropene (1,3-DCP), tetrachloroethene (PCE), trichloroethene (TCE), and vinyl chloride.

The Upper and Lower 180-foot aquifers are hydraulically separated by the Intermediate 180-foot aquitard; however, low concentrations of COC are occasionally detected below aquifer cleanup levels (ACL) in the Lower 180-foot aquifer. Concentrations of COCs detected in the Lower 180-foot aquifer have not consistently exceeded ACLs and thus the Lower 180-foot aquifer was not identified for groundwater remediation in the Record of Decision (ROD). Lower 180-foot aquifer groundwater monitoring is conducted on a quarterly basis and continues to indicate that COC are below ACLs.

1.1.2 Groundwater Remedy Description

The Sites 2/12 groundwater remedy is defined by the ROD (Army, 1997) and consists of a groundwater pump and treat system designed to remediate Upper 180-foot aquifer groundwater containing COC above ACLs. Treated water is recharged back to the Upper 180-foot aquifer as part of the Sites 2/12 groundwater remedy. Table 1 presents the ACL and treated water discharge levels for the Sites 2/12 COC.

The groundwater remedy was designed to extract groundwater from Site 12 at a system rate of about 300 gallons per minute (gpm) and recharge the Upper 180-foot aquifer at a system total rate of about 600 gpm. The additional 300 gpm of aquifer recharge water was to be provided by the OU 2 system. The aquifer extraction / recharge system is designed to reverse the groundwater flow gradient to flow toward the southeast in the Site 2 area and facilitate groundwater flow from Site 2 to the Site 12 extraction wells. The performance goal of the design was to facilitate groundwater extraction and hydraulic capture of the COC plume while maintaining a groundwater mound at Site 2 adjacent to Monterey bay.

The Sites 2/12 groundwater remedy consists of eight extraction wells located at Site 12, the groundwater treatment plant (2/12 GWTP), and five Upper 180-foot aquifer recharge structures (2 injection wells and 3 infiltration galleries) (Plate 1). System operation consists of Upper 180-foot aquifer groundwater extraction from wells at Site 12. Extracted groundwater is piped to the 2/12 GWTP where COCs are removed by adsorption to granular activated carbon (GAC). The treated water undergoes pH adjustment by sulfuric acid addition and is piped to the five Site 2 aquifer recharge structures. Treated water from the Operable Unit 2 groundwater remedy (OU 2) is piped to the 2/12 GWTP and added to the Sites 2/12 treated water for transfer to the Site 2 aquifer recharge structures.

The eight extraction wells are arranged in four groups of two extraction wells per group. Extraction wells in a group are either screened in the upper part of the Upper 180-foot aquifer or screened in the lower part of the Upper 180-foot aquifer. Extraction wells designated with a "U" at the end of the well name, extract groundwater from the upper portion of the aquifer. Wells designated with a "M" at the end of the well name, extract groundwater from the lower portion of the aquifer.

The five Upper 180-foot aquifer recharge structures consist of three infiltration galleries and two injection wells. Treated water from Site 2 extraction and OU 2 extraction is combined at the 2/12 GWTP and piped to five aquifer recharge structures for the purpose of treated water discharge to the Upper 180-foot aquifer.

Groundwater extraction and treatment first occurred at Sites 2/12 on April 13, 1999. Continuous groundwater extraction and treatment began on May 3, 1999. Diversion of treated effluent from OU2 GWTP to the Sites 2/12 aquifer recharge structures began on June 23, 1999. Since system startup in April 1999, the system has been operating for about 37 months through June 2002.

1.1.3 Vinyl Chloride Presence in Groundwater

Vinyl chloride was originally detected at a limited number of locations at Site 12 during site investigation activities. The vinyl chloride was originally observed in groundwater samples collected from PZ-12-04-180M and hydropunch samples collected during installation MW-12-10-180U, MW-12-10-180M, MW-12-11-180U, and MW-12-11-180M. Groundwater samples from monitoring wells MW-12-10-180U and MW-12-10-180M, MW-12-10-180U, and MW-12-11-180U, and MW-12-10-180M, installed after collection of hydropunch samples did not contain vinyl chloride. Monitoring wells MW-12-10-180U, MW-12-10-180M, MW-12-11-180U, and MW-12-11-180M were converted into Extraction Wells EW-12-01-180U, EW-12-01-180M, MW-12-02-180U, and MW-12-02-180M. After conversion into extraction wells and continuous extraction operation, extracted groundwater contained vinyl chloride at elevated concentrations, which were unanticipated based on previous data associated with wells during monitoring well status.

Throughout system operation, vinyl chloride concentrations greater than anticipated during treatment system design were observed in extracted groundwater from individual extraction wells and in the combined influent to the GAC treatment system. The elevated vinyl chloride concentrations could not adequately be treated by the GAC treatment system and exceeded the discharge compliance limit of 0.1 micrograms per liter (μ g/L) at the treatment system effluent sampling point.

Operational changes to maintain system operation and discharge compliance consisted of turning off extraction wells with elevated vinyl chloride and adjusting the discharge compliance sampling location to incorporate the effect of treated OU2 water sent to the Site 2 aquifer recharge structures. Extraction pumps in EW-12-04-180U and EW-12-04-180M were replaced with larger pumps to increase pumping rates. The current extraction and treatment rate of 240 gpm is achieved by operating EW-12-03-180U, EW-12-04-180U, and EW-12-04-180M.

1.2 Purpose of the In-Situ Chemical Oxidation Pilot Study

The purpose of the pilot study was to determine if in-situ chemical oxidation of vinyl chloride using potassium permanganate is a feasible technology to reduce vinyl chloride concentration in groundwater to a point compatible with the existing groundwater treatment system. The pilot study was designed to provide data for evaluation of effectiveness of in-situ chemical oxidation, and to provide preliminary design parameters for potential full-scale application of the approach.

1.3 In-Situ Chemical Oxidation Pilot Study Objectives

Objectives of the chemical oxidation pilot study were (1) to evaluate the effectiveness of in-situ chemical oxidation were; (2) develop preliminary design parameters for full-scale operation; and (3) to provide site-specific data. Site specific parameters evaluated during the pilot study were as follows:

- Determination of effectiveness of in-situ chemical oxidation of vinyl chloride
- Determination of optimum potassium permanganate concentrations to oxidize vinyl chloride to acceptable levels
- Determination of extraction and injection well locations and flow rates suitable for in-situ oxidation of vinyl chloride.

1.4 Organization of the In-Situ Chemical Oxidation Pilot Study Report

The remainder of this report presents the pilot study methods (Section 2.0), the pilot study results (Section 3.0), data analysis and interpretation (Section 4.0), and conclusions (Section 5.0). The response to regulatory agency comments on the draft submittal are provided in Appendix C.

2.0 PILOT STUDY METHODS

The pilot study methods consisted of construction of the pilot study system (Section 2.1) and operation of the pilot study system (Section 2.2).

2.1 Pilot Study System Construction

The pilot study system construction consisted of: 1) modifying existing groundwater extraction wells and, 2) installation of piping and a chemical addition system.

On February 20, 2002, a pre-construction meeting was held between members of the Army Corps of Engineers, AHTNA, and Harding ESE. Topics discussed during the meeting included installation of the potassium permanganate injection system, operation and maintenance of the system, and health and safety practices during installation, operation, and maintenance of the system. Following the pre-construction meeting, procurement of the components for the potassium permanganate injection system began. System component procurement and installation was completed on March 22, 2002. Plate 2 shows the final injection system configuration. A temporary fence was placed around the pilot study wells, piping, and chemical addition components for site security.

2.1.1 Well Modifications

As described in the Work Plan, the highest vinyl chloride concentrations consistently observed in extracted groundwater occur in the vicinity of extraction wells EW-12-01-180M and EW-12-02-180M. Of these two wells, EW-12-01-180M is located closest to the suspected source area and furthest up gradient within the hydraulic capture zone of the currently operating groundwater extraction wells (EW-12-03-180U, EW-12-04-180U, and EW-12-04-180M). The monitoring wells PZ-12-04-180U and EW-12-01-180M are 64 and 22 feet away from EW-12-01-180U, respectively. Because of the accessibility of the area, the up gradient location, two available monitoring points, and the high vinyl chloride concentration, the pilot study was conducted at Wells EW-12-01-180U and EW-12-01-180M.

Wells EW-12-01-180M and EW-12-01-180U required minor modifications for the in-situ chemical injection pilot study. Well EW-12-01-180M and its existing extraction pump were used as the extraction well. Well EW-12-01-180U was modified for use as the injection well by connecting to the 1-inch diameter, polyvinyl chloride (PVC) existing water level sounding tube. The existing extraction pump in EW-12-01-180U was maintained as operational and used to collect groundwater samples from EW-12-01-180U. Harding ESE and AHTNA technical staff performed the necessary field equipment installation and modifications.

2.1.2 Pilot Study Chemical Addition System

A schematic of the potassium permanganate chemical addition system is shown on Plate 3. The pilot study chemical addition system consisted of a 500-gallon cross-link polyethylene open top tank, liquid metering pump, and groundwater chemical mixing and injection piping. Potassium permanganate solution was metered from the tank by a variable speed, metering pump. The metering pump automatically added potassium permanganate solution to the extracted groundwater. To facilitate mixing of the potassium permanganate solution with the groundwater, the solution was added to the groundwater upstream of a 1 1/2-inch in-line PVC static-tube mixer. The in-line mixer accomplished complete mixing of the groundwater and the potassium permanganate solution prior to injection into the subsurface. Groundwater with potassium permanganate was injected in the well using the 1-inch PVC sounding tube.

The potassium permanganate chemical addition system consisting of the metering pump, mixer, and piping were installed inside of the Well EW-12-01-180U well vault to contain any possible spill of potassium permanganate solution in the event of a system malfunction. Upon final installation of the potassium permanganate chemical addition system, the chemical tank and supply lines was filled with potable water and tested for leaks before adding potassium permanganate.

After the first week of operation of the groundwater extraction and injection system, a 0.5 percent potassium permanganate solution was prepared in the 500-gallon batch tank by manually adding approximately 20.82 pounds of potassium permanganate and 500 gallons of water from a domestic source. Due to the high solubility of the potassium permanganate, manual stirring of the solution was sufficient to achieve complete dissolution of the potassium permanganate.

As discussed in the Work Plan, the anticipated mass loading of vinyl chloride and chlorinated hydrocarbons at the source area was 54.56 grams per day (g/d). Stoichiometric weight ratios for oxidation of chlorinated hydrocarbons dictated that 202.5 g/d (0.141 g/min) of potassium permanganate was required for treating groundwater containing VOCs and pumping at a rate of 10 gallons-per-minute (gpm). However, upon startup of the groundwater pumping and injection system, the observed rate was 14 gpm.

The increase in the groundwater extraction rate from 10 gpm to 14 gpm required a liquid metering rate of approximately 0.5 gallons per hour (gal/hr) for a 0.5 percent potassium permanganate to achieve the 3 ppm solution concentration as described in the Work Plan. Injection of the 0.5 percent potassium permanganate solution began on April 1, 2002.

To create an approximate 100 ppm solution, a 4.2 percent potassium permanganate solution was added at a rate of 2.0 gal/hr to the 14 gpm groundwater flow. The combination of the extracted groundwater at 14 gpm, and the chemical addition rate of 2.0 gal/hr resulted in a calculated 100 ppm concentration of potassium permanganate solution being injected into the subsurface.

Two different sources of potassium permanganate were used during the pilot test. After the decision was made to extend the chemical injection phase and increase the injected chemical concentration, an alternative source of potassium permanganate was identified and used due to inability of the original supplier to supply potassium permanganate. The potassium permanganate used initially was Potassium Permanganate Free Flow Grade Lot #: A-000710, made in India for Carrus Inc. and distributed by Great Western Chemical. The second supply of potassium permanganate was Potassium Permanganate Technical Grade Batch #: 269-274, made in Czech Republic by Spolek Pro Chemicov A Hutni Uyrobu and distributed by LA Chemical (formerly known as Great Western Chemical). The initial chemical supply was used from the beginning until May 16, 2001, when the second chemical supply was used to prepare the potassium permanganate solution for the remainder of the test.

2.2 Pilot Study System Operation

The pilot study system operation is organized into two subsections. Section 2.2.1 describes the mechanical system operation. Section 2.2.2 describes the chemical monitoring activities.

2.2.1 Mechanical System Operation

The potassium permanganate injection system was inspected daily during business days and injection flow rate/volume data and groundwater flow rate/volume data was collected to verify system operation performance during each groundwater sampling event. Additional potassium permanganate solution was prepared on an as needed basis to maintain solution supply and continuous system operation. Solution was prepared at a frequency dependent upon chemical feed rate and overall system operability. Approximately 660 pounds of potassium permanganate dissolved into 2,080 gallons of water were added by the chemical addition system to approximately 1,491,148 gallons of groundwater during the pilot test.

Procedures for conducting the pilot study are described in detail in Section 3.0 of the Work Plan. During the course of the pilot test, operational changes from those described in the Work Plan occurred. The following sections describe the pilot test procedures and deviation from the Work Plan during each phase (pre-startup, potassium permanganate injection, and post injection) of the pilot test.

Pre-Startup

The pre-startup phase of the pilot test took place as described in the Work Plan. The groundwater extraction/injection system was operated for one week (March 25 through March 30, 2002) prior to injection of the potassium permanganate solution.

Chemical Injection

The chemical injection phase of the pilot study consisted of continuous groundwater extraction, potassium permanganate chemical addition, and groundwater injection. As originally outlined in the Work Plan, this phase of the study was to be conducted for a continuous period of 45 days which would subsequently be followed by a post-injection monitoring phase for an additional 45 days. The intent of pilot study plan was to inject the chemical oxidant in the upper well for a period of time and observe the arrival of the chemical oxidant in water extracted from the lower well. Because no evidence of potassium permanganate breakthrough was observed at EW-12-01-180M during the initial 32 days of the 45 day chemical injection phase, the chemical injection phase was extended for an additional 47 days and the concentration of the potassium permanganate solution was increased from approximately 3 ppm to 100 ppm. A 100 ppm solution was selected because it was determined to be maximum concentration that could be created using the existing solution tank, injection pump, and staffing resources. The chemical concentration was increased to compensate for uncertainties associated with the spurious oxidant consumption capacity of the aquifer material that could have been preventing the arrival of the injected chemical oxidant at the lower extraction well.

Injection of the 3 ppm potassium permanganate solution at a continuous rate of 14 gpm began on April 1, 2002, and took place for the first 32 days of operation. On May 2, 2002, the potassium permanganate solution concentration was increased to 100 ppm and the groundwater pumping rate was maintained at 14 gpm for an additional 47 days. On June 20, 2002, after 81 days of chemical addition, the potassium permanganate chemical addition and groundwater extraction and injection was ended after collection of the final set of groundwater samples.

The actual potassium permanganate concentrations measured at the injection well were less than the calculated concentrations. The concentrations measured using the photo spectrometer during the 3 ppm chemical injection phase ranged from 0.6 to 1.2 ppm and averaged 1 ppm. The concentrations measured during 100 ppm phase ranged from 53.6 to 80.6 ppm and averaged 65.7 ppm. The average measured concentrations ranged from 66-percent to 33-percent of the calculated concentration. The potential reason for this discrepancy include error associated with the assumed 14.0 gpm flow rate, error in the chemical feed rate of the metering pump, error in actual potassium permanganate chemical concentrations in chemical solution tank, and error associated collection of water samples. Of the previous listed sources of potential error, the most likely causes of the decreased concentrations are the assumed 14 gpm flow rate, chemical metering pump rate, and chemical solution concentration.

The chemical injection system malfunctioned on three different occasions during system operation. Chemical injection system malfunctions resulted in interruption of potassium permanganate addition to the 14 gpm groundwater flow. The potassium permanganate feed interruptions were relatively short in duration and the systems were repaired and restarted upon recognition of the problem. The following are descriptions of chemical feed malfunction events:

- On Monday May 13, 2002, AHTNA personnel discovered that the tank containing the potassium permanganate solution had run out of solution during the weekend. It is uncertain as to exactly when the injection of potassium permanganate solution stopped during the weekend and an approximate estimate is 12:00 AM May 12, 2002. The potassium permanganate solution tank was refilled and the injection of potassium permanganate solution resumed on May 13, 2002. The groundwater pumping system was not interrupted by the potassium permanganate supply problem. Groundwater samples were collected on May 13, 2002, while the potassium permanganate solution feed interruption the groundwater sample collected on May 13, 2002, from Well EW-12-01-180U reflected the lack chemical oxidizer and contained VOC concentrations similar to the source water from Well EW-12-01-180M.
- On May 15, and May 25, 2002, AHTNA personnel discovered that the potassium permanganate injection feed line had separated from the metering pump and that the potassium permanganate supply had stopped. Based on the volume of potassium permanganate solution that was metered into the well vault the duration of the supply interruptions were estimated to be 12 and 6 hours for the May 15 and May 25 events, respectively. The well vault contained the potassium permanganate solution. Upon discovery of the malfunction, the injection line was reconnected to the metering pump and injection of the potassium permanganate solution resumed. The groundwater pumping system was not interrupted to repair the injection line. The potassium permanganate solution feed interruptions were discovered and repaired in between groundwater sampling events. No apparent effects were observed in the VOC concentration results from subsequent groundwater sampling events.

Post Chemical Injection Phase

No post-chemical injection phase was implemented following the high-concentration potassium permanganate injection phase. Operation of the potassium permanganate chemical addition system was completed on June 20, 2002. Post chemical addition monitoring data was not conducted by the pilot study. Post chemical addition monitoring data is provided by the monthly groundwater sampling of the eight Site 12 extraction wells including EW-12-01-180M, EW-12-01-180U, and EW-12-02-180U associated with Sites 2 and 12 groundwater treatment system operation.

2.2.2 Chemical Monitoring

The monitoring strategy for the pilot study consisted of sampling groundwater at the extraction point EW-12-01-180M and injection point EW-12-01-180U for evidence of potassium permanganate oxidation of vinyl chloride. Groundwater monitoring was also conducted at PZ-12-04-180U and PZ-12-04-180M (nearest groundwater monitoring points) to identify additional evidence of oxidation of vinyl chloride (and other VOCs). Groundwater chemistry data from monthly groundwater treatment system sampling of Sites 2/12 extraction wells was also used to evaluate pilot study effects. Table 2 lists the chemical test methods, associated analytes list, and practical quantitation limits.

Extracted groundwater from EW-12-01-180M was monitored to characterize the pilot study source water prior to chemical addition. Injected water consisting of the source water with the addition of potassium

permanganate was collected from EW-12-01-180U using the extraction well pump while injection was taking place and used to evaluate the effect of chemical addition and injection. The piezometers PZ-12-04-180U and PZ-12-04-180M were monitored to evaluate spatial distribution of chemical parameters. The down gradient extraction well EW-12-02-180U results were monitored to evaluate spatial distribution of in-situ oxidation.

Pilot study water samples were analyzed for; volatile organic compounds (VOC), total organic carbon (TOC), chloride, and dissolved metals including manganese, chromium, and hexavalent chromium to evaluate oxidation process. Water samples were analyzed for potassium permanganate concentrations in the field using a Spectronic Genesys 10 visible light photo spectrometer. Other field parameters collected during water sampling included dissolved oxygen (DO), oxidation-reduction potential (Redox), electrical conductivity, pH, and temperature.

Additional analyses were performed on water samples to evaluate general water quality trends associated with the pilot test. Samples were analyzed for chloride, total dissolved solids (TDS), and total suspended solids (TSS). These data were used to evaluate general chemistry, saltwater intrusion, and mixing phenomena.

Table 3 lists the groundwater sample schedule for samples collected during the pilot study. Rationale for the sample collection schedule is further described in the Work Plan in Section 3.0. Field sampling procedures and laboratory analysis requirements are presented in Section 4.0 of the Work Plan.

3.0 PILOT STUDY RESULTS

The pilot study results consist of chemical analytical data and field parameter data. The organic and inorganic laboratory analytical data collected at EW-12-01-180U and EW-12-01-180M are listed in Table 4 and Table 5, respectively. The organic and inorganic laboratory analytical data collected at PZ-12-04-180U and PZ-12-04-180M are listed in Table 6 and Table 7, respectively. The organic laboratory analytical data collected at EW-12-02-180U is listed in Table 8.

The pilot study monitoring results from the four wells are also presented graphically as charts of concentration over time to allow for data analysis. Plate 4 through 8 are time concentration graphs of organic analytes; vinyl chloride, cis-1,2-DCE, TCE, PCE and TOC. Plates 9 through 11 are time concentration graphs of dissolved metals: manganese, chromium, and hexavalent chromium. Plates 12 through 14 are graphs of chloride, TDS, and TSS. The reporting limit is used to represent concentration on time concentration graphs in cases where chemicals were not detected.

3.1 Laboratory Water Chemistry Data

Groundwater samples were collected and submitted to Sequoia Analytical (Sequoia) in Petaluma and in Morgan Hill, California. Submitted samples were analyzed for volatile organic compounds (VOCs) by EPA Test Method 8260 and total organic carbon (TOC) by EPA Test Method 415.1. Samples were analyzed for inorganic analytes consisting of dissolved metal concentrations by EPA Test Method 6010B, hexavalent chromium by EPA Test Method 7196A, mercury by Test Method 7470A, and chloride by EPA Test Method 300.0. In addition, analyses for total dissolved solids (TDS) by EPA Test Method 160.1 and total suspended solids (TSS) by EPA Test Method 160.2 were also conducted.

All analytical data generated during the pilot study were reviewed and validated according to the procedures specified in the *Draft Final Chemical Data Quality Management Plan* (CDQMP), *Former Fort Ord Complex, Monterey County, California* (*HLA, 1997*), as well as the *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review* (October 1999) and *USEPA Contract Laboratory Program National Functional Functional Guidelines for Inorganic Data Review* (February 1994). Laboratory Data Consultants (LDC), an independent subcontract to Harding ESE, performed the data validation task. Data validation results are presented in the form of qualifiers associated with the chemical data presented in Tables 4 through 7 and in Appendix A.

Organic Compounds

The pilot study collected 84 samples for VOC analyses from the four monitoring locations over March 25 through June 20, 2002 88-day pilot study period. The chemicals PCE, TCE, and cis-1,2-DCE were detected in all 84 samples. As anticipated, the highest levels of VOC concentrations were detected in samples from wells EW-12-01-180M and PZ-12-04-180M, which are screened in the lower portion of the Upper 180-foot aquifer and have historically contained the highest concentrations at Sites 2/12. A total of 56 samples were analyzed for TOC during the pilot study.

The VOC data from the four pilot study sampling locations displayed cyclical concentration patterns consistent with tidal fluctuations previously observed in the area (Plate 4 though 7). The concentration fluctuations are thought to be the result of changing groundwater flow gradients and flow direction in the vicinity of monitoring points associated with the incoming and outgoing tides.

The highest VOC concentrations monitored at EW-12-01-180M were TCE and cis-1,2-DCE at 260 μ g/l and 190 μ g/l, respectively. The highest VOC concentrations monitored at PZ-12-04-180M were TCE and

cis-1,2-DCE at 370 μ g/l and 460 μ g/l, respectively. Vinyl chloride concentrations were detected in 59 of the 84 samples collected. The maximum vinyl chloride concentration detected at EW-12-01-180M was 3.4 μ g/l and at PZ-12-04-180M was 5.4 μ g/l.

Groundwater samples collected from well EW-12-01-180U reflected the effects of potassium permanganate addition and contained reduced levels of VOCs as compared to the pilot study source water collected from EW-12-01-180M. The highest reported TCE and cis-1,2-DCE,concentrations were 200 μ g/l and 150 μ g/l, respectively. Vinyl chloride concentrations were not detected, or detected at reduced concentrations, in samples from EW-12-01-180M reflecting the effects of chemical oxidation.

The maximum vinyl chloride concentration of 2.0 μ g/l measured at EW-12-01-180U was associated with a malfunction of the chemical addition system. Vinyl chloride detection limits for samples from EW-12-01-180U varied throughout the project as a result of sample dilution required for analysis of other target compounds. The analytical laboratory successfully reduced EW-12-01-180U vinyl chloride detection limits as the study proceeded allowing for quantification of vinyl chloride concentration reductions not possible due to elevated detection limits present in the beginning of the study.

Potassium permanganate (Appendix Table B1) and VOC chemical data (Table 4) collected May 13, 2002, following an approximately 1-day interruption in the potassium permanganate addition indicates that potassium permanganate concentrations dropped from 53.6 ppm to 2.3 ppm and VOC concentrations increased at the injection well to approximately equal those from the extraction well. The only VOC that did apparently decrease with out the addition of potassium permanganate was vinyl chloride, which decreased from 2.1 to 2.0 μ g/l. The vinyl chloride concentration reduction of approximately 5-percent is less than the 10 percent range of sampling error typically accepted and associated with this highly volatile compound. The potassium permanganate supply interruption event demonstrates the instantaneous effects associated with ending potassium permanganate addition, and shows that injection well monitoring does not dilute or reduce VOC concentrations, permanganate concentrations decrease relatively quickly, and the instantaneous VOC oxidation process stops.

The TOC concentrations declined over time for all four wells monitored during the pilot study (Plate 8). TOC concentrations ranged from a high of 64 mg/L in well PZ-12-02-180U to a low of 1.5 mg/L in well EW-12-01-180U. By the end of the pilot study, TOC concentrations for all four wells ranged from 2.2 mg/L to 4.1 mg/L.

Inorganic Compounds

The pilot study collected 56 sets of inorganic analyses from the four locations over the 88-day period. Samples were analyzed for dissolved metals including manganese, chromium, hexavalent chromium, chloride ion, TDS, and TSS.

Barium, manganese, hexavalent chromium, chromium, zinc, and mercury were the most frequently detected dissolved metals during the pilot study. Barium was detected in 100 percent of samples analyzed. Manganese was detected in 70 percent of samples analyzed. Hexavalent chromium was detected in 37 percent of samples analyzed. Chromium was detected in 32 percent of samples analyzed. Zinc was detected in 19 percent samples analyzed. Mercury was detected in 16 percent of samples analyzed.

Dissolved barium was detected in all samples analyzed well below the MCL of 2000 μ g/l. Barium concentrations remained relatively constant for the four wells throughout the study. The highest barium concentration was detected in well PZ-12-04-180M at 77 μ g/l.

Hexavalent chromium was detected in 21 of 56 samples analyzed with a maximum value of 100 μ g/l detected in the last sample collected from PZ-12-04-180U. The pattern of detected concentrations remained relatively constant for four wells during the pilot study with PZ-12-04-180U experiencing the most frequent number of detections. Elevated detection limits for the last three sample from EW-12-01-180U obscure the fact that hexavalent chromium was not detected in this well during the study (Plate 11).

Chromium was detected in 18 of 56 samples analyzed with 4 samples from PZ-12-04-180U exceeding the MCL of 100 μ g/l. Dissolved chromium concentrations increased at EW-12-01-180U, EW-12-01-180M and PZ-12-04-180U during the pilot study (Plate 10). The dissolved chromium concentrations remained relatively unchanged during the first 51 days of the pilot study. The chromium concentration at PZ-12-04-180U increased significantly 51 days into the study and reached a maximum value of 240 μ g/l at the end of the study. The chromium concentrations in Well EW-12-01-180U increased from less than 10 μ g/l to as high as and 52 μ g/l during the last 20 days of the pilot study. The chromium concentration in well EW-12-01-180M increased during the last 13 days of the pilot study, from less than 10 μ g/l to the highest value of 43 μ g/l at the end of the study.

Zinc was detected in 11 of 56 samples analyzed with a maximum value of 180 μ g/l in a sample from PZ-12-04180U well below the MCL of 5000 μ g/l.

Mercury was detected in 9 of 56 samples analyzed with the majority of the detection occurring in samples from PZ-12-04-180U. The maximum mercury concentration was $3.1 \,\mu g/l$, which was also the only result exceeding the MCL of 2 $\mu g/l$. The isolated elevated mercury concentration occurred at PZ-12-04-180U after 51 days of the pilot study.

Thallium was detected in 2 of 56 samples analyzed with the only detections occurring in samples from EW-12-01-180U. The thallium concentrations detected were 100 and 110 μ g/l approximately at the EPA Method 6010 PQL of 100 μ g/l. The detected thallium concentrations exceeded the MCL of 2 μ g/l. The thallium concentrations were detected in samples collected on June 6 and June 13 at EW-12-01-180U. The large majority of non-detectable concentrations of thallium at all the wells suggest that the two instances of detectable concentrations are anomalous.

Chloride results for wells EW-12-01-180U, EW-12-01-180M, and PZ-12-04-180M indicated an increase in concentrations during the pilot study. The chloride concentration over time (Plate 12) clearly shows the concentration increase. Chloride levels in EW-12-01-180U and EW-12-01-180M increase from a low of 45 mg/l and 50 mg/l, respectively, to a high of 86 mg/l and 84 mg/l, respectively by the end of the pilot study. Well PZ-12-04-180M had the highest chloride levels ranging from 44 mg/l to 140 mg/l. Chloride levels in well PZ-12-04-180U decreased from 100 mg/l to 84 mg/l at the end of the pilot study.

The TDS concentration results for wells EW-12-01-180U, EW-12-01-180M, and PZ-12-04-180M indicated an increase in concentrations during the pilot study. The TDS concentration over time (Plate 13) shows the concentration increased slightly for wells EW-12-01-180U and EW-12-01-180M. TDS for wells EW-12-01-180U and EW-12-01-180M ranged from 320 mg/l to 480 mg/l and 260 mg/l to 440 mg/l, respectively. Well PZ-12-04-180M had the greatest increase in TDS concentration, which ranged from 270 mg/l to as high as 710 mg/l. The last collected groundwater sample from PZ-12-01-180M contained a 530 mg/l TDS concentration. The TDS concentrations for well PZ-12-04-180U remained relatively stable, and ranged from 380 mg/l to 480 mg/l

The TSS concentration for wells EW-12-01-180U, EW-12-01-180M, and PZ-12-04-180M remained relatively constant throughout the pilot study (Plate 14). The TSS concentrations declined in well PZ-12-04-180U from 320 mg/l in the initial sample to 25 mg/l by the end of the pilot study. The TSS

concentrations in well PZ-12-04-180M varied throughout the study from a high of 100 mg/L to a low of 23 mg/L.

3.2 Pilot Study Field Parameter Data

Field parameters collected during the pilot study included potassium permanganate ion concentration, dissolved oxygen, Redox, electrical conductivity, pH, and temperature. Field parameter data collected during the pilot study along with time concentration graphs are in Appendix B.

Photo Spectrometric Analysis of Potassium Permanganate Ion

Dissolved potassium permanganate concentrations were analyzed using standard photo spectrometric methods. A calibration curve was developed by measuring absorbency of various potassium permanganate solutions at a wavelength of 533 nanometers (as recommended by the equipment manufacturer). Standard potassium permanganate solutions were prepared at various concentrations and a concentration versus absorbency curve was plotted. Once plotted, a best-fit, straight trend line was plotted over the obtained curve and a liner equation derived from the straight trend line. The equation was then used to obtain potassium permanganate ion concentration of collected field samples into parts per million (ppm). Separate calibration curves were prepared for the two separate potassium permanganate supplies used during the study.

Measured potassium permanganate ion concentration at the injection well EW-12-01-180U varied from 0.6 ppm to 1.2 ppm during the 3 ppm concentration injection phase and 51.5 ppm to 80.6 ppm during the 100 ppm concentration injection phase. Potassium permanganate ion concentrations remained relatively constant throughout the study at extraction well EW-12-01-180M and monitoring well PZ-12-04-180M.

Visual evidence of potassium permanganate ion concentrations were observed (pink color) and measured in groundwater collected from monitoring well PZ-12-04-180U on May 23, 2002 after 52 days of chemical addition. The presence of potassium permanganate at PZ-12-04-180U was subsequently observed throughout the remainder of the pilot study. Measured potassium permanganate ion concentration for PZ-12-04-180U ranged from 2.1 ppm to 13.4 ppm.

Visual evidence of potassium permanganate ion (pink color) was also observed during the June 24, 2002 sampling of EW-12-02-180U. The visual observation of the presence of potassium permanganate was not verified by conducting a field photo spectrometric analysis.

Dissolved Oxygen and Redox Data

Dissolved oxygen (DO) and Redox data were collected during each groundwater sampling event. DO readings indicated an average increase of DO concentrations between wells EW-12-01-180M (extraction well) and EW-12-01-180U (injection well) of 65%. Measured DO readings ranged from 2.91 mg/L to 6.94 mg/L for EW-12-01-180M and 5.38 mg/L to 9.32 mg/L for EW-12-01-180U. In addition, collected readings also indicated an increase of DO in well PZ-12-04-180U. DO readings for PZ-12-04-180U ranged from 2.34 mg/L (baseline) to as high as 6.7 mg/L. Well PZ-12-04-180M DO readings were the lowest and fluctuated from 0.93 mg/L to 4.03 mg/L throughout the pilot study.

Redox data collected during the latter part of the pilot study indicated an increase of Redox in all the wells. Redox measurement collected between April 11 and April 20 are inaccurate due to a meter operation problem that was corrected starting with the April 22 sampling. Baseline Redox readings collected on March 28, 2002 were 153 millivolts (mv) 9 mv, 135 mv, 118 mv, and 31 mv for wells EW-12-01-180U, EW-12-01-180M, PZ-12-04-180U, and PZ-12-04-180M, respectively. Highest measured

Redox readings during the high potassium permanganate concentration injection phase were 668 mv, 369 mv, 600 mv, and 512 mv for wells EW-12-01-180U, EW-12-01-180M, PZ-12-04-180U, and PZ-12-04-180M, respectively. Measured Redox readings for well EW-12-01-180U increased from 190 mv to as high of 668 mv.

Conductivity, pH, and Temperature

Conductivity, pH, and temperature readings collected during the pilot study remained relatively constant for each of the monitoring locations. Conductivity readings fluctuated between 500 micro siemens per centimeter (μ s/cm) and 700 μ s/cm with the exception of well PZ-12-04-180M, which increased from 400 μ s/cm to 800 μ s/cm by the end of the pilot study. The increase of conductivity could be attributed to influx of salt water captured by the groundwater extraction/reinjection system. Temperature and pH readings remained constant for all four wells throughout the study and ranged from 15° C to 20° C and 6 to 8, respectively.

4.0 DATA ANALYSIS AND INTERPRETATION

The pilot study data was evaluated for evidence of in-situ chemical oxidation of vinyl chloride and information relevant to its application as a treatment technology for Sites 2/12. The data was evaluated to address the following aspects of the in-situ chemical oxidation process:

- Relative oxidation of VOC compounds in groundwater
- Effectiveness of relative potassium permanganate solution concentrations
- Inorganic chemistry implications of in-situ chemical oxidation process
- Horizontal groundwater transport of injected potassium permanganate and VOC plume reduction
- Vertical groundwater transport of injected potassium permanganate and VOC plume reduction.

The following five sections address the five issues previously described.

4.1 Relative Oxidation of VOCs in Groundwater

The pilot study results display evidence of VOC mass reduction resulting from the addition of potassium permanganate. Evidence of VOC mass reduction was observed at EW-12-01-180U, PZ-12-04-180U, and EW-12-02-180U. Evidence of VOC mass reduction was in the form of either decreasing concentrations associated with the addition of potassium permanganate (EW-12-01-180U) or decreasing VOC concentrations associated with the arrival of potassium permanganate at the monitoring point (PZ-12-04-180U) and EW-12-02-180U).

Well EW-12-01-180U

Beginning on April 1, 2002 following the collection of groundwater monitoring samples, the addition of potassium permanganate was initiated to the water being injected into EW-12-01-180U. Comparison of VOC data from EW-12-01-180U with EW-12-01-180M was done for each of the 26 sets of samples collected after initiating potassium permanganate addition. The data were used to estimate percent reduction of a VOC concentration for a sample set. All samples showed VOC percent reduction with the only exception being equal (zero percent decrease) TCE concentrations monitored on May 13, 2002, when the potassium permanganate feed system malfunctioned.

The 26 sets of VOC percent mass reduction data were used to estimate average percent mass reduction statistics. Table 9 lists the sampling event and average percent reduction of vinyl chloride, cis-1,2-DCE, and TCE at EW-12-01-180U.

Inspection of Table 9 and Plates 4 through 6 indicate that, vinyl chloride, cis-1,2-DCE and TCE were consistently reduced in correlation with the potassium permanganate addition. The apparent VOC mass reduction appeared to be greater with the 3 ppm potassium permanganate then the subsequent 100 ppm potassium permanganate. The average percent mass reduction of 63-percent for vinyl chloride generally equated to vinyl chloride concentrations ranging from 2.0 to 3.4 μ g/l consistently being reduced to less than 1.0 μ g/l.

The well EW-12-01-180U was used to inject EW-12-01-180M extracted groundwater containing relatively high concentrations of VOCs for a 7-day period before initiating the potassium permanganate

chemical addition. During the initial 7-day pumping period, groundwater samples collected from EW-01-01-180U contained VOC concentrations that increased with time and approached the chemical concentrations of the source water from EW-12-01-180M. The TCE concentration monitored at EW-12-01-180U increased from 5.5 μ g/l to 190 μ g/l, approaching the 220 μ g/l monitored in the source water from EW-12-01-180M. The vinyl chloride concentration monitored at EW-12-01-180U increased from non detect at 0.01 µg/l to 1.1 µg/l approaching the 1.9 µg/l monitored in the source water from EW-12-01-180M. The TCE and vinyl chloride data suggests that the initial process of injecting water with high concentrations of VOCs into the upper portion of the aquifer at 14 gpm requires more than 7 days of operation to create conditions where injected water reflects chemistry of extracted water. The apparent mass reduction associated with sampling is greatest for vinyl chloride and is less than 20 percent during beginning of the study and less than 5-percent during the May 13, 2002, sampling event. Although concentration reduction associated with sample error is apparent, the 5-percent mass reduction observed in the May 13 results is considered representative of the study and is much less than the 63-percent apparent mass reduction associated with the potassium permanganate oxidation. The 5-percent error associated with vinyl chloride sampling is within the range of acceptable sampling error and represents the most significant level of error associated with the VOC mass reduction estimates.

Well PZ-12-04-180U

Initial potassium permanganate arrival at PZ-12-04-180U was observed in the form of increased Redox readings on May 9, 2002, after 39 days of potassium permanganate addition. Visual confirmation of potassium permanganate was observed on May 23, 2002, after 53 days of system operation. In association with the apparent arrival of potassium permanganate oxidation front on May 9, VOC mass reduction was observed in 6 subsequent sets of weekly samples collected from May 16, 2002, through June 20, 2002. The 6 sets of VOC percent mass reduction data were used to estimate average percent mass reduction statistics. Table 10 lists the sampling events and average percent mass reduction of cis-1,2-DCE and TCE for PZ-12-04-180U. Vinyl chloride percent mass reduction could not be determined because of the lack of detectable concentrations of vinyl chloride at PZ-12-04-180U. The average percent mass reduction of 23-percent for cis-1,2-DCE equated to a concentration of 26 μ g/l observed on May 9, 2002 being sequentially reduced to concentrations ranging from 20 to 4.3 μ g/l.

Potassium permanganate chemical arrival at PZ-12-04-180U occurred 7 days after initiating the 100 ppm potassium permanganate injection. The potassium permanganate concentration increase may have increased the area of potassium permanganate influence by either advancing the oxidation front previously established by the 3 ppm solution injection or by physically increasing the dissolved solution plume due to the solution concentration increase.

Well EW-12-02-180U

Evidence of potassium permanganate arrival was observed as a color change in extracted groundwater collected from EW-12-01-180U as part of monthly system monitoring. The vinyl chloride, cis-1,2-DCE and TCE concentrations observed in June 24, 2002, sampling results were much lower than those observed in the preceding monitoring events (Table 8). The apparent percent mass reduction between the May 2002 and June 2002 sample results for vinyl chloride, cis-1,2-DCE and TCE was 86 percent, 99.9 percent and 99.5 percent, respectively. This apparent VOC percent mass decrease may be related to the operation of EW-12-04-180U as an extraction well. EW-12-02-180U was turned off on June 5, 2002 due to treatment plant operations. The 19-day period of no pumping from this well prior to the June 24, 2002 sampling could bias the direct comparison of May and June results.

4.2 Potassium Permanganate Concentration Effects

The pilot study tested two different potassium permanganate concentrations of approximately 3 ppm and 100 ppm. Observations regarding the relative effectiveness of the two testing concentrations are limited to results from injection well EW-12-01-180U. As previously described in Section 4.1, the apparent instantaneous VOC mass reduction appeared to be greater using the 3 ppm solution than with the subsequent 100 ppm solution.

Oxidant transport is reaction limited because the oxidants are being depleted as they move through the subsurface. Injection of higher concentrations of permanganate can provide greater diffusion and can result in greater permanganate persistence. However injection of greater permanganate concentrations can also result in lower treatment efficiency because the matrix demand can be greater at larger oxidant concentrations (*ITRC*, 2001).

4.3 Inorganic Chemistry Issues

Inorganic chemistry phenomena were identified during review of the pilot study inorganic chemistry data or were identified for evaluation in the Work Plan. Inorganic chemistry issues are presented according to chemical analyte and location observed.

Dissolved Chromium and Hexavalent Chromium

Dissolved chromium and/or hexavalent chromium were detected at concentrations exceeding either State or Federal MCLs in multiple samples collected at PZ-12-01-180U and a single sample collected at EW-12-01-180U.

PZ-12-041-80U

Hexavalent Chromium was detected at a concentration of 73 μ g/l above the California MCL for total chromium of 50 μ g/l in the background sample collected from PZ-12-04-180U before potassium permanganate chemical addition was initiated. The PZ-12-04-180U background sample collected on March 28, 2002 displayed hexavalent chromium and dissolved chromium results that did not agree with each other. Hexavalent chromium was detected at 73 μ g/l and the dissolved chromium was not detected at a reporting limit of 10 μ g/l. The reason for the discrepancy in analytical results is unknown. Hexavalent chromium was detected in the majority of samples (10 of 13) collected from PZ-12-04-180U at concentrations up to 100 μ g/l. Dissolved chromium was detected in conjunction with hexavalent chromium in 5 of the 10 samples.

Dissolved chromium was first detected at 110 ug/l in the May 9, 2002 sample collected at PZ-12-04-180U in association with the arrival of the chemical oxidation front and onset of VOC reduction. Dissolved chromium was detected in all the subsequent samples collected at PZ-12-04-180U at concentrations exceeding the California total chromium MCL of 50 μ g/l up to a maximum concentration of 240 μ g/l in the last sample collected during the pilot study.

The presence of hexavalent chromium in the PZ-12-04-180U initial background sample and subsequent samples may be related to the well construction. The three piezometers PZ-12-04-180U, PZ-12-04-180M, and PZ-12-04-180L were constructed in a common borehole. Each piezometer was constructed of 2-inch diameter galvanized steel pipe with a 10-foot long stainless steel well screen. The galvanized steel piezometer pipe and stainless screen material are likely affected by galvanic reactions between the metal materials and brackish groundwater associated with local sea-water intrusion. The stainless steel well screen material and the electrochemical environment are a likely source of the hexavalent chromium and

dissolved chromium observed as PZ-12-04-180U. The mobilization of chromium from the well materials would be exacerbated by the arrival of the potassium permanganate oxidation front.

Chromium is a metal that is more mobile in an oxidized state and is a recognized redox sensitive metal that can be mobilized under oxidizing conditions. Typically metals, including chromium, mobilized by in-situ oxidization activities are reabsorbed/precipitate after the oxidizer is consumed and the groundwater returns to background redox conditions.

EW-12-01-180U

Dissolved chromium was detected at a concentration of 52 μ g/l above the State of California MCL of 50 μ g/l in 1 out of 15 samples collected at EW-12-01-180U. Hexavalent chromium was not detected in any of the samples collected at EW-12-01-180U. Dissolved chromium was detected in 8 of the 12 samples collected at EW-12-01-180U and with the exception of the one MCL exceedance the observed chromium concentrations were below regulatory action levels.

Possible sources of the dissolved chromium observed at EW-12-01-180U include: 1) the stainless steel extraction well components including the well screen, submersible pump, and discharge pipe, 2) trace metal contamination of the potassium permanganate chemical supply, and 3) chromium bearing minerals in aquifer material. The pattern of chromium detection and chromium concentration increase suggests that the elevated occurrence of chromium to concentrations exceeding the MCL may be related to potassium permanganate chemical supply used during the final three weeks of chemical addition.

Dissolved Manganese

Dissolved manganese concentrations increased at EW-12-01-180U and PZ-12-04-180U to levels exceeding the secondary MCL of 50 μ g/l. The elevated dissolved manganese concentrations observed at wells EW-12-01-180U and PZ-12-04-180U were as high as 22,000 μ g/l and 3,500 μ g/l, respectively. The elevated manganese concentration of 22,000 μ g/l observed at EW-12-01-180U is less than 34,600 μ g/l, which is the estimated manganese concentration associated with a 100 ppm potassium permanganate concentration. The exceedance of the secondary MCL of 50 μ g/l for manganese is directly related to the potassium permanganate chemical addition. The dissolved manganese concentrations are expected to decrease to levels below the secondary MCL as permanganate (MnO₄) is decomposed via the oxidation process and manganese is precipitated as relatively insoluble manganese oxide.

Dissolved Mercury

Dissolved mercury was detected at PZ-12-04-180U above the MCL of 2 μ g/l on one occasion at a concentration of 3.10 μ g/l. The single instance of a mercury concentration exceeding the MCL occurred with the initial arrival of the potassium permanganate solution at PZ-12-04-180U. The subsequent samples collected from PZ-12-04-180U contained consistent but lower mercury concentrations ranging from 0.33 to 0.42 μ g/l well below the MCL. The anomalous instance of elevated mercury is thought to reflect the solution oxidation front moving through the piezometer area, and representative of typical conditions associated with the chemical oxidation process. Similar to the anomalous detections of hexavalent chromium at PZ-12-04-180U, the piezometer construction and well materials may be the source of the elevated mercury.

Dissolved Thallium

Dissolved thallium was detected in 2 of the 12 samples collected from EW-12-01-180U. The dissolved thallium EPA Method 6010 PQL of 100 μ g/l is well above the MCL of 2 μ g/l. The dissolved thallium was detected in two samples collected sequentially during the last three weeks of chemical addition. Trace metal contamination of the potassium permanganate chemical supply may have been the source of the detected dissolved thallium. The relatively infrequent detection of dissolved thallium at EW-12-01-180U suggests that thallium is not persistently present at this location. Future sampling and analysis for thallium should be conducted using analytical methods such as EPA Method 7841, which provide PQLs that are lower than the MCL.

Other Dissolved Metals

Dissolved antimony, arsenic, barium, beryllium, copper, molybdenum, nickel, selenium, silver, vanadium, and zinc concentrations were not observed to detrimentally affect groundwater quality during the pilot study.

Additional testing and monitoring of chromium and hexavalent chromium concentration should be conducted at EW-12-01-180U, PZ-12-04-180U, and EW-12-02-180U to evaluate the long-term impacts of the potassium permanganate chemical oxidation test. Test results would document persistence of chromium and hexavalent chromium concentrations.

4.4 Horizontal Solution Transport and Reaction

Evidence of horizontal potassium permanganate solution transport and VOC oxidation were observed at PZ-12-04-180U and at EW-12-02-180U.

PZ-12-04-180U

Evidence of potassium permanganate arrival at PZ-12-04-180U was in the form of increased Redox reading in the sample collected on May 9, 2002, evidence of VOC reduction first observed on May 16, 2002, visual identification and increased dissolved manganese concentrations observed on May 23, 2002 along with reductions of VOCs.

The horizontal distance between EW-12-01-180U and PZ-12-04-180U is approximately 63 feet. The first evidence of potassium permanganate arrival at PZ-12-04-180U took approximately 39 days after initiating the potassium permanganate injection. The potassium permanganate transport velocity was approximately 1.6 feet per day based on 63-foot distance and 39 day duration. The orientation of EW-12-01-180U to PZ-12-04-180U is approximately cross gradient to average regional groundwater flow.

EW-12-02-180U

The arrival of potassium permanganate solution was based on the visual recognition of discolored water during the June 24, 2002 monthly groundwater treatment system sampling. The apparent arrival of potassium permanganate at EW-12-02-180U was coincident with a significant reduction in VOCs. The horizontal distance between EW-12-01-180U and EW-12-02-180U is approximately 750 feet. The potassium permanganate arrived at EW-12-02-180U approximately 86 days after initiating the potassium permanganate injection. The potassium permanganate transport velocity was approximately 8.7 feet per day based on 750-foot distance and 86 day duration. Well EW-12-02-180U is directly down gradient of EW-12-01-180U and the solution transport reflects a combination of the ambient groundwater flow gradient and the hydraulic capture of the operating Sites 2/12 groundwater remediation system. The

preliminary results from the July 2002 monthly operations and maintenance program sampling suggest that significant reduction of VOCs at this extraction point.

4.5 Vertical Solution Transport and Reaction

Although the groundwater extraction and groundwater injection system was operated at 14 gpm for 88 days, no evidence of vertical transport or chemical reaction was observed. The lack of evidence for vertical chemical transport suggests that anisotropic hydraulic conductivity and groundwater flow preferentially favor horizontal groundwater flow to vertical groundwater flow.

Assumptions made in the Work Plan (Section 2.5.2) concerning vertical hydraulic conductivity ranging from 20 to 200 feet per day are reduced based on pilot study results to estimates ranging from 0.2 to 2 feet per day for future vertical groundwater flow analysis.

5.0 CONCLUSIONS AND RECOMMENDATIONS

The results of the pilot study indicate that potassium permanganate solutions of approximately 3 to 100 ppm are effective at reducing average groundwater vinyl chloride concentrations up to a maximum of 63 percent by mass at the point of injection. The pilot test results indicate that instantaneous oxidation reaction effectiveness is greater at the 3 ppm injection concentration than for the 100 ppm injection concentration.

Based on the results observed at PZ-12-04-180U, the potassium permanganate solution appears to disperse into the surrounding aquifer and effectively reduce VOCs along with other total organic carbon in groundwater. The inorganic chemical results indicate that with the exception of manganese, chromium mercury, and thallium, the potassium permanganate solution is compatible with local geochemical conditions. The data indicate that dissolved manganese concentrations in groundwater exceed the secondary MCL as a direct result of potassium permanganate addition; however, the concentration of manganese is expected to decline to acceptable levels as the source of the manganese (potassium permanganate) is consumed by chemical oxidation reactions and as manganese oxide precipitates out of solution. The data suggest that dissolved the chromium and hexavalent chromium observed at PZ-12-04-180U is related to the piezometer construction materials. Elevated dissolved chromium and dissolved thallium concentrations exceeding MCLs observed at EW-12-01-180U are considered to be anomalous and potentially related to potassium permanganate chemical supply contamination. The single dissolved mercury detection exceeding MCLs observed at PZ-12-04-180U during the study was considered to be anomalous and potentially related to piezometer construction and materials. Given these metals detections, the presence and persistence of dissolved chromium, mercury, and thallium should be further evaluated by additional monitoring over time to confirm concentration trends.

The pilot test results indicate that local aquifer conditions do not allow for the creation of vertical groundwater recirculation loops using the existing groundwater extraction wells and 14 gpm pumping rates. The data indicate that anisotropic groundwater flow conditions result in preferential horizontal groundwater flow. This information regarding preferential horizontal flow suggests that future in-situ chemical oxidation should incorporate horizontal groundwater flow for chemical delivery.

Recommendations

A second phase of pilot testing is necessary to fill data gaps identified during the initial pilot study to finalize the use of this approach at this site. The second phase of pilot testing will include the following tasks:

- 1) Resample for total and hexavalent chromium in wells EW-12-01-180U, EW-12-01-180M, EW-12-02-180U and EW-12-02-180M to confirm lower concentrations following equilibration to pre-test conditions.
- 2) Evaluate potential trace level contaminants in the potassium permanganate chemical supply.
- 3) Evaluate regional dissolved oxygen (DO) and oxidation reduction potential (ORP) levels to confirm the location of the source area of vinyl chloride. Downhole monitoring in existing suitable monitoring locations is recommended on a periodic basis.
- 4) Provided favorable results are achieved from items 1-3 above, perform a second phase of pilot testing with potassium permanganate using the existing extraction wells EW-12-01-180M and EW-12-02-180M. An addendum to the "Sites 2 and 12 In-Situ Chemical Oxidation Pilot Study Work Plan" will

be prepared describing pilot study wells, pumping rates, monitoring parameters, etc. for second phase of pilot testing.

6.0 REFERENCES

Carus, 2001. Carus Chemical Company Technical Information CD-Rom: Groundwater & Soil Remediation, Volume 1. May 2001.

Harding ESE/IT, 2001a. Semiannual Evaluation Report, Revision 0, Sites 2 and 12 Groundwater Remedy, Former Fort Ord, California. Prepared June 29.

, 2002a. Sites 2 and 12 In-Situ Chemical Oxidation Pilot Study Work Plan (Work Plan) Prepared January 4.

, 2002b. *Revision 0, Sites 2 and 12 Groundwater Remedy, Operating Properly and Successfully Evaluation Report, Former Fort Ord California.* Prepared June 7.

, 2002c. Annual Evaluation Report, Revision 0, October 2000 through December 2001, Sites 2 and 12 Groundwater Remedy, Former Fort Ord, California. Prepared June 12.

Hood, E.R., N.R. Thompson, G.J. Farquhar, 1998. *In Situ Oxidation: An Innovative Treatment Strategy to Remediate Trichloroethylene and Perchloroethylene DNAPLs in Porous Media*. Presented at the 6th Symposium on Groundwater and Soil Remediation, Montreal, Quebec. March.

IT Corporation (IT), 1999. Draft Technical Memorandum Number 2 Remedial Action Option Recommendation, Sites 2 and 12 Groundwater Remediation, (Former) Fort Ord, California. Prepared for USACE Sacramento. November.

Interstate Technology Regulatory Cooperation (ITRC), 2001. *Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater*. June

Schnarr, M., C. Truax, G. Farquhar, E. Hood, T. Gonullu, and B. Stickney, 1996. *Laboratory and Controlled field Experiments Using Potassium permanganate to Remediate Trichloroethylene and Perchloroethylene DNAPLs in Porous Media*. Journal of Contaminant Hydrology. December.

U.S. Environmental Protection Agency (EPA), 1993. USEPA Contract Laboratory Programs National

Functional Guidelines for Organic Data Review. February.

_____, 1994. USEPA Contract Laboratory Programs National Functional Guidelines for Inorganic Data Review. February.

West, O.R., S.R. Cline, W.L. Holden, F.G. Gardner, B.M. Schlosser, J.E. Thate, D.A. Pickering, 1997. A *Full-Scale Demonstration on In Situ Chemical Oxidation Through Recirculation at the X-701B Site, Field Operations and TCE Degradation*. Prepared for the U.S. Department of Energy. Oak Ridge National Laboratory, Environmental Sciences Division, Publication No. 4727. December.

DISTRIBUTION

Sites 2 and 12 In-Situ Chemical Oxidation Pilot Study Report Former Fort Ord, California

April 14, 2003

Copy No. ____

Copies 1 - 4: Mr. Chris Smith AHTNA Government Services Corporation 1115 Shore Street West Sacramento, California 95691

Copies 5 - 10: Harding ES

Harding ESE files

Quality Control Reviewer

Donald R Smallback

Donald R. Smallbeck Managing Principal

BK/AA;kb/KB59117-F.DOC-FO

TABLES

PLATES

APPENDIX A

QUALITY CONTROL SUMMARY REPORT

APPENDIX B

FIELD PARAMETER DATA

APPENDIX C

RESPONSES TO AGENCY COMMENTS

APPENDIX C

RESPONSES TO AGENCY COMMENTS

Agency comments are listed below regarding the Draft In-Situ Chemical Oxidation Pilot Study Report for Sites 2 and 12, Former Fort Ord (*AGSC, November 12, 2002*) and AGSC responses are shown in **bold.**

General Response – Based on the comments received (listed below) as well as further analysis of the data collected from the pilot test and the objectives of the pilot testing activities, the Army is proposing to temporarily or permanently delay the second pilot test. Instead, the Army is proposing to perform a more detailed evaluation of the biogeochemical environment present at Sites 2 and 12. The goal of this evaluation will be to characterize the ambient biogeochemical environment present in the areas of impacted groundwater, specifically targeting the development of a more definitive determination of the causes for the persistence of vinyl chloride (VC) in Extraction Wells EW-12-01-180M, EW-12-02-180M, and EW-12-03-180M and the potential for reductivce dechlorination in this area. This information will in turn support two objectives for the project as a whole:

- Further the understanding of the biogeochemical environment in the area near Extraction Wells EW-12-01-180M, EW-12-02-180M, and EW-12-03-180M which will allow for a more effective design and testing of potential insitu VC removal or reduction techniques. The persistence of VC in Extraction Wells EW-12-01-180M, EW-12-02-180M, and EW-12-03-180M as well as specific observation from the in-situ chemical oxidation (ISCO) pilot testing suggest that the environment may have a higher than expected 'reductive poise' (i.e., unexpected demand for oxidants). If this is the case, alternative in-situ treatment techniques may be more suitable for use, assuming the potential use of in-situ treatment is still an objective for the Site.
- Provide a better understanding of the biogeochemical environment of the impacts at Sites 2 and 12, which will be useful for evaluating other groundwater remediation enhancements on an area wide basis.

In support of this proposed approach, the Army plans to submit a workplan under separate cover. The workplan will outline the proposed monitoring parameters, sampling locations and frequencies.

Comments by the US Environmental Protection Agency dated October 2, 2002:

M:\Job Folders\30019\2-12pilot study\Pilot Test Report\Draft Final\KB59117-F.doc

GENERAL COMMENTS

 The value of a proposed second pilot test is not clear. It appears from the data that the permanganate oxidation of vinyl chloride in site groundwater may not be significant, or in fact, that the addition of permanganate may be counter-productive. The vinyl chloride concentrations detected in groundwater samples collected from downgradient piezometer PZ-12-04-180M go up by almost an order of magnitude during the test indicating that the permanganate addition may be degrading groundwater quality - the sharp increase in vinyl chloride concentrations at PZ-12-04-180M occurs at about the same time that the permanganate reaches the location of PZ-12-04-180M, but the vinyl chloride concentrations are far higher at PZ-12-04-180M than at either the injection or extraction wells.

It is very unlikely that the addition of the permanganate during the pilot study had any effect on the chemical results observed at PZ-12-04-180M. No evidence of permanganate was observed at PZ-12-04-180M. The observed increase in VC concentrations in PZ-12-04-180M were likely the result of saline groundwater movement into the area of PZ-12-04-180M due to either tidal activity, onset of spring groundwater extraction in the Salinas Valley, or groundwater extraction from EW-12-01-180M. The TDS and VOC chemical concentrations observed at PZ-12-04-180M displayed an upward trending oscillating pattern that suggested salt water intrusion and tidal fluctuations. The concentrations of VC observed at PZ-12-04-180M during the pilot study were less than the maximum value observed historically at this location (10 ug/L, 7/25/95) and are consistent with what is known to exist in this area.

In addition, the reduction of vinyl chloride observed in extracted groundwater (between the extraction and injection point) is not particularly convincing as vinyl chloride is extremely volatile and much of the observed concentration decrease may have been due to agitation rather than oxidation. That air stripping rather than chemical oxidation was the primary remedial force is further indicated by the negligible decrease in TCE and PCE concentrations between the extraction and injection points. Because the stated objective is to remove vinyl chloride by permanganate oxidation, please explain the significance of the only slight decreases in chlorinated VOC concentrations over the some 90 days of the pilot study and the observed order of magnitude increase in vinyl chloride concentrations at PZ-12-04-180M. In addition, please address how well the chlorinated VOCs were destroyed insitu versus the amount destroyed at mixing. Please also provide the numerical remedial objective for vinyl chloride and other VOCs that will determine whether permanganate oxidation significantly improves the treatment system.

The preferential oxidation of VC followed by TCE and then PCE by a chemical oxidizer, such as potassium permanganate, is well documented in literature and the results observed during the test are consistent with the understood phenomena. If VC was being removed by traveling through pumps, piping, and

sample handling, the VC would be uniformly reduced at all the sampling points. The pattern of VC results observed during the study are consistent with the very large set of historic VC results collected monthly as part of system operation and are believed to be accurate. The relatively instantaneous reduction of VC by chemical oxidation observed in the injection well is consistent throughout the pilot test and is further demonstrated by the rise in VC in the injection well occurring when the oxidant supply was temporarily halted.

The dilution effect upon chlorinated VOCs in groundwater sampled from the injection well produced by the mixing of the permanganate solution (at an approximate rate of 0.033 gpm) to the injected water (at an approximate rate of 14 gpm) is approximately 0.24 percent and considered negligible. The dilution effect upon chlorinated VOCs in groundwater sampled from the injection well associated with native groundwater mixing with the injected water is unknown, but assumed to be negligible. The validity of the assumption of negligible dilution from mixing of injected water with native groundwater is expected to increase throughout the testing period as the native groundwater surrounding the well is displaced by the injected water. It should be noted that at the end of the study a total of approximately 1.5 million gallons of water was placed into the injection well and surrounding aquifer area.

If further pilot testing is proposed in the future (See General Response) the numerical remedial objective for VC will be to reduce the concentration of VC in the extracted water from wells EW-12-01-180M, EW-12-02-180M and EW-12-03-180M to less than 0.1 ug/L in order to meet treatment plant discharge criteria. Other VOCs do not warrant specific treatment objectives as they can be easily removed from the extracted groundwater via the existing treatment plant.

- 2. At 300 gallons per minute, if the effluent from the Sites 2/12 groundwater treatment system still contains vinyl chloride at a concentration of 0.5 ug/l, it would seem that this water could be run through an air-stripper for several years for less money than the cost of this pilot study. It would also have to be evaluated whether the 1-gram per day of vinyl chloride that would be off-gassed from the air stripper would require collection or treatment. Please revise the pilot study report to address whether air stripping as a polishing step for the Sites 2/12 groundwater treatment system is feasible. The Army has considered air stripping and other ex-situ treatment alternatives in the past and is proposing to further evaluate VC influent concentrations with respect to improved system performance and alternative VC treatment technologies. This analysis will include evaluation of off-gas treatment, because such treatment is anticipated to be required by the regional air quality district regardless of mass discharge rates.
- 3. The evaluation of chlorinated VOC removal appears to rely on comparing the

concentrations of the source water (from the extraction well) and the reinjected water after permanganate dosing. Chlorinated VOC removal would then be a function of the contact time between permanganate dosing and the time when the water was reinjected. Please provide an estimate of this contact time to allow an assessment of the permanganate oxidation rate of the chlorinated VOC. The permanganate and VOC-containing groundwater contact time reflected in samples collected from Injection Well EW-12-01-180U was very short and in the range of several seconds to a few minutes which is described as instantaneous in the report. The contact time between permanganate and VOC-containing groundwater in samples collected at Piezometer PZ-12-04-180U is estimated to be at a minimum 39 days using the elapsed time from initiating injection at EW-12-01-180U and the initial observation of oxidation front at the piezometer.

SPECIFIC COMMENTS

1. Section 2.2.1, Mechanical System Operation, Chemical Injection, Page 11, end of first paragraph: The statement that "100 ppm [potassium permanganate] ... was the maximum concentration that could be created using the existing solution tank, injection pump and staffing resources" is unclear, and given the reported results it is likely that much higher concentrations of oxidant will be required to remove vinyl chloride with a certainty suitable to treatment system design. Please address this issue in any recommendations for future pilot studies. Please also recognize that the "uncertainties associated with the spurious oxidant consumption capacity of the aquifer material" are due to the inherent properties of the groundwater system as much as to any anthropogenic contamination, and their presence and variability in the site groundwater must be included in the design of any chemical or biological treatment system. Successful in-situ treatment of VC was observed at EW-12-01-18U in 23 sets of monitoring results collect during the 81 days of monitoring. The direct observation of VC mass reduction at other monitoring locations was not possible due to its absence from all of the upper aquifer monitoring points affected by the mixture of permanganate and lower aquifer VC-contaminated groundwater. The reduction of VC mass is expected to be a function of oxidant concentration, contact time, and competing oxidant demand from aquifer materials and groundwater. It is for these reasons (as well as others described in the General Response) that the Army is proposing to perform an evaluation of the biogeochemical environment present in the VC-contaminated lower portion of the aquifer at Sites 2 and 12 as outlined in the General Response. Data collected during this characterization will help assure proper design of in-situ VC treatment, if these types of enhancements are considered for use in the future.

ERRATA

1. To avoid reporting negative concentrations (e.g., Plates 9, 11), please turn off the line-

smoothing for the plots of contaminant concentrations versus time. Comment noted and graphs are corrected. The corrected graphs (Plates 9 and 11) are provided in the draft final report.

Comments by the California Department of Toxic Substances Control and Regional Water Quality Control Board, dated September 17, 2002:

Summary/Conclusions

The specific objectives of the PSR were to:

- Determine the effectiveness of ISCO in treating vinyl chloride
- Determine the optimum potassium permanganate concentration required to oxidize vinyl chloride to acceptable levels
- Determine extraction and injection well locations and associated flow rates suitable for ISCO of vinyl chloride

The Engineering Services Unit does not consider the limited amount of data provided in the PSR sufficient enough to support an assessment of the effectiveness of ISCO in treating vinyl chloride in the upper aquifer at this site.

The ESU indicated in a review of the ISCO Workplan, dated January 4, 2002, that in order to adequately assess the effectiveness of the ISCO for the application described a significant addition of planned monitoring infrastructure in the form of multi-depth monitoring wells installed in multiple locations would be required.

However, the PSR indicates the pilot study (PS) was implemented without the addition of any monitoring wells. The results of the PS are based on an assessment of data from only two downgradient monitoring wells. The intent of this pilot study was to use existing infrastructure and funding was not available for additional well installations. If the first phase of pilot testing was favorable, the financial investment for collection of additional lithologic information and multi-depth monitoring points would be considered for future tests.

The data collected from one of these downgradient monitoring wells, EW-12-01-180M, indicated there was no connection between the upper and middle part of the upper aquifer (U/M). Conversely, the data from monitoring well PZ-12-04, located in the same part of the aquifer as EW-12-01-180M, appears to indicate a significant increase in COCs over time and a direct relationship to PS activities as defined by the anomaly related to chemical addition malfunction found on almost every graph (Plates 4-9), specifically Plate 4, Vinyl Chloride vs. Time. It is very unlikely that the addition of permanganate during the pilot study had any effects on the chemical results observed at PZ-12-04-180M. No evidence of permanganate was observed at PZ-12-04-180M. The observed increase in VC concentrations in PZ-12-04-180M were likely the result of saline groundwater movement into the area of PZ-12-04-180M due to either tidal activity, onset of spring groundwater extraction in the Salinas Valley, or groundwater extraction from EW-12-01-180M. The TDS and VOC chemical concentrations observed at PZ-12-04-180M displayed an upward trending oscillating pattern that suggested salt water intrusion and tidal fluctuations. The concentrations of VC observed at PZ-12-04-180M during the pilot study

were less than the maximum value observed historically at this location (10 ug/L 7/25/95) and are consistent with what is known to exist in this area. Although COCs concentrations increased the most at PZ-12-04-180M (Plates 4-9) at about the same time as the chemical (potassium permanganate) supply to EW-12-01-180U was interrupted, the spatial separation between the two locations and the lack of any evidence suggesting that injected groundwater containing potassium permanganate arrived at PZ-12-04-180M indicates that the correlation is coincidental and not causative.

The increase in manganese can be attributed to the use of the chosen oxidant. The PSR indicates a review of data supports the appearance of elevated levels of chromium attributed to the interaction of monitoring well construction materials and the oxidant.

The ESU was unable to find any data to support this premise but found only a statement indication this type of reaction was a possibility. In addition, plate 10 of the PSR indicates an increase in chromium levels in PZ-12-04-180U, while a similar monitoring well, PZ-12-04-180M, exposed to similar levels of the oxidant as shown in plate B1, does not indicate an increased level of chromium. The comment's statement that PZ-12-04-180U and PZ-12-04-180M were exposed to similar levels of oxidant is incorrect. There is no evidence that groundwater containing potassium permanganate was transported to the vicinity of PZ-12-04-180M. There is evidence that groundwater containing potassium permanganate was transported to PZ-12-04-180U and there is an approximate correlation between the increase in manganese at PZ-12-04-180U (5/23/02) arrival of groundwater containing potassium permanganate as arriving at PZ-12-04-180U and the initial detection of chromium (5/15/02). The literature reference describing the ability of stainless steel well materials to leach metals including chromium into groundwater is the "Potential of Common Well Casing Materials to Influence Aqueous Metals Concentrations" by Alan D Hewitt, reported in the Spring 1992 Groundwater Monitoring and Remediation edition.

Based the limited monitoring capabilities provided for the PS and the questionable PSR conclusions based on the PS data, the ESU does not consider the PS as a viable means to assess the effectiveness of ISCO in treating saturated zone vinyl chloride at this site.

Without sufficient data to insure this treatment technology can be effective, the evaluation of the remaining objectives cannot be accomplished.

The alternative to ISCO of vinyl chloride would be to add a secondary treatment system, such as air stripping, to the existing groundwater treatment system. Based on the throughput (300 gpm) and vinyl chloride concentration (4 ug/l) given in the PSR, the ESU has estimated the capital cost of an air stripping unit at approximately 100K. In addition, a means to address the vinyl chloride vapor effluent, such as a thermal oxidizer, would be required.

This would appear to support the further evaluation of this treatment technology as an adjunct to the existing system as means to address the increased level of vinyl chloride in

groundwater. The Army has considered air stripping and other ex-situ treatment alternatives in the past and is proposing to further evaluate VC influent concentrations with respect to improved system performance and alternative VC treatment technologies. This analysis will include evaluation of off-gas treatment, because such treatment is anticipated to be required by the regional air quality district regardless of mass discharge rates.

However, any further action taken to evaluate this treatment technology will require the resolution of the issues discussed above in development of a PS that can:

1. Completely evaluate the lithology of the PS portion of the site and the affect of lithology on the injection of the subject oxidant.

2. Provide additional monitoring infrastructure that can better assess the ISCO process in the form of:

a. Additional multi-depth monitoring wells and the associated drill logs to evaluate the site lithology and provide data that can be used to evaluate the effectiveness of the ISCO process.

b. Monitoring wells of the type described located such that both the aerial and vertical extent of influence of an injection well can be determined for the basis of a full scale design.

3. Adequately evaluate the presence of elevated levels of metals in the saturated zone during the implementation of a PS. The minimum requirement would the inclusion of data supporting the production of elevated chromium levels due to interaction of oxidant with well construction materials indicated in the PSR.

4. Adequately evaluate the possibility of the creation of partial by-products, including vinyl chloride, which may be produced by the partial oxidation of the COCs present in the saturated zone as noted in the PSR.

5. Provide additional data supporting a more in-depth analysis of the optimum concentration of oxidant required to oxidize vinyl chloride to acceptable levels. The ESU does not consider the use of two concentrations that are two orders of magnitude apart, 3 ppm and 100 ppm, as an adequate evaluation to determine this optimum concentration.

6. Develop sufficient data to adequately evaluate the last objective, determination of injection and extraction well locations and associated flow rates.

General Response – Based on the comments received and the objectives of the pilot testing activities, the Army is proposing to temporarily or permanently delay the second pilot test of potassium permanganate ISCO. If an additional ISCO pilot testing were to be proposed, the above recommendations would be considered in the planning process. As an alternative, the Army is proposing to perform a more

detailed evaluation of the biogeochemical environment present in the lower aquifer area at Sites 2 and 12. The goal of this evaluation will be to characterize the ambient biogeochemical environment present in the areas of impacted groundwater, specifically targeted at developing a more definitive determination of the causes for the persistence of VC in the lower aquifer area and the potential for reductive dechlorination. This information will in turn support two objectives for the project as a whole:

- Further the understanding of the biogeochemical environment in the lower aquifer area, which will allow for more effective design and testing of potential in-situ VC removal or reduction techniques. The persistence of VC in the lower aquifer area as well as specific observation from the ISCO pilot testing suggests that the environment may have a higher than expected 'reductive poise' (i.e., unexpected demand for oxidants). If this is the case, other in-situ treatment techniques may be more suitable for use, assuming the potential use of in-situ treatment is still an objective for the Site.
- Provide a better understanding of the biogeochemical environment of the impacts at Sites 2 and 12, which will be useful for evaluating other groundwater remediation enhancements on an area-wide basis.

In support of this proposed approach, the Army plans to submit a workplan, under separate cover. The workplan will outline the proposed monitoring parameters, sampling locations and frequencies.