

Lawrence Livermore National Laboratory

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Five-Year Review Report for the Building 834 Operable Unit at Lawrence Livermore National Laboratory **Site 300**

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March 2012

*Weiss Associates, Emeryville, California **Weiss Associates, Emeryville, California and University of California, Berkeley



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Certification

I certify that the work presented in this report was performed under my supervision. To the best of my knowledge, the data contained herein are true and accurate, and the work was performed in accordance with professional standards.



10/10/12 Date CP John Valett

California Professional Geologist No. 7154 License expires: June 30, 2013 California Certified Hydrogeologist No. 826 License expires: June 30, 2013

Approval for the Five-Year Review for the Building 834 Operable Unit at Lawrence Livermore National Laboratory Site 300

Prepared by:

The United States Department of Energy Livermore Site Office Livermore, California

Approved:

inde Dct. 10, 2012 **Claire S. Holtzapple**

Date

Site 300 Remedial Project Manager U.S. Department of Energy National Nuclear Security Administration Livermore Site Office



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY REGION IX 75 Hawthorne Street San Francisco, CA 94105

September 28, 2012

Via USPS and email

Claire Holtzapple U.S. Department of Energy Livermore Environmental Programs Division Lawrence Livermore National Laboratory P.O. Box 808, L-574 Livermore, California 94551

Re: U.S. EPA Concurrence with Five-Year Review Report for OU2 (Building 834) Lawrence Livermore National Laboratory Site 300, March 2012

Dear Ms. Holtzapple:

The U.S. Environmental Protection Agency (EPA) has reviewed the Five-Year Review Report for OU2, the Building 834, at the Lawrence Livermore National Laboratory (LLNL) Site 300, dated March 2012. Based upon this review, EPA agrees with the overall findings, conclusions and recommendations in the report. The remedy is protective of human health and the environment for the site's industrial land use. While the long-term remedial action is operating, the remedy is protective of human health because exposure pathways that could result in unacceptable risk to onsite workers are being controlled by the implementation of institutional controls, the LLNL Site 300 Health and Safety Plan, and the LLNL Site 300 Contingency Plan.

The cleanup standards for groundwater are drinking water Maximum Contaminant Levels (MCLs). For contaminants in subsurface soil, the cleanup standards are based on reduction of concentrations to mitigate risk to onsite workers and prevent further impacts to groundwater to the extent technically and economically feasible. Because some contaminants may remain in subsurface soil following the achievement of these cleanup standards, the Record of Decision includes a land use control prohibiting the transfer of lands with unmitigated contamination that could cause potential harm under residential or unrestricted land use. This prohibition will remain in place until and unless a risk assessment is performed in accordance with current EPA risk assessment guidance and is agreed to by the Department of Energy, EPA, and the State agencies as adequately showing no unacceptable risk for unrestricted use and unlimited exposure scenarios.

This Five-Year Review identifies five recommendations which will be implemented as part of the routine administrative or programmatic processes that are already in place to optimize the operation of the remedy. Since these issues do not directly impact remedy protectiveness, we do not include them as Five-Year Review protectiveness issues. For the next 5-Year Review, please clarify the institutional roles and/or responsibilities of the various DOE/LLNL Site 300 entities. EPA also requests that DOE develop a formal plan to consolidate the individual FYR documents into logical pairings, with the goal ultimately of producing one, site-wide document for future deliverables.

We appreciate the opportunity to work with you on this project and look forward to continued success at LLNL Site 300. If you have any questions regarding this letter, please feel free to contact Andrew Bain at (415) 972-3167.

Sincerely,

Michael M. Montgomery Assistant Director, Superfund Division Federal Facilities and Site Cleanup Branch

cc by EMail: Ariel Robertson, DOE Leslie Ferry, LLNL Jacinto Soto, DTSC Aimee Phiri, CVRWQCB

Five-Year Review Summary Form

Site Identification						
Site name: Lawrence Livermore National Laboratory Site 300, Building 834 Operable Unit						
EPA ID: CA 2890090002						
Region: IX State: California		ifornia	City/County: San Joaquin/Alameda			
Site Status						
NPL status: Final						
Remediation status: Operating						
Multiple OUs: Yes		Construction completion date: December 2004				
Has the site been put into reuse: No						
1.0 REVIEW STATUS						
Reviewing agency: U.S. Department of Energy						
Author name: J. Valett						
Author title: Project Hydrogeolog		gist	Author affiliation: Weiss Associates Emeryville, California			
Review period: July 2006 to June 2011						
Date(s) of site inspection: March 30, 2010						
Type of review: Statutory						
Review number: 3						
Triggering action: Five-Year Review for the Building 834 OU						
Triggering action date: February 11, 2002						
Due date: March 16, 2012						

Five-Year Review Summary Form (continued)

Deficiencies:

No deficiencies in the remedy were identified during this evaluation.

Recommendations and Follow-up Actions:

The following recommendations to be carried out by the United States (U.S.) Department of Energy (DOE) were developed during the review process:

- 1. Assess the cost-benefit of expanding *in situ* bioremediation at T2 by implementing a recirculation cell with biostimulation/bioaugmentation injection wells and extraction wells to distribute sodium or ethyl lactate and dechlorinating bacteria to further promote biotransformation of trichloroethene to ethene.
- 2. Monitor Building 834 contaminants of concern (COCs) including volatile organic compounds (trichloroethene, cis-1,2-dichloroethene, chloroform, tetrachloroethene, and 1,1,1-trichloroethane) tetrabutyl orthosilicate/tetrakis (2-ethylbutyl) silane, and nitrate concentrations in Tps-Tnsc₂ HSU monitoring wells W-834-A1 and -2119 during the next five years. Additional actions, including installation of extraction wells in the vicinity of these wells, may be considered if these wells exhibit stable or increasing VOC trends.
- 3. Monitor COC concentrations in wells W-834-B4 and W-834-C5 during the next five years. Additional actions, including installation of extraction wells in the vicinity of these wells, may be considered if these wells exhibit stable or increasing VOC trends.
- 4. Monitor COC concentrations in well W-834-2113 during the next five years. Additional actions, including conversion of this well to an extraction well, installation of an extraction well in the vicinity of W-834-2113, or implementing *in situ* bioremediation in this area, may be considered if this well exhibits stable or increasing VOC trends.
- 5. Evaluate the implications of the September 28, 2011 change to EPA's TCE toxicity value for the TCE inhalation risk at the Building 834 OU which will be discussed in the next five-year review report for the Building 834 OU that will encompass the time period (July 2011 to June 2016) during which this change occurred.

No other follow-up actions were identified related to this Five-Year Review. As discussed below, these recommendations do not affect the protectiveness of the remedy.

DOE will: (1) estimate costs and the timeframe necessary to accomplish the new work scope; (2) prioritize new work scope and present these priorities to the regulatory agencies; (3) incorporate the new work scope into upcoming fiscal year budget requests; and (4) develop a schedule for implementing the work.

Protectiveness Statement:

The remedy at the Building 834 Operable Unit (OU) is protective of human health and the environment for the site's industrial land use. The remedy protects human health because exposure pathways that could result in unacceptable risk to onsite workers are being controlled by the implementation of institutional controls, the Health and Safety Plan, and the Contingency Plan.

The cleanup standards for Building 834 OU ground water are drinking water standards. Because drinking water standards do not differentiate between industrial and residential use, the ground water cleanup remedy will be protective under any land use scenario.

The cleanup standards for volatile organic compounds (VOCs) in subsurface soil are to reduce concentrations to mitigate risk to onsite workers and prevent further impacts to ground water to the extent technically and economically feasible. Because some VOCs may remain in subsurface soil following the achievement of these cleanup standards, a land use control prohibits the transfer of lands with unmitigated contamination that could cause potential harm under residential or unrestricted land use. This prohibition is included in the Site-Wide Record of Decision. This prohibition will remain in place until and unless a risk assessment is performed in accordance with current U.S. Environmental Protection Agency (EPA) risk assessment guidance and is agreed by the DOE, the EPA, the California Department of Toxic Substances Control and the Regional Water Quality Control Board as adequately showing no unacceptable risk for residential or unrestricted land use.

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Appendix A. T2 Area Enhanced Bioremediation Treatability Study

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Attachment A. Building 834 Five-Year Review Inspection Checklist

1. Introduction

The United States (U.S.) Department of Energy (DOE) has conducted a Five-Year Review of the remedial actions implemented at the Building 834 Operable Unit (OU) at Lawrence Livermore National Laboratory (LLNL) Site 300. Environmental cleanup is conducted under the oversight of the U.S. Environmental Protection Agency (EPA), the California Department of Toxic Substances Control (DTSC), and the California Regional Water Quality Control Board (RWQCB) – Central Valley Region. DOE is the lead agency for environmental restoration at LLNL. The review documented in this report was conducted from July 2006 through June 2011. Parties providing analyses in support of the review include:

- U.S. DOE, Livermore Site Office.
- LLNL, Environmental Restoration Department (ERD).
- Weiss Associates.

The purpose of a Five-Year Review is to evaluate the implementation and performance of a remedy to determine whether the remedy will continue to be protective of human health and the environment. The Five-Year Review report presents the methods, findings, and conclusions of the review. In addition, the Five-Year Review identifies issues or deficiencies in the selected remedy, if any, and presents recommendations to address them. The format and content of this document is consistent with guidance issued by DOE (DOE, 2002) and the U.S. EPA (EPA, 2001).

Section 121 of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), as amended by the Superfund Amendment Reauthorization Act (SARA), requires that remedial actions that result in any hazardous substances, pollutants, or contaminants remaining at the site be subject to a Five-Year Review. The National Contingency Plan further provides that remedial actions which result in any hazardous substances, pollutants, or contaminants remaining at the site above levels that allow for unlimited use and unrestricted exposure be reviewed every five years to ensure protection of human health and the environment. Consistent with Executive Order 12580, Federal agencies are responsible for ensuring that Five-Year Reviews are conducted at sites where five-year reviews are required or appropriate.

This is the third Five-Year Review for the Building 834 OU (OU 2). The first and second Five-Year Reviews were completed in 2002 (Ferry et al., 2002a) and 2007 (Dibley et al., 2007), respectively. This review is considered a statutory review because: (1) contamination will remain onsite upon completion of the remedial action, (2) the Record of Decision was signed after October 17, 1986 (the effective date of the SARA), and (3) the remedial action was selected under the CERCLA. Since cleanup was initiated at this OU as a treatability study, the triggering action for the first review was the September 26, 1995 signature date of the Interim Record of Decision (ROD) for the Building 834 OU (DOE, 1995).

Five-year reviews are conducted individually for each OU at Site 300, with the exception of OUs 3 and 8 which will be combined. The Remedial Action Completion Report (Holtzapple, 2008) and Final Site-Wide ROD (U.S DOE, 2008) are the triggers for the five-year reviews for OUs 3 and 8, respectively, in accordance with EPA guidance. At the other OUs where

construction began prior to the Site-Wide ROD as treatability studies and/or removal actions, DOE and the regulatory agencies agreed to use the completion of the OU-specific Remedial Design report as the trigger for the first five-year review.

The background and description of the Building 834 OU are presented in Section 3 and the location is shown in Figure 1. The following sections include the descriptions and status of the other OUs and areas where environmental restoration activities are occurring at Site 300. The locations of these OUs at Site 300 are shown in Figure 2.

1.1. General Services Area (GSA) OU (OU 1)

The GSA OU has been separated into the Central GSA and the Eastern GSA based on differences in hydrogeology and the distribution of environmental contaminants. DOE has performed three Five-Year Reviews for the GSA OU (Ferry et al., 2001b; Dibley et al., 2006a; and Valett et al., 2011). The fourth Five-Year Review is scheduled for 2016.

1.1.1. Central GSA

Chlorinated solvents, mainly trichloroethene (TCE), were used as degreasing agents in craft shops in the Central GSA. Rinse water from these degreasing operations was disposed of in dry wells that were gravel-filled holes about 3 to 4 feet (ft) deep and two ft in diameter. As a result, subsurface soil and ground water was contaminated with volatile organic compounds (VOCs). There are no contaminants of concern (COCs) in surface soil in the central GSA. The Central GSA dry wells were used until 1982. In 1983 and 1984, these dry wells were decommissioned and excavated.

Ground water cleanup began in the Central GSA in 1992 and soil vapor extraction started in 1994 as removal actions. In 1997, a Final ROD for the GSA OU (U.S. DOE, 1997) was signed and ground water and soil vapor extraction and treatment continued as a remedial action. The selected remedy for the Central GSA includes monitoring, risk and hazard management, and ground water and soil vapor extraction and treatment. The remedial design was completed in 1998 and construction completion for the OU was achieved in September 2005.

Operation of the ground water and soil vapor extraction and treatment systems to remove VOCs from the subsurface is ongoing. Remediation has reduced maximum VOC concentrations in ground water from 272,000 micrograms per liter (μ g/L) in 1992 to a first semester 2011 maximum concentration of 700 μ g/L (April 2011) and has mitigated the risk to onsite workers from inhalation of VOCs inside Building 875.

1.1.2. Eastern GSA

The source of contamination in the Eastern GSA is an abandoned debris burial trench that received craft shop debris. Leaching of solvents from the debris resulted in the release of VOCs to ground water.

Ground water cleanup began in the Eastern GSA in 1991 as a removal action. In 1997, a Final ROD for the GSA OU was signed and ground water extraction and treatment continued as a remedial action. The remedial design was completed in 1998 and construction completion for the OU was achieved in September 2005. A ground water extraction and treatment system operated from 1991 to 2007 to remove VOCs from ground water.

As of February 2007, remediation had reduced VOC concentrations in on- and offsite ground water to meet cleanup standards. The treatment system was shut off and placed on standby. Post-shutdown monitoring is being conducted to determine if VOC concentrations rebound above cleanup standards. If VOC concentrations remain below cleanup standards for five years, the treatment system and associated wellfield will be decommissioned.

1.2. Pit 6 Landfill (OU 3)

From 1964 to 1973, approximately 1,900 cubic yards (yd³) of waste from LLNL Livermore Site and Lawrence Berkeley Laboratory was buried in nine unlined trenches and animal pits at the Pit 6 Landfill. Infiltrating rainwater leached contaminants from pit waste resulting in tritium, VOC, and perchlorate contamination in ground water. Nitrate contamination in ground water results from septic system effluent. No COCs were identified in surface or subsurface soil.

In 1971, DOE excavated portions of the waste contaminated with depleted uranium. In 1997, a landfill cap was installed as a CERCLA removal action to prevent infiltrating precipitation from further leaching contaminants from the remaining waste. Because of decreasing VOC concentrations in ground water, the presence of trichloroethene (TCE) degradation products, and the short half-life of tritium (12.3 years), the selected remedy for VOCs and tritium at the Pit 6 Landfill is monitored natural attenuation (MNA). Because ground water monitoring data for perchlorate and nitrate are limited, DOE will continue to monitor ground water to determine if and when an active remedy for these contaminants might be necessary. The remedy also includes risk and hazard management. Construction completion was achieved in October 2002. No Remedial Design document was required for this area.

The extent of contamination at the Pit 6 Landfill is limited and continues to decrease with concentrations/activities near and below cleanup standards. Natural attenuation has reduced total VOCs in ground water from a historic maximum of 250 μ g/L in 1988 to a first semester 2011 maximum concentration of 9.3 μ g/L (April 2011). Tritium activities are well below the cleanup standard and continue to decrease towards background levels. Perchlorate is not currently detected in any wells above the cleanup standard. The extent of nitrate at concentrations exceeding the cleanup standard continues to be limited to one well. Installation of the landfill cap mitigated the onsite worker inhalation risk.

The first Five-Year Review for this OU is scheduled for 2012.

1.3. High Explosives (HE) Process Area (OU 4)

From 1958 to 1986, surface spills at the drum storage and dispensing area for the former Building 815 steam plant resulted in the release of VOCs to ground water, subsurface soil, and bedrock. HE compounds, nitrate, and perchlorate detected in ground water are attributed to wastewater discharges to former unlined rinse water lagoons that occurred from the 1950s to 1985. VOCs, nitrate, and perchlorate have also been identified as COCs in ground water near the former HE Burn Pits. VOCs are COCs in surface water at Spring 5. HE compounds are COCs in surface soil. HE compounds and VOCs are COCs in subsurface soil. No further action was selected as the remedy for VOCs and High-Melting Explosive (HMX) in surface and subsurface soil.

The HE Open Burn Facility was capped under the Resource Conservation and Recovery Act (RCRA) in 1998. In 1999, DOE implemented a CERCLA removal action to extract ground

water at the site boundary and prevent offsite TCE migration. The HE Process Area remedy includes: (1) ground water extraction and treatment for VOCs, HE compounds, and perchlorate, and (2) MNA for nitrate (except at Building 829 where nitrate is extracted and treated), (3) monitoring, and (4) risk and hazard management. The remedial design was completed in 2002. Construction completion for the OU was achieved in September 2007. Six ground water extraction and treatment systems currently operate in the OU.

Ground water remediation efforts have reduced total VOC concentrations from a historic maximum of 450 μ g/L in 1992 to a first semester 2011 maximum of 53 μ g/L (April 2011). Perchlorate concentrations have decreased from a historic maximum of 50 μ g/L in 1998 to a first semester 2011 maximum of 29 μ g/L (May 2011). Research Department Explosive (RDX) in ground water has also been reduced from a maximum historic concentration of 350 μ g/L to a first semester 2011 maximum concentration of 106 μ g/L (March 2011). Natural denitrification processes are reducing nitrate concentrations in ground water to background levels. Remediation has also mitigated risk to onsite workers in the HE Process Area OU.

DOE has performed a Five-Year Review for the High Explosives Process Area OU (Dibley et al., 2007b). The second Five-Year Review is scheduled for 2013.

1.4. Building 850/Pit 7 Complex (OU 5)

This OU has been divided into two areas for cleanup evaluation purposes: (1) the Building 850 Firing Table area, and (2) the Pit 7 Complex.

The first Five-Year Review for this OU is scheduled for 2016.

1.4.1. Building 850 Firing Table (OU 5)

High-explosives experiments were conducted at the Building 850 Firing Table from 1958 to 2008. Tritium was used in some of these experiments, primarily between 1963 and 1978. As a result of the destruction and dispersal of test assembly debris during detonations, surface soil was contaminated with metals, polychlorinated biphenyls (PCBs), dioxins, furans, HMX, and depleted uranium. Leaching from firing table debris has resulted in tritium and depleted uranium contamination in subsurface soil and ground water. Nitrate and perchlorate are also COCs in ground water. Tritium is the only COC in surface water (Well 8 Spring).

Gravel was removed from the firing table in 1988 and placed in the Pit 7 Landfill. PCB-contaminated shrapnel and debris were removed from the area around the firing table in 1998. The Building 850 remedy consists of MNA, monitoring, and risk and hazard management. A remedial design was completed in 2004. The remedial design included the excavation and offsite disposal of contaminated surface soil and sand pile. This remedy was not implemented due to a large increase in transportation and offsite disposal costs. DOE and the regulatory agencies agreed to perform remediation of contaminated surface soil as a non-time critical removal action. An Engineering Evaluation/Cost Analysis (Dibley et al., 2008a) and Action Memorandum (Dibley et al., 2008b) were completed in 2008. A removal action was completed in 2010 for the excavation and solidification of PCB-, dioxin-, and furan-contaminated soil and sand pile. Metals, HMX, and uranium in surface soil at Building 850 do not pose a risk to human health or threat to ground water, therefore a no further action remedy was selected. However, these constituents in surface soil were removed during the soil excavation/solidification removal action. Natural attenuation has reduced tritium activities from a historic maximum of 566,000 picoCuries per liter (pCi/L) in 1985 to a first semester 2011 maximum of 53,300 pCi/L (May 2011). Uranium activities are below the cleanup standard and are within the range of natural background levels. The extent of nitrate with concentrations above cleanup standards is limited and does not pose a threat to human health or the environment. The maximum perchlorate concentration in the first semester 2011 is 74 μ g/L (April 2011), and a treatability study to evaluate *in situ* biodegradation of perchlorate is underway.

1.4.2. Pit 7 Landfill Complex (OU 5)

The Pit 3, 4, 5, and 7 Landfills are collectively designated the Pit 7 Landfill Complex. Firing table debris containing tritium, depleted uranium, and metals was placed in the pits in the 1950s through the 1980s. The Pit 4 and 7 Landfills were capped in 1992. During years of above-normal rainfall (i.e., 1997-1998 El Niño event), ground water rose into the bottom of the landfills and the underlying contaminated bedrock. This resulted in the release of tritium, uranium, VOCs, perchlorate, and nitrate to ground water. There are no COCs in surface water or surface soil. Tritium and depleted uranium are COCs in subsurface soil.

DOE and the regulatory agencies agreed that the Pit 7 Complex required additional study; accordingly, this area was not included in the 2001 Interim Site-Wide ROD and an area-specific Remedial Investigation/Feasibility Study (Taffet et al., 2005) was completed. An Amendment to the Interim ROD for the Pit 7 Complex was signed in 2007 (U.S. DOE, 2007) that described the selected remedy for the Pit 7 Complex including monitoring, risk and hazard management, MNA, ground water extraction and treatment, and source control. The interim remedial design was completed in 2008. A hydraulic drainage diversion system was constructed in 2008 to control contaminant sources by preventing ground water from rising into the pit waste and underlying contaminated bedrock. Also, a ground water extraction and treatment system was constructed in 2009-2010 to treat uranium, nitrate, perchlorate, and VOCs in ground water.

Natural attenuation has reduced tritium activities in ground water from a historic maximum of 2,660,000 pCi/L in 1998 to a first semester 2011 maximum of 575,000 pCi/L (April 2011) and has mitigated risk to onsite workers from inhalation of tritium vapors. Uranium activities have also decreased from a historic maximum of 781 pCi/L in 1998 to a first semester 2011 maximum of 417 pCi/L (April 2011). VOC concentrations are currently near or below cleanup standards. Nitrate concentrations in ground water remain relatively stable, while perchlorate concentrations have decreased.

1.5. Building 854 (OU 6)

TCE was released to soil and ground water through leaks and discharges of heat-exchange fluid, primarily between 1967 and 1984. Nitrate and perchlorate are also COCs in ground water. HE compounds, PCBs, dioxins, furans, tritium, and metals were identified as COCs in surface soil. No further action was selected as the remedy for metals, HMX, and tritium in surface soil.

In 1983, TCE-contaminated soil was excavated at the northeast corner of Building 854F. Ground water extraction and treatment has been conducted since 1999 to reduce VOC, nitrate, and perchlorate concentrations in ground water. PCB-, dioxin-, and furan-contaminated soil in the Building 855 former rinse water lagoon was excavated in 2005 (Holtzapple, 2005). The selected remedy for this OU includes monitoring, risk and hazard management, and ground water and soil vapor extraction and treatment. The interim remedial design was completed in

2003. Construction completion for the OU was achieved in September 2007. Three ground water extraction and treatment systems and one soil vapor extraction and treatment system currently operate in the OU.

Ground water remediation has reduced total VOC concentrations from a historic maximum of 2,900 μ g/L in 1997 to a first semester 2011 maximum of 110 μ g/L (April 2011). Nitrate concentrations have decreased from a historic maximum of 260 milligrams per liter (mg/L) in 2003 to a first semester 2011 maximum of 50 mg/L (June 2011). Perchlorate concentrations in ground water have also decreased from 27 μ g/L in 2003 to a first semester 2011 maximum of 15.9 μ g/L (June 2011). Risks to onsite workers from inhalation of VOC vapors and from exposure to PCBs, dioxins, and furans in surface soil have been mitigated.

A Five-Year Review of remediation in the Building 854 OU was completed in January 2009 (Dibley et al., 2009a). The second Five-Year-Review is scheduled for 2014.

1.6. Building 832 Canyon (OU 7)

Contaminants were released from Buildings 830 and 832 through piping leaks and surface spills during past activities at these buildings. VOCs, nitrate, and perchlorate are COCs in ground water. VOCs are COCs in surface water at Spring 3. VOCs, nitrate, and HMX are COCs in subsurface soil. HMX is also a COC in surface soil. No further action was selected as the remedy for HMX and nitrate in surface and subsurface soil.

Ground water and soil vapor extraction and treatment have been conducted since 1999 to reduce contamination in ground water and subsurface soil. The Building 832 Canyon OU remedy includes monitoring, risk and hazard management, MNA for nitrate, and ground water and soil vapor extraction and treatment. The interim remedial design was completed in 2006. Construction completion for the OU was achieved in September 2007. Three ground water extraction and treatment systems and two soil vapor extraction and treatment systems currently operate in the OU.

Remediation has reduced total VOC concentrations from a historical maximum of 13,000 μ g/L in 2003 to a first semester 2011 maximum of 3,600 μ g/L (April 2011). Perchlorate concentrations have been reduced from a historical maximum of 51 μ g/L in 1998 to a first semester 2011 maximum of 14 μ g/L (March 2011). Nitrate concentrations in ground water remain fairly stable, and are possibly the result of the ongoing contribution of nitrate from septic systems and natural bedrock sources. However, natural denitrification processes continue to reduce nitrate concentrations to background levels near the site boundary. Remediation has also mitigated the risk to onsite workers in several locations in the Building 832 Canyon OU.

A Five-Year Review of remediation in the Building 832 Canyon OU was completed in August 2011 (Helmig et al., 2011). The second Five-Year-Review is scheduled for 2016.

1.7. OU 8

Operable Unit 8 includes the contaminant release sites that have a monitoring-only remedy: the Building 801 Dry Well and Pit 8 Landfill, Building 833, Building 845 and Pit 9 Landfill, the Building 851 Firing Table, and the Pit 2 Landfill. OU 8 release sites have a monitoring-only interim remedy because either: (1) contaminants in surface and subsurface soil/bedrock do not pose a risk to humans or plant and animal populations or a threat to ground water, (2) there is no ground water contamination, (3) contaminant concentrations in ground water do not exceed

cleanup standards, and/or (4) the extent of contamination in ground water is limited. The first Five-Year Review for this OU is scheduled for 2013. These release sites are summarized below.

1.7.1. Building 801 Dry Well and the Pit 8 Landfill (OU 8)

The Building 801 Firing Table was used for explosives testing and operations resulting in contamination of adjacent soil with metals and uranium. Use of this firing table was discontinued in 1998, and the firing table gravel and some underlying soil were removed. Waste fluid was discharged to a dry well (sump) located adjacent to Building 801D from the late 1950s to 1984. The dry well was decommissioned and filled with concrete in 1984. VOCs, perchlorate and nitrate are COCs in ground water due to the past releases from the Building 801 Dry Well. VOC and nitrate concentrations in ground water are currently near or below cleanup standards or at background levels. Perchlorate is not currently detected in ground water. VOCs are COCs in subsurface soil, but do not pose a risk to human health. The adjacent Pit 8 Landfill received debris from the Building 801 Firing Table until 1974, when it was covered with compacted soil. There is no evidence of contaminant releases from the landfill.

The selected remedy for this area includes monitoring and risk and hazard management. No further action was selected as the remedy for VOCs in subsurface soil at Building 801.

No Remedial Design documents are required for this area.

1.7.2. Building 833 (OU 8)

TCE was used as a heat-exchange fluid in the Building 833 area from 1959 to 1982 and was released through spills and rinse water disposal, resulting in TCE-contamination of subsurface soil and shallow perched ground water. No contamination has been detected in the deeper regional aquifer. No COCs were identified surface soil at Building 833.

The selected remedy for Building 833 includes monitoring and risk and hazard management. No Remedial Design document is required for this area. Ground water monitoring at Building 833 has shown a decline in total VOC concentrations from a historic maximum of 2,100 μ g/L in 1992 to a first semester 2011 maximum of 150 μ g/L (February 2011).

1.7.3. Building 845 Firing Table and the Pit 9 Landfill (OU 8)

The Building 845 Firing Table was used from 1958 until 1963 to conduct explosives experiments. Leaching from firing table debris resulted in minor contamination of subsurface soil with depleted uranium and HMX but no unacceptable risk to human or ecological receptors or threat to ground water was identified. No contaminants have been detected in surface soil or in ground water at the Building 845 Firing Table. Debris generated at the Building 845 Firing Table was buried in the Pit 9 Landfill. There has been no evidence of contaminant releases from the Pit 9 Landfill.

The selected remedy for Building 845 and the Pit 9 Landfill includes monitoring and risk and hazard management. No further action was selected as the remedy for uranium and HMX in subsurface soil at Building 845. No Remedial Design documents are required for this area.

1.7.4. Building 851 Firing Table (OU 8)

The Building 851 Firing Table has been used for high-explosives research since 1962. VOCs and uranium-238 were identified as COCs in subsurface soil, and RDX, uranium-238, and metals as surface soil COCs. However, there is no risk to humans or animal populations, or threat to ground water associated with these contaminants in surface and subsurface soil. Uranium-238 was identified as a COC in ground water. However, it poses no risk to human or ecological receptors, and uranium activities are well below cleanup standards and within the range of background levels.

In 1988, the firing table gravel was removed and disposed in Pit 7. Gravel has been replaced periodically since then. The selected remedy for Building 851 includes monitoring and risk and hazard management. No further action was selected as the remedy for VOCs and uranium in surface and subsurface soil, and for RDX and metal in surface soil at Building 851. No Remedial Design document is required for this area.

1.7.5. Pit 2 Landfill (OU 8)

The Pit 2 Landfill was used from 1956 until 1960 to dispose of firing table debris from Buildings 801 and 802. Ground water data indicate a discharge of potable water to support a red-legged frog habitat located upgradient from the landfill may have leached depleted uranium from the buried waste. The frogs were relocated and the water discharge was discontinued, thereby removing the leaching mechanism. No contaminants were identified in surface or subsurface soil at the Pit 2 Landfill. No risk to human or ecological receptors has been identified at the Pit 2 Landfill.

The selected remedy for the Pit 2 Landfill includes monitoring and risk and hazard management. Monitoring data indicate that uranium activities remain below the cleanup standard. No Remedial Design document is required for this area.

1.8. Building 812 (OU 9)

The Building 812 Complex was built in the late 1950s-early 1960s and was used to conduct explosives tests and diagnostics until 2008. A Characterization Summary Report for this area was completed in 2005 (Ferry and Holtzapple, 2005). The Building 812 Complex was designated as OU 9 in March 2007 based on characterization results that indicated the presence of uranium, VOCs, HE compounds, nitrate, and perchlorate in environmental media. In 2008, a draft Remedial Investigation/Feasibility Study (RI/FS) describing the results of characterization activities and remedial alternatives for the Building 812 OU was submitted to the regulatory agencies. A DOE task force reviewed the soil-washing alternative and determined that it would not be effective at Site 300, therefore a soil-washing treatability study will not be performed. DOE is currently evaluating a new remedial strategy for contaminated soil at Building 812. Additional characterization began in 2011. A new RI/FS will be prepared following the completion of the characterization. A Proposed Plan will subsequently present the alternatives and a preferred remedy for public comment. A remedy will then be selected in an Amendment to the Final Site-Wide ROD.

1.9. Building 865/Advanced Test Accelerator

Building 865 facilities were used to conduct high-energy laser tests and diagnostics in support of national defense programs from 1980 to 1995. The Building 865 Complex housed a

275-foot linear electron accelerator called the Advanced Test Accelerator (ATA). The ATA was designed to produce a repetitively pulsed electron beam for charged particle beam research. In 2006, a Characterization Summary Report for this area was submitted to the regulatory agencies (Ferry and Holtzapple, 2006). Freon 113, Freon 11, and tetrachloroethene (PCE) were identified as COCs in ground water. The remediation pathway for Building 865 is currently being negotiated.

2. Site Chronology

A chronology of important environmental restoration events at the Building 834 OU is summarized below.

Late 1950s

• Experiments involving the thermal-cycling (i.e., repeated heating and cooling) of weapon components started at the Building 834 Complex.

1962-1978

• During the course of these experiments, VOCs, primarily TCE, were released through spills and piping leaks. TCE was used as the primary heat-transfer fluid during these experiments and was sometimes mixed with tetrabutyl orthosilicate (TBOS) and tetrakis (2-ethylbutyl) silane (TKEBS) to prevent degradation of pump seals and gaskets.

1982–1983

- DOE/LLNL excavated approximately 100 cubic yards of TCE-contaminated soil resulting from spills and piping leaks.
- Site investigations began at Building 834.

1986

• Ground water and soil vapor extraction began as treatability studies.

1989

• Ground water and soil vapor extraction treatability studies ended and construction of a full-scale facility began at Building 834.

1990

• LLNL Site 300 was placed on the National Priorities List.

<u>1991</u>

• DOE/LLNL conducted a treatability study using an electron accelerator to treat VOCs in extracted vapor. This technology was later screened out in the Site-Wide Feasibility Study (Ferry et al., 1999) due to the production of undesirable byproducts, including phosgene.

<u>1992</u>

• A Federal Facility Agreement for Site 300 was signed. The parties to the Agreement included DOE, EPA, the California DTSC, and California RWQCB.

- DOE/LLNL conducted an evaluation of a technology to treat extracted soil vapor using ultraviolet light and hydrogen peroxide. This technology was later screened out in the Site-Wide Feasibility Study due to the high energy and operation costs.
- A pilot study involving electrical soil heating (Joule heating) was performed. This technology was later screened out in the Site-Wide Feasibility Study due to limited applicability at Building 834.

1993

• The heat-exchange system was dismantled in 1993–1994.

1994

- The Site-Wide Remedial Investigation report for Site 300 (Webster-Scholten et al., 1994) was issued.
- A Feasibility Study for the Building 834 OU was issued.

1995

• An Interim ROD for the Building 834 OU was signed. Ground water extraction began as an interim remedial action. DOE also agreed to test innovative cleanup technologies at Building 834.

1998

- Soil vapor extraction began as an interim remedial action.
- DOE/LLNL began treatability studies to evaluate the role of intrinsic *in situ* biodegradation in reducing TCE mass and concentration. This process was found to be important in removing TCE from the subsurface.
- A surfactant injection/extraction (push-pull) treatability test was performed. This technology was subsequently screened out in the Site-Wide Feasibility Study due to difficulty in ensuring complete capture of mobilized contaminants and resulting risk of enhanced migration.
- A laboratory-scale treatability test was performed using soil from Building 834 to test the capability of potassium permanganate injection to destroy VOCs *in situ*. These tests indicated potential problems with injection and distribution of the potassium permanganate. Therefore, this technology was subsequently screened out in the Site-Wide Feasibility Study.
- Surface water drainage was diverted to prevent infiltration of precipitation in the Building 834 contaminant source area.

1999

• The Site-Wide Feasibility Study for Site 300 was issued that included the Building 834 OU.

2000

• Additional extraction well configuration testing was conducted at Building 834 to optimize interim remedial action performance.

2001

- An Interim Site-Wide ROD for Site 300 was signed that superseded the 1995 Interim ROD for the Building 834 OU. The Interim Site-Wide ROD specified continued ground water and soil vapor extraction, administrative controls (e.g., risk and hazard management), and monitoring as the components of the selected interim remedy for the Building 834 OU. The Interim Site-Wide ROD did not contain ground water cleanup standards. These standards were established in the Final Site-Wide ROD for Site 300.
- A Remedial Design Work Plan (Ferry et al., 2001b) was issued that contained the strategic approach and schedule to implement the remedies in the Interim Site-Wide ROD.
- DOE/LLNL performed treatability studies at the Building 834 OU that indicated that the existing air-sparging ground water treatment system could be replaced by an aqueous-phase granular activated carbon (GAC) system.

2002

- The Interim Remedial Design document for the Building 834 OU was issued.
- The Compliance Monitoring Plan/Contingency Plan for the Interim Remedies (Ferry et al., 2002b) was issued.
- The first Five-Year Review for the Building 834 OU was issued.

2004

- Building 834 build-out and upgrade of the ground water and soil vapor extraction and treatment systems were completed.
- Construction completion was achieved.

2005

- The EPA performed the OU construction completion inspection on July 13, 2005.
- A ground water tracer test and microcosm study was conducted to evaluate the feasibility of accelerating ground water cleanup through *in situ* bioremediation.

2007

• The second Five-Year Review for the Building 834 OU was issued.

2008

• The Final Site-Wide ROD with selected remedies and cleanup standards for Site 300 was signed. The remedy for the Building 834 OU did not change between the 2001 Interim Site-Wide ROD and the 2008 Final Site-Wide ROD, with the exception that ground water cleanup standards were added in the 2008 Final Site-Wide ROD.

2009

• The revised Compliance Monitoring Plan/Contingency Plan for Interim Remedies was issued (Dibley et al., 2009b).

2010

• The ground water *in situ* bioremediation study was concluded.

3. Background

3.1. Physical Characteristics

3.1.1. Site Description

LLNL Site 300 is a U.S. DOE experimental test facility operated by the Lawrence Livermore National Security (LLNS), Limited Liability Corporation. It is located in the Eastern Altamont Hills 17 miles east of Livermore, California (Figure 1). At Site 300, DOE conducts research development, and testing associated with high-explosive materials. Historic Site 300 operations involved the release of a number of contaminants to the environment. These releases occurred primarily from spills, leaking pipes, leaching from unlined landfills and pits, high explosive test detonations, and disposal of waste fluids in lagoons and dry wells (sumps). The climate at Site 300 is semi-arid; approximately 10 to 15 inches of precipitation falls each year, mostly in the winter.

The Building 834 Complex is approximately 50 acres, located on an isolated hilltop in the southeast portion of Site 300 (Figure 1). Facilities at the Building 834 Complex have been in use since the late 1950s for thermal-cycling experiments conducted on weapon components. These experiments were performed in four main buildings surrounded by a ring of eight smaller test cells (Figure 3). Aboveground pipes carried TCE-based heat-exchange fluid from storage tanks at the main buildings to the test cells. From 1962 to 1978, intermittent spills and piping leaks resulted in contamination of the subsurface with TCE and the silicone oils (TBOS/TKEBs) at eight release points. Nitrate associated with septic system effluent is also present in ground water.

The Building 834 OU is informally divided into three areas: the core, leachfield (septic system), and distal areas (Figure 3). The core area generally refers to the vicinity of the buildings and test cells in the center of the Building 834 Complex where the majority of contaminant releases occurred. The leachfield area is located immediately southwest of the core area. The distal area refers to the area downgradient (south) of the core and leachfield areas. A portion of the distal area, located near the T2 wells, has been used as an enhanced *in situ* bioremediation treatability study area since 2005 and is also identified on Figure 3.

The ground water and soil vapor extraction and treatment systems are currently in place and operating to remediate VOCs, nitrate, and TBOS/TKEBs. Ground water is monitored for VOCs, nitrate, and TBOS/TKEBs in 82 wells to evaluate the progress of remediation. The locations of existing monitor, extraction and water-supply wells and treatment facilities are shown on Figure 3.

3.1.2. Hydrogeologic Setting

The vadose zone and primary hydrostratigraphic units (HSUs) in the Building 834 OU are described below, from shallowest to deepest. A north-south oriented hydrogeologic cross-section through the Building 834 OU is presented in Figure 4.

3.1.2.1. Vadose (Unsaturated) Zone

The vadose zone consists of unconsolidated to highly cemented gravel, sand, silt, and clay sediments beneath the Building 834 Complex that are unsaturated to a depth of approximately 30 feet (ft) below ground surface (bgs).

3.1.2.2. Saturated Zone

The HSUs in the Building 834 OU are described below:

Perched Water-Bearing Zone: Miocene non-marine unit (Tpsg HSU)

This unit consists of a variably saturated, discontinuous perched water-bearing zone in Tertiary sand and gravel lenses (defined as the Tpsg HSU) below the vadose zone. In many portions of the OU, including the T2 distal area, the gravels are cemented with hard calcium carbonate and exhibit low permeability. Extraction wells in this HSU are very low yielding, even under vacuum-enhanced conditions, averaging 0.25 or less gallons per minute (gpm). The sands are typically well-sorted, medium-grained, and fairly permeable. The saturated thickness of the perched zone is up to 8 ft. Ground water in the perched Tpsg HSU generally flows toward the south. Perched ground water in this HSU is spatially and temporally variable depending on seasonal rainfall and evapotranspiration along the surrounding hillslopes. The lateral extent of the perched zone is limited by the steep slopes to the north, east, and west of the Building 834 Complex. A potentiometric surface map for the Tpsg HSU is presented as Figure 5. Ground water in this HSU is of poor quality due to naturally high total dissolved solids (TDS) concentrations in ground water ranging from 270 to 6,300 mg/L and natural nitrate that ranges in concentration from 0.44 to 749 mg/L.

Perching Horizon: Pliocene Non-marine Unit — Miocene Neroly Formation — Upper Siltstone/claystone Member (Tps-Tnsc₂ HSU)

Downward ground water and contaminant movement from the perched zone is inhibited by the underlying low-permeability Tps-Tnsc₂ clay and claystone HSU perching horizon. The thickness of the perching horizon ranges from 10 to 40 ft. Saturation within this HSU is highly variable and is locally dependent on the presence of fractures and/or discrete thin sand intervals. A ground water elevation map for the Tps-Tnsc₂ HSU is presented as Figure 6. Ground water in this HSU is of poor quality due to naturally high TDS concentrations in ground water ranging from 520 to 3,300 mg/L and natural nitrate that ranges in concentration from 0.5 to 150 mg/L.

Regional Aquifer: Lower Member of the Neroly Lower Blue Sandstone (Tnbs1 HSU)

Approximately 280 ft of unsaturated, interbedded claystone $(Tnsc_1)$ and sandstone $(Tnbs_2 and Upper Tnbs_1)$ lie below the Tps-Tnsc_2 perching horizon. A laterally extensive regional aquifer (Lower Tnbs_1 HSU) occurs at a depth of over 300 ft bgs.

3.2. Land and Resource Use

Prior to DOE establishing Site 300 as a remote testing facility in 1955, the area was used for cattle grazing. Site 300 is currently an operating facility, and will remain under DOE control for the reasonably anticipated future. There have been no changes in land, building, or ground water use in the Building 834 OU since the Interim Site-Wide ROD and none are anticipated. The Building 834 Complex is still used for thermal cycling experiments and is accessible only to DOE/LLNL workers. Building 834D, where an unacceptable risk for VOC inhalation was

identified, is still used only for storage and building occupancy restrictions remain in place as discussed in Section 4.4.

Current offsite land use near the OU includes agriculture, private residences, and an ecological preserve. The nearest major population center (Tracy, California) is 8.5 miles to the northeast. While there is offsite development proposed adjacent to and north of Site 300 (the Tracy Hills Development), this development does not border the Building 834 OU. There is no known planned modification or proposed development of the offsite land adjacent to the OU.

Ground water underlying the Building 834 Complex is present in a shallow, perched HSU and is not used for water supply due to extremely low well yields, limited extent of saturation, and naturally poor water quality. At Site 300, the regional aquifer (Tnbs₁ HSU) is a source of water for drinking, processing of explosives, and fire suppression. Offsite, the regional aquifer supplies water for domestic and agricultural uses. There are no onsite or private offsite water supply wells in use or planned near the OU.

There are no environmentally sensitive areas within the Building 834 OU. However, the American badger (a California Department of Fish and Game species of special concern) and the big tarplant (an annual plant on the California Native Plant Society's List 1B) do occur in the Building 834 area. The California Department of Fish and Game operates an ecological preserve east of the OU along Corral Hollow Creek, but contaminant releases from the OU are not anticipated to affect the preserve.

3.3. History of Contamination

The Building 834 facilities have been used since the 1950s for experiments involving the thermal cycling of weapon components. From 1962 to 1978, intermittent spills and piping leaks resulted in contamination of the subsurface with VOCs, including TCE, cis-1,2-dichloroethylene (cis-1,2-DCE), chloroform, PCE, and 1,1,1-trichlorethane (1,1,1-TCA), and silicone oils (TBOS/TKEBS). DOE estimates that approximately 550 gallons of TCE were released, either directly to the ground surface and/or to floor drains leading to a nearby septic system leach field. It is likely that a significant fraction of the total amount of TCE released volatilized without infiltrating into the subsurface. Elevated nitrate concentrations in ground water result from a combination of anthropogenic and natural sources. The amount of silicone oil and nitrate released has not been determined. Diesel, benzene, toluene, and ethylbenzene have been detected sporadically in ground water in the core area. The source of these contaminants is an underground fuel storage tank that was excavated in 1994 and closed with the concurrence of the State of California regulatory agencies; no further action is required.

3.4. Initial Response

DOE/LLNL began environmental investigations in the Building 834 area in 1983. Since then, 117 boreholes have been drilled in the Building 834 OU; 82 of these boreholes were completed as ground water monitor or extraction wells (Figure 3). Eleven wells have since been abandoned. The geologic and chemical data from these wells and boreholes are used to characterize the site hydrogeology and to monitor temporal and spatial changes in saturation and dissolved contaminants. Site characterization also included conducting soil vapor and geophysical surveys, installing test pits, and hydraulic testing. As summarized in Section 2, remediation activities at the Building 834 OU conducted prior to the 2001 Interim Site-Wide ROD included soil excavation, numerous treatability studies, soil vapor and ground water extraction, and diverting surface water drainage from contaminant source areas.

3.5. Contaminants of Concern

COCs in ground water in the Building 834 OU include: (1) VOCs including, TCE, cis-1,2-DCE, chloroform, PCE, and 1,1,1-TCA, (2) TBOS/TKEBs, and (3) nitrate. VOCs have also been identified as COCs in subsurface soil/rock. Historical and current concentrations of these COCs are discussed in Section 7.5.2. No COCs were identified in surface soil or surface water.

The predominant contaminant in the vadose zone and ground water is TCE, a suspected human carcinogen. Due to the high concentrations detected, TCE is suspected to be present as a discontinuous, diminishing, dense non-aqueous phase liquid (DNAPL) residual source in the subsurface. The baseline human health risk assessment (Webster-Scholten et al., 1994) estimated a maximum excess cancer risk of 1×10^{-3} to onsite workers, assuming continuous inhalation of VOC vapors volatilizing from the subsurface and migrating into indoor air at Building 834D over a 30-year period. The baseline risk assessment also identified a human cancer risk of 6×10^{-4} for onsite workers continuously inhaling VOC vapors volatilizing from the vadose zone into outdoor air in the vicinity of Building 834D over a 30-year period.

The baseline ecological risk assessment for the Building 834 OU identified a hazard index greater than one for inhalation of VOCs in burrow air and for cadmium in surface soil for ground squirrels and the San Joaquin kit fox.

Significant concentrations of cis-1,2-DCE and low concentrations of vinyl chloride and ethane have been detected in ground water. The presence of these breakdown products is primarily the result of the *in situ* biodegradation of TCE. PCE has also been detected in ground water samples.

Silicone oils (TBOS/TKEBS) occur as a light non-aqueous phase liquid (LNAPL) floating on perched ground water. Silicone oils are relatively non-toxic, and no health risks have been identified for these compounds.

Elevated nitrate concentrations in ground water results from a combination of natural and anthropogenic sources including septic system effluent. Nitrate can cause non-carcinogenic health effects if ingested at elevated concentrations.

The ground water COCs are present in two shallow HSUs: the Tpsg HSU perched waterbearing gravel zone and the underlying Tps-Tnsc₂ HSU clay/claystone perching horizon. The Tpsg perched HSU is highly contaminated with VOCs and TBOS/TKEBS beneath the core area. Discontinuous VOC plumes extend into distal areas in this HSU. Nitrate is present in the Tpsg HSU in the vicinity of the septic tank leach field. Some VOC contamination is also present in the Tps-Tnsc₂ HSU clay perching horizon. COCs have not been detected in the unsaturated portion of the Tnbs₁ sandstone or in ground water in the lower Tnbs₁ regional aquifer.

During December 2003, three passive soil vapor VOC monitoring devises (Gore-Sorbers) were used to detect the presence of VOC vapors in the unsaturated zone between the contaminated Tpsg and Tps perched water-bearing zones and the regional aquifer. One Gore-Sorber was installed in well W-834-1712 screened in the shallow vadose zone (Tpsg) beneath

Building 834 D. Total VOCs were measured at 123 μ g/sorber, which was predominately TCE. A second Gore-Sorber was placed in monitor well W-834-D9A, which is completed in the unsaturated Tnbs₂ geologic unit, that underlies the Tps clay perching horizon. Analytical results from this Gore-Sorber indicated total VOCs at 489 μ g/sorber, also predominately TCE. A third Gore-Sorber was placed into monitor well W-834-D2, which is completed in the upper unsaturated portion of the Tnbs₁ geologic unit. TCE was not detected above the 0.05 μ g/sorber analytical laboratory limit of detection. These data suggest that VOC contamination has not migrated into the unsaturated zone overlying the regional aquifer.

Total VOC concentrations in ground water in the Tpsg and Tps-Tnsc₂ HSUs are shown on Figures 7 and 8, respectively. TBOS/TKEBs concentrations in the Tpsg and Tps-Tnsc₂ HSUs are shown on Figures 9 and 10, respectively. Nitrate concentrations in the Tpsg and Tps-Tnsc₂ HSUs are shown on Figures 11 and 12, respectively.

3.6. Summary of Basis for Taking Action

Remedial actions were initiated in the Building 834 OU to address unacceptable human health risks associated with onsite worker inhalation exposure to TCE volatilizing from the subsurface soil to indoor air within and outdoor air in the vicinity of Building 834D. The remedial actions were also initiated to remediate ground water in this area to meet cleanup standards. The remedial action objectives for the Building 834 OU cleanup are discussed in Section 4.1.

4. Remedial Actions

4.1. Remedy Selection

The remedy selected for the Building 834 OU is intended to achieve the following Remedial Action Objectives (RAOs):

For Human Health Protection:

- Restore ground water containing contaminant concentrations above cleanup standards.
- Prevent human ingestion of ground water containing contaminant concentrations (single carcinogen) above cleanup standards.
- Prevent human inhalation of VOCs volatilizing from subsurface soil to air that pose an excess cancer risk greater than 10^{-6} or hazard index greater than 1, a cumulative excess cancer risk (all carcinogens) in excess of 10^{-4} , or a cumulative hazard index (all noncarcinogens) greater than 1.
- Prevent human exposure to contaminants in media of concern that pose a cumulative excess cancer risk (all carcinogens) greater than 10⁻⁴ and/or a cumulative hazard index greater than one (all noncarcinogens).

For Environmental Protection:

• Restore water quality to ground water cleanup standards within a reasonable timeframe and to prevent plume migration to the extent technically and economically practicable. Maintain existing water quality that complies with ground water cleanup standards to the extent technically and economically practicable. This will apply to both individual and multiple constituents that have additive toxicology or carcinogenic effects.

- Ensure ecological receptors important at the individual level of ecological organization (listed threatened or endangered, State of California species of special concern) do not reside in areas where relevant hazard indices exceed 1.
- Ensure existing contaminant conditions do not change so as to threaten wildlife populations and vegetation communities.

In the 2001 Interim Site-Wide ROD, the remedy for the Building 834 OU was selected based on its ability to contain contaminant sources, prevent further plume migration, remove contaminant mass from the subsurface, and protect human health and the environment. The interim remedy was selected as the final remedy in the 2008 Final Site-Wide ROD.

The selected remedy for the Building 834 OU consisted of:

- 1. Monitoring soil vapor and ground water to evaluate the effectiveness of the remedial action in achieving cleanup standards, plus post-remediation monitoring.
- 2. Risk and hazard management to prevent onsite workers exposure to VOCs volatilizing from subsurface soil and impacts to animals until risk and hazard is mitigated through active remediation. Annual risk re-evaluation indicated that the inhalation risk for VOCs volatilizing from subsurface soil into outdoor air in the vicinity of Building 834D has been mitigated through remediation. Therefore, risk and hazard management for this exposure pathway is no longer necessary. These risk re-evaluation results are documented in the 2003 and 2004 Annual Compliance Monitoring Report for LLNL Site 300 (Dibley et al., 2004a and 2005a). Institutional/land use controls will be implemented to prevent human exposure to contamination and to protect the integrity of the remedy
- 3. Extracting and treating soil vapor and ground water to mitigate risk and hazards posed by VOCs in the subsurface soil and reduce VOC, nitrate, and TBOS/TKEBS concentrations in ground water and VOCs in subsurface soil to cleanup standards.
- 4. Continue evaluating innovative technologies to improve remediation of VOCs in lowpermeability sediments and expedite cleanup.

4.2. Remedy Implementation

Ground water and soil vapor extraction and treatment systems have been operating in the Building 834 OU since 1986; first as treatability studies and later as interim remedial actions. The location of ground water and soil vapor extraction wells and treatment systems are shown in Figure 3. Full-scale ground water extraction and treatment began in the Building 834 core (source) area in 1995 to reduce VOC concentrations and mass in ground water. Full-scale soil vapor extraction and treatment began in 1998 to reduce VOC concentrations and mass in the vadose zone. Although the ground water treatment system (GWTS) can be operated alone, the soil vapor treatment system (SVTS) is not operational without ground water extraction due to the upconing of the ground water in the well that covers the well screen and prevents soil vapor flow. Typically, soil vapor extraction is more effective in removing VOCs than ground water extraction. In addition, the negative pressure (i.e., vacuum) created in the well casing during dual-phase extraction enhances the yield of ground water from the Tpsg HSU.

Due to the very low ground water yield from individual extraction wells (less than 0.1 gallons per minute [gpm]), the ground water treatment system has been operated in batch mode. The GWTS extracts ground water at an approximate combined flow rate of 0.23 gpm and the SVTS extracts soil vapor at a combined flow rate of approximately 103 scfm. The current GWTS configuration includes floating hydrocarbon adsorption devices to remove the floating silicon oil, TBOS/TKEBs, and any floating diesel, followed by aqueous-phase GAC to remove VOCs, dissolved-phase TBOS/TKEBs, and diesel from ground water. Nitrate-bearing treated effluent is then discharged via a misting tower onto the landscape for uptake and utilization of the nitrate by indigenous grasses. The current SVTS configuration includes vapor-phase GAC for VOC removal. Treated vapors are discharged to the atmosphere under an air permit from the San Joaquin Valley Unified Air Pollution Control District.

Per the Federal Facility Agreement milestones to "Initiate build-out and upgrade of the B834-SRC ground water and soil vapor treatment facility in the Building 834 OU" for December 2, 2002 and "Complete Building 834 treatment facility modifications and extraction wellfield buildout" for December 30, 2004, modifications were made to improve the performance of both the ground water treatment system and the extraction wellfield at the Building 834 OU. In 2004, the following modifications were completed to the ground water treatment system:

- Replacement of the oil-water separator with floating hydrocarbon adsorption devices (pigs) placed in the influent ground water storage tank to remove any floating product that is extracted.
- Conversion from air stripping with vapor-phase GAC treatment to the use of aqueousphase GAC to remove VOCs from ground water.
- Installation of monitoring equipment to measure the volume of ground water and soil vapor extracted from each well.

The core area extraction wellfield was also modified, reducing the number of extraction wells from 16 to 9 wells. This modification was based on individual well performance data collected during a series of zone-of-influence tests conducted on core area extraction wells. Test data indicated seven extraction wells were not contributing significantly to mass removal. These seven wells were converted to performance monitoring wells and the remaining nine core area extraction wells extract both ground water and soil vapor. The currently active extraction wellfield in the core area consists of wells W-834-B2, W-834-B3, W-834-D4, W-834-D6, W-834-D7, W-834-D12, W-834-D13, W-834-J1, and W-834-2001.

In 2004, the ground water and soil vapor extraction wellfield was expanded to the VOC plume in the leachfield area to accelerate ground water cleanup. The currently active extraction wellfield in the leachfield area consists of wells W-834-S1, W-834-S12A, and W-834-S13. Additionally, in 2004, extraction wellfield piping was extended to the T2 portion of the distal area, but pumping from the T2 area was delayed to conduct studies to evaluate the potential of utilizing *in situ* bioremediation in this area. Since 2005, an enhanced bioremediation treatability study has been conducted in this area and results of this test are presented in Appendix A.

4.3. System Operations/Operation and Maintenance

The Building 834 OU ground water and soil vapor extraction and treatment systems are operating as designed and no significant operations, performance, maintenance, or cost issues were identified during this review. All required documentation is in place, and treatment system operations and maintenance (O&M) activities are consistent with established procedures and protocols.

O&M procedures are contained in the following documents:

- Health and Safety Plan and Quality Assurance/Quality Control Plan for the O&M of the Building 834 Treatment Facilities, contained within the Interim Remedial Design document (Gregory et al., 2002).
- Building 834 Treatment Facility Operations and Maintenance Manual (LLNL, in progress).
- Operations and Maintenance Manual for Miniature Treatment Units, Ground Water Treatment Units, and Solar Treatment Units, Volume 13 (Martins, 2007).
- Operations and Maintenance Manual, Volume 1: Treatment Facility Quality Assurance and Documentation (LLNL, 2004).
- Integration Work Sheet Safety Procedure #11341: Ground Water and Soil Vapor Treatment Facility Operations at Site 300.
- Integration Work Sheet Safety Procedure #11314: Environmental Restoration Department (ERD) Site 300 Ion Exchange Resin Emplacement.
- Integration Work Sheet Safety Procedure #11313: ERD Site 300 Off-Road Driving Training.
- Integration Work Sheet Safety Procedure #11343: ERD Routine Ground Water Sampling & Water Level Monitoring at Site 300.
- Integration Work Sheet Safety Procedure #14984: ERD Routine Electronic Operations at Site 300.
- Integration Work Sheet Safety Procedure #11339: ERD Site 300 Hydraulic Pump Operation.
- Integration Work Sheet Safety Procedure #11346: Spent Aqueous and Vapor-phase Granular Activated Carbon (GAC) Replacement at Site 300.
- LLNL Livermore Site and Site 300 Environmental Restoration Project Standard Operating Procedures (Goodrich and Lorega, 2009).
- Building 834 Substantive Requirements and the Monitoring and Reporting Program issued by the California RWQCB.
- Building 834 Permit to Operate issued by the San Joaquin Valley Unified Air Pollution Control District.
- Site-Wide Compliance Monitoring Plan/Contingency Plan for Interim Remedies at LLNL Site 300 (Ferry et al., 2002) until superseded by Site-Wide Compliance Monitoring Plan/Contingency Plan for Remedies at LLNL Site 300 (Dibley et al., 2009).

Monitoring and optimizing the performance and efficiency of the extraction and treatment systems comprises a large portion of the O&M activities. Extracted ground water is sampled throughout the treatment process to ensure compliance with discharge requirements. Treatment system parameters such as pressure and flow are routinely recorded to anticipate potential mechanical problems and monitor system performance.

The major O&M activities for the Building 834 ground water and soil vapor treatment systems include:

- Maintaining the particulate filters, blower, and compressor.
- Maintaining the misting towers used to discharge treated ground water.
- Protecting the unit from freezing in cold weather.
- Replacing and properly disposing of spent GAC.
- Routinely inspecting and maintaining extraction well pumps, pipelines, the soil vapor extraction blower, and temperature and air flow sensors.
- Ensuring the temperature within the vapor-phase GAC units remains within the optimal range.
- Collecting condensate from vapor extraction lines and vapor-phase GAC units to maximize GAC adsorption capacity.

The treatment systems have consistently operated in compliance with all permits and regulatory requirements, including the requirements for discharge of treated ground water, during the Five-Year Review period.

The budgeted and actual environmental restoration costs for the Building 834 OU are tracked closely and are consistently within or near the allocated budget. Table 1 presents the actual costs for the last five fiscal years, 2007 through 2011.

4.4. Institutional Controls

Institutional/land use controls are non-engineered actions or measures used to prevent or limit the potential for human exposure to contamination at the Building 834 OU and to protect the integrity of the remedy. The general types of institutional/land use controls that are used to prevent human exposure to contamination at the Building 834 OU include:

- Access controls Measures such as fences, signs, and security forces that are used to prevent exposure by controlling and/or restricting access to areas of contamination.
- Administrative controls Measures such as pre-construction review and controls for limiting or restricting access to contaminated areas and prohibitions on water supply well drilling.

Table 2 presents a description of: (1) the institutional/land use control objective and duration, (2) the risk necessitating land use controls, and (3) the specific institutional/land use controls and implementation mechanisms used to prevent exposure to contamination at the Building 834 OU. Figure 13 shows the specific areas of the Building 834 OU where the institutional/land use controls will be implemented and maintained.

Monitoring and inspection of the Building 834 OU will be performed throughout the remediation period to determine whether the institutional/land use controls remain protective and
consistent with all remedial action objectives. In addition, DOE will review facility and land use to evaluate changes in exposure pathway conditions that could affect the risk assessment assumptions and calculations.

Institutional/land use controls are included in the Risk and Hazard Management Program contained in the Site-Wide Compliance Monitoring Plan (Dibley et al., 2009). Any new or modified institutional/land use controls resulting from the Five-Year Review process will be incorporated in the Risk and Hazard Management Program contained in the revised Site-Wide Compliance Monitoring Plan. Risk and hazard monitoring results conducted during the year are submitted to the U.S. EPA and State regulatory agencies in the Annual Site 300 Site-Wide Compliance Monitoring Reports. In addition, DOE will work with LLNL Site 300 Management to incorporate these institutional/land use controls into the Site 300 Integrated Strategic Plan or other appropriate institutional planning documents.

The land use controls and requirements described herein are only applicable to the Building 834 OU and associated contaminated environmental media that are being addressed through the CERCLA process. DOE will implement, maintain, and enforce these institutional/land use controls at the Building 834 OU for as long as necessary to keep the selected remedy protective of human health and the environment.

If DOE later transfers these procedural responsibilities to another party by contract, property transfer agreement, or through another means, DOE will retain ultimate responsibility for the integrity of the remedy. In the event that the property is transferred in the future, DOE will execute a land use covenant at the time of transfer in compliance with California Code of Regulations Title 22, Division 4.5, Chapter 39, Section 67391.1. If the Site 300 property were to be transferred to an entity outside the U.S. DOE, the necessary institutional/land use controls would be determined prior to the property transfer based on: (1) the intended land use subsequent to the property transfer, and (2) contamination and associated risk, if any, remaining at the Building 834 OU.

The institutional controls were reviewed and are still effective for preventing exposure to contaminated media. The 2011 institutional controls inspection found all institutional controls were in place and properly implemented. The checklist will be presented in the 2011 Annual Compliance Monitoring Report.

5. Progress Since Last Review

This section describes the Protectiveness Statement and recommendations and follow-up actions from the 2007 Building 834 OU Five-Year Review. It also describes the status of the actions recommended in this previous review.

5.1. Protectiveness Statement from Last Review

The 2007 Building 834 OU Five-Year Review determined that the remedy for the OU was protective of human health and the environment. The Health and Safety Plan and the Contingency Plan are in place, sufficient to control risks, and properly implemented. Ground water and soil vapor extraction and treatment are effectively controlling the migration of contaminants, and reducing contaminant concentrations in the subsurface as needed to meet

cleanup standards in the time frame anticipated at the time of the Final Site-Wide ROD. Institutional controls are in place to prevent use of contaminated ground water.

No deficiencies in the remedy were identified during the 2007 Five-Year Review.

5.2. Recommendations and Follow-up Actions from the 2007 Five-Year Review

The recommendations in the 2007 Five-Year Review and the status of the follow-up actions taken in response to the recommendations are as follows:

1. *Recommendation:* DOE/LLNL will sample and analyze all monitor wells in the Building 834 OU for perchlorate and report the results in the 2007 Annual Site-Wide Compliance Monitoring Report for Site 300. Based on the results of the analysis, specific wells may continue to be monitored for perchlorate in ground water.

Follow-up Action: The perchlorate sampling history of each Building 834 well is summarized in Table 3. Information for each well in the table includes the number of historical perchlorate samples collected, the range in perchlorate concentrations (in $\mu g/L$), and comments regarding whether perchlorate sampling was discontinued and the associated rationale. As part of the perchlorate evaluation in 2007, DOE/LLNL did not attempt to collect perchlorate samples from 36 of the 65 total wells listed in Table 3, due to either previous perchlorate non-detections in these wells, or in one case (W-834-T7A), a previous very low concentration (4.5 μ g/L). Of the 29 remaining wells where sampling for perchlorate was attempted in 2007, 13 were dry and sampling for perchlorate has not been conducted since 2007 due to dry conditions. Of the remaining 16 wells that were sampled for perchlorate in 2007, only two (W-834-2118 and W-834-S7) yielded detectable perchlorate concentrations. As reported in the 2007 Annual Compliance Monitoring Report, well W-834-2118 yielded a perchlorate concentration of 4 µg/L (August 2007) and W-834-S7 yielded concentrations of 8.8 µg/L (March 2007) and 9.9 µg/L (August 2007). Since 2007, perchlorate samples have been collected semiannually from these two wells. Perchlorate has been detected once at a concentration above the 6 µg/L cleanup standard in well W-834-2118 (6.4 µg/L in June 2006). Current perchlorate concentrations in this well are slightly above the 4 µg/L reporting limit (4.9 µg/L in February 2011). From 2007 to 2009, perchlorate was detected in well W-834-S7 at concentrations ranging from 8.8 to 11 µg/L. DOE/LLNL have been unable to collect samples for perchlorate analysis in well W-834-S7 since 2009 due to insufficient water in the well from which to collect samples. Perchlorate will continue to be sampled semiannually from these two wells to determine if perchlorate is consistently present above the cleanup standard.

2. **Recommendation:** DOE/LLNL will continue to evaluate other remedial technologies, such as *in situ* bioremediation, that could shorten cleanup time, especially those that will facilitate remediation of the low-permeability sediments. However, even if these technologies are implemented, it may not be possible to fully remediate volatile organic compounds in the low-permeability sediments.

Follow-up Action: Since 2005, a long-term enhanced *in situ* bioremediation treatability study has been ongoing in the T2 portion of the Building 834 distal area. The objective of this study was to assess the performance of passive *in situ* bioremediation of TCE at

concentrations greater than 10,000 μ g/L in the low-yielding Tpsg HSU in this area. The long-term study was conducted in various phases and involved tracer testing, nutrient and bacteria injection, and performance monitoring. Details of the procedures and findings of the treatability study are presented in Appendix A, as well as recommendations for implementing this technology to assist in long-term cleanup

3. *Recommendation:* Because some VOCs may remain at the Building 834 OU following the achievement of the proposed cleanup standards for VOCs in subsurface soil, a land use control will be added that prohibits the transfer of lands with unmitigated contamination that could cause potential harm under residential or unrestricted land use. This prohibition will be codified in the Final Site-Wide ROD scheduled for 2008. The Final Site-Wide ROD will also reference the LLNL Site 300 Integrated Strategic Plan or other appropriate institutional planning document into which this prohibition will be incorporated.

Follow-up Action: A land use control that prohibits the transfer of lands with unmitigated contamination that could cause potential harm under residential or unrestricted land use was included in the Final Site-Wide ROD.

4. *Recommendation:* The action-specific ARAR change identified in Section 7.2, and ARARs related to ground water cleanup will be established in the Final Site-Wide ROD scheduled for 2008.

Follow-up Action: The action-specific ARAR change identified in Section 7.2 was the California Code of Regulations, Title 22, Section 67391.1, adopted April 19, 2003. It contains requirements for imposing legal limitations on future site uses and activities through a land use covenant. A land use control that prohibits the transfer of lands with unmitigated contamination that could cause potential harm under residential or unrestricted land use was included in the Final Site-Wide ROD.

No other follow-up actions were identified related to this Five-Year Review.

5.3. Status of Other Prior Issues

There are no other prior issues.

6. Five-Year Review Process

The Five-Year Review of the Building 834 OU at LLNL Site 300 was led by Claire Holtzapple, Site 300 Remedial Project Manager for the DOE/NNSA-Livermore Site Office. The following team members assisted in the review:

- Leslie Ferry, Program Leader, LLNS.
- Valerie Dibley, Deputy Program Leader, LLNS.
- Vic Madrid, Hydrogeologic Team Leader, LLNS.
- John Valett, Hydrogeologist, Weiss Associates.
- Mark Buscheck, Hydrogeologist, Weiss Associates.

This Five-Year Review consisted of examining relevant project documents and site data:

- Final Site-Wide Remedial Investigation for Lawrence Livermore National Laboratory Site 300 (Webster-Scholten, 1994).
- Final Site-Wide Feasibility Study for Lawrence Livermore National Laboratory Site 300 (Ferry et al., 2006).
- Interim Site-Wide Record of Decision for Lawrence Livermore National Laboratory Site 300 (U.S. DOE, 2002).
- Site-Wide Record of Decision for Lawrence Livermore National Laboratory Site 300 (U.S. DOE, 2008).
- Remedial Design Work Plan for Interim Remedies at Lawrence Livermore National Laboratory Site 300 (Ferry et al., 2001).
- Interim Remedial Design for the Building 834 Operable Unit at Lawrence Livermore National Laboratory Site 300 (Gregory et al., 2002).
- Five-Year Review Reports for the Building 834 Operable Unit Lawrence Livermore National Laboratory Site 300 (Ferry et al., 2002; Dibley et al., 2007).
- Site-Wide Remediation Evaluation Summary Report for Lawrence Livermore National Laboratory Site 300 (Ferry et al., 2006).
- Semi-annual Site-Wide Compliance Monitoring Reports that include evaluations of remediation progress in the Building 834 OU (Dibley et al., 2006b, 2007c, 2007d, 2008c, 2009c, 2009d, 2010a, 2010b and 2011; LLNL 2008.

This Five-Year Review evaluates subsurface contaminant concentration and remediation system performance data collected through the first semester of calendar year 2011.

The completed report will be placed in the Administrative Record file and the Information Repositories located in the LLNL Discovery Center in Livermore, California and in the Tracy Public Library in Tracy, California. Notice of its initiation and completion will be placed in two publications: *The Tracy Press* and *East County Times*. The initial notice was published in *The Tracy Press* on January 5, 2012 and the *East County Times* on January 6, 2012.

7. Five-Year Review Findings

7.1. Interviews and Site Inspection

DOE/LLNL meets monthly with the EPA, RWQCB, and DTSC Remedial Project Managers (RPMs) and quarterly with a community action group at Technical Assistance Grant Meetings to discuss remediation activities, issues, and cleanup status and progress.

There is a continuous presence of Site 300 Environmental Restoration Program staff at Site 300 that routinely inspect the: (1) extraction wellfield and treatment facilities weekly, and (2) monitoring wellfield during sampling activities. The Site 300 Environmental Restoration Program conducts self-assessment inspections of facilities and DOE conducts quarterly inspections of remediation activities at Site 300. The RWQCB RPM performs site inspections twice a year, and EPA and DTSC RPMs perform site inspections as requested. The EPA performed the construction completion inspection on July 13, 2005. The Five-Year Review

Inspection was performed by DOE/LLNL on March 30, 2010. The Five-Year Review Inspection Checklist is included as Attachment A.

Operational issues and resulting corrective actions identified during routine inspections associated with the Building 834 treatment systems and extraction wellfields are: (1) described in detail in the Site 300 Compliance Monitoring Reports that are issued semi-annually, and (2) discussed and presented in the RPM Project Updates that are issued prior to and discussed with the regulators at the monthly RPM meetings. The contents of the Project Updates are incorporated into the RPM meeting minutes that are distributed following the meetings.

7.2. Changes in Cleanup Standards and To-Be-Considered Requirements

The following action-specific applicable or relevant and appropriate requirements (ARARs) have been adopted since the Interim Site-Wide ROD was signed in 2001:

- The California Code and Regulations, Title 22, Section 67391.1 was adopted April 19, 2003. It contains requirements for imposing legal limitations on future site uses and activities through a land use covenant. There is no impact on the protectiveness of the remedy related to the new requirement for a land use covenant at the time of property transfer.
- The State of California established a Maximum Contaminant Level (MCL) (6 μg/l) for perchlorate on October 18, 2007.

This action-specific ARAR and ARARs related to ground water cleanup were included in the 2008 Final Site-Wide ROD.

The EPA National Pollution Discharge Elimination System (NPDES) Pesticide Rule changed in 2011, however, no Site 300 treatment systems currently discharge to the ground surface or fall under an NPDES permit.

There have been no changes in cleanup standards since the 2008 Final Site-Wide ROD.

7.3. Changes in Land, Building, or Ground Water Use

There have been no changes in land, building, or ground water use in the Building 834 OU since the Site-Wide ROD was signed in 2008. The OU is still accessible only to DOE/LLNL workers. The Building 834 Complex is still used for thermal cycling experiments. Building 834D, where an unacceptable risk for VOC inhalation was identified, is still used only for storage and building occupancy restrictions remain in place as discussed in Table 2. Ground water underlying the Building 834 Complex is present in a shallow, perched HSU and is not used for water supply.

7.4. Changes in Exposure Pathways, Toxicity, and Other Contaminant Characteristics

During the review period, the State of California Office of Environmental Health Hazard Assessment (OEHHA) reclassified ethylbenzene as a carcinogen in 2007. Ethylbenzene in subsurface soil in the Building 834 OU was evaluated in the baseline risk assessment as a non-carcinogen.

The maximum concentration of ethylbenzene detected in subsurface soil at Building 834 was 0.0035 mg/kg. In the baseline risk assessment, the non-carcinogenic hazard for ethylbenzene volatilizing from subsurface soil to both indoor and outdoor air at Building 834D was calculated to be 0.0001 (HI<1). The maximum concentration of ethylbenzene in subsurface soil (0.0035 mg/kg) is well below the EPA 2008 Regional Screening Level for industrial soil of 29 mg/kg, which includes an air inhalation pathway component. In addition, the baseline risk assessment calculated concentrations of ethylbenzene volatilizing from subsurface soil into indoor and outdoor air at Building 834D of 0.0056 μ g/m³ and 0.0053 μ g/m³, respectively. These concentrations are well below EPA's 2008 Regional Screening Level for ethylbenzene in industrial air of 4.9 μ g/m³. Therefore, no further action regarding ethylbenzene in subsurface soil at Building 834 is required, and the protectiveness of the remedy is not affected by this change.

There were no other changes in exposure pathways, toxicity, or other contaminant characteristics in the Building 834 OU during this review period.

However, EPA issued a change to their TCE toxicity value on September 28, 2011. While this does not represent a "Change in Exposure Pathways, Toxicity, and Other Contaminant Characteristics" for this review period (July 2006 to June 2011), DOE will evaluate the implications of the September 28, 2011 change to EPA's TCE toxicity value for the TCE inhalation risk at the Building 834 OU which will be discussed in the next five-year review report for the Building 834 OU that will encompass the time period (July 2011 to June 2016) during which this change occurred.

7.5. Data Review and Evaluation

Table 4 summarizes the pre-remediation and current (first semester 2011) COC concentrations in soil vapor and ground water in the core, leachfield, and distal areas. A discussion of remedial progress in the vadose zone and ground water is presented in Sections 7.5.1 and 7.5.2, respectively.

7.5.1. Vadose Zone Remediation Progress

Ongoing performance of the Building 834 soil vapor extraction system is evaluated by reviewing temporal trends in soil vapor extraction well concentrations during both active extraction and non-active rebound periods.

Full-scale soil vapor extraction and treatment began in 1998 to reduce VOC concentrations and mass in the vadose zone using eight vapor extraction wells. In the source area, ground water extraction is used to dewater the Tpsg HSU, creating a larger volume of soil available from which to extract VOCs in soil vapor. Typically, soil vapor extraction is more effective in removing VOCs than ground water. In 2004, soil vapor extraction was initiated from three dualphase extraction wells located in the leachfield area.

Recent (first semester 2011), TCE soil vapor concentrations from the core area SVE wells ranged from 0.021 to 30 parts per million on a volume per volume basis ($ppm_{v/v}$). These TCE vapor concentrations have decreased by two orders-of-magnitude from the maximum preremediation core area concentration of 3,200 $ppm_{v/v}$ (W-834-D4, 1989). Figure 14 shows long-term TCE vapor concentration trends in treatment facility influent and core area vapor extraction wells (Figure 14a) W-834-B2, W-834-B3, and W-834-J1; (Figure 14b) W-834-D6, W-834-D7, and W-834-D12; and (Figure 14c) W-834-D4, W-834-D13, and W-834-2001, as well as monthly facility vapor flow volume. All three time-series graphs show general decreasing trends in TCE concentrations. As described in Section 4.2, the vapor system was shut down from July 2002 to September 2004 for wellfield modifications and this time period was used to measure rebound of TCE vapor concentrations in both treatment facility influent and individual vapor extraction wells. As shown on Figure 14, significant rebound of TCE concentrations was detected in all vapor extraction wells, as well as the treatment facility influent, immediately after this approximate two-year long time period. Within the last five years, two additional shut down periods occurred: (1) from late June to early November of 2007 the system was off for carbon change-out and related contractual issues, and (2) from November 2010 to April 2011 the system was off for blower replacement. After the first (2007) shutdown period, rebound of VOC concentrations in soil vapor occurred in both northern core area wells (W-834-B2 and W-834-B3 shown in Figure 14a), and one central core area well (W-834-D12 shown in Figure 13b). After the second (2010/2011) shutdown period, rebound occurred in all the central core area wells (Figure 14 (b and c)).

Recent (first semester 2011) TCE soil vapor concentrations from the leachfield area SVE wells ranged from 1.1 to 5.6 ppm_{v/v}, significantly lower than the 710 ppm_{v/v} maximum preremediation concentration measured in 2004 (W-834-S13). Figure 15 shows long-term TCE vapor concentration trends in leachfield vapor extraction wells W-834-S1, W-834-S12A, and W-834-S13, as well as monthly facility vapor flow volume. As noted, the Building 834 soil vapor extraction wellfield was expanded in 2004 to include the leachfield wells, thereby significantly increasing the total vapor flow. As shown in Figure 15, all three wells show significant decreasing trends in TCE concentrations since soil vapor extraction began in 2004. Additionally, as shown on Figure 15, rebound appeared in W-834-S1 and -S12A after the 2007 shutdown period, and in W-834-S12A and W-834-S13 after the 2010/2011 shut down period.

As shown on Figure 16, the vapor extraction and treatment system has removed approximately 322 kilograms (kg) of VOCs as of the end of 2010. In the future, DOE/LLNL will continue to conduct rebound testing to assess source area cleanup performance.

7.5.2. Ground Water Remediation Progress

Ground water data were evaluated to assess the effectiveness of extraction and treatment to remediate VOCs, TBOS/TKEBS, and nitrate in ground water in the Building 834 OU. Remediation progress was evaluated by:

- Comparing historic maximum ground water COC concentrations and plume extent to current concentrations and extent,
- Reviewing ground water COC performance well concentration trends, and
- Evaluating extraction wellfield capture zones.

Remediation progress in the Tpsg and Tps-Tnsc₂ HSUs is discussed in Sections 7.5.2.1 and 7.5.2.2, respectively.

7.5.2.1. Remediation Progress in the Tpsg HSU

TCE, cis-1,2-DCE, chloroform, PCE, and 1,1,1-TCA are the VOC contaminants of concern in Building 834 OU ground water. In the Tpsg HSU, TCE has decreased from a historical maximum concentration of 800,000 μ g/L (W-834-D3 in 1993) to a first semester 2011 maximum of 17,000 μ g/L (W-834-D13, April). The cleanup standard (state and federal MCL) for TCE is

5 μ g/L. Cis-1,2-DCE has decreased from a historical maximum concentration of 540,000 μ g/L (W-834-D4, 1990) to a current maximum of 19,000 μ g/L (W-834-D4, March). The cleanup standard (state MCL) for cis-1,2-DCE is 6 μ g/L.

Chloroform has decreased from a historical maximum concentration of 950 µg/L (W-834-S1, 1989) to a current maximum concentration of 1.5 µg/L (W-834-D6, March), below the cleanup standard (state and federal MCL for total trihalomethanes [THMs]) of 80 µg/L. PCE has decreased from a historical maximum concentration of 10,000 µg/L (W-834-D3, 1993) to a current maximum concentration of 150 µg/L (W-834-D13, March). The cleanup standard (state and federal MCL) for PCE is 5 µg/L. 1,1,1-TCA has decreased from a historical maximum concentration of 33,000 µg/L (W-834-J1, 1991) to a current concentration of below the 0.5 µg/L reporting limit. The cleanup standard (state MCL) for 1,1,1-TCA is 200 µg/L. The highest VOC concentrations in Tpsg HSU ground water at the Building 834 OU are detected in the core area. Active remediation has reduced total VOC ground water concentrations in the Tpsg HSU from a historical (pre-remediation) maximum of 1,060,000 µg/L (W-834-D3, 1993) to a first semester 2011 maximum concentration of 19,383 µg/L (W-834-D4, March). The maximum total VOC concentration shown on Figure 7 (second semester of 2010) is 54,000 µg/L in monitoring well W-834-C5. Figure 17 shows long-term VOC trends in extraction and monitoring wells in (a) the northern core area and (b) the southern core area. Extraction wells are defined as (EW) in the legend and are shown as dashed lines. Monthly ground water treatment facility flow volume (in gallons) is also shown. In the northern core area, extraction wells W-834-B2 and W-834-B3 and all but two monitoring wells show a general decreasing trend from pre-remediation levels. The two monitoring wells with the highest concentrations (W-834-B4 and W-834-C5) show fairly stable trends indicating that these two wells may not be influenced by northern core area extraction wells W-834-B2 and W-834-B3. Concentrations in wells W-834-B4 and W-834-C5 will continue to be closely monitored. If concentrations remain stable or increase, the installation of extraction wells in the vicinity of these two wells may be considered to reverse these trends. In the southern core area, extraction well W-834-J1 and nearby monitoring wells show a significant decreasing trend from pre-remediation levels. After the recent O&M shutdown in early 2011, the southern core area wells generally show more rebound in VOC concentrations than the northern core area wells. Figure 18 shows long-term VOC trends in extraction and monitoring wells in (a) the west-central core area and (b) the east-central core area. In both subareas, all extraction and monitoring wells show a general decreasing trend from pre-remediation levels. After the recent O&M shutdown in early 2011, most of these wells show moderate to significant rebound in VOC concentrations.

Because the GWTS and SVTS systems were off intermittently in December 2006 and January 2007 due to both electrical repairs and for freeze protection, the monthly facility flow for those months were much lower than average. VOC concentrations in some other wells also increased after January 2007, although not as much. The December 2006 and January 2007 monthly flows in extraction wells near W-834-D11 and -D5 (such as W-834-B2, -D4, and -S13) were generally lower than other core area extraction wells.

In the leachfield area, total VOCs in the Tpsg HSU have decreased by approximately an order-of-magnitude, from a pre-remediation maximum of 179,200 μ g/L (W-834-S1, 1988) to a first semester 2011 maximum concentration of 12,000 μ g/L (W-834-2113, February). The maximum total VOC concentration in the leachfield area shown on Figure 7 (second semester of 2010) is 20,000 μ g/L in monitoring well W-834-2113. Figure 19 shows long-term VOC trends

in the leachfield area extraction wells (W-834-S1, W-834-S12A, and W-834-S13) and performance monitoring well W-834-2113. As noted on this figure, increased facility flow in late 2004 is due to the initiation of extraction from the leachfield wells as part of the wellfield expansion at that time. As shown, all three leachfield area extraction wells generally exhibit significant decreasing VOC trends after late 2004. Performance monitoring well W-834-2113 was drilled in January 2005 and generally exhibits a stable VOC trend indicating that this well is most likely not influenced by the leachfield area extraction wells.

In the distal area, total VOC concentrations in the Tpsg HSU have decreased from a historic maximum of 86,000 μ g/L (W-834-T2A, 1988) to a first semester 2011 maximum of 11,052 μ g/L (W-834-T2A, February). The maximum total VOC concentration in the distal area shown on Figure 7 (second semester of 2010) is 8,600 μ g/L in monitoring well W-834-T2A. As mentioned in subsection 4.2, extraction wellfield infrastructure was extended to the T2 portion of the distal area in 2004 as part of the overall wellfield expansion at that time, however, pumping at the T2 portion was delayed in order to conduct studies to evaluate the potential of utilizing *in situ* bioremediation in this area. Since 2005, a long-term enhanced bioremediation treatability study has been conducted in the T2 portion of the distal area. The treatability study process, conclusions, and recommendations (including VOC trend graphs for key wells) are presented in detail in Appendix A. The primary recommendation from Appendix A for further remediation of Tpsg HSU ground water in the distal area is to convert the T2 portion into a re-circulation cell(s) whereby multiple closely spaced injection/extraction well pairs are used to deliver and distribute reagents in the subsurface to promote biotransformation of TCE to benign end products.

Figure 20 shows a comparison of the distribution of total VOCs in ground water in the Tpsg HSU in second semester 2005 versus second semester 2010. Only extraction wells are shown. Although the overall extent of total VOCs in ground water with concentration above the 0.5 μ g/L reporting limit has not changed significantly, the area of highest concentration has been reduced. In the core area, the portion of the total VOC plume greater than 10,000 μ g/L has been reduced by approximately one third. In the leachfield and distal areas, the portion of the plume greater than 10,000 μ g/L has also been significantly reduced.

Figure 7 shows the hydraulic capture zones for the ground water extraction and treatment remedy in the Tpsg HSU where active extraction is occurring in the core and leachfield areas. The hydraulic capture zones are based on pumping water levels from extraction wells and nearby performance monitor wells. Capture zones presented in Figure 6 were prepared using data from the second semester of 2010. Extraction well hydraulic capture is constrained in portions of the core and leachfield areas, primarily due to the low yields and spacing of the extraction wells. As shown on Figure 7, the closely spaced extraction wells in the central core area are capturing the highest VOC concentrations in that area. As mentioned above, the two extraction wells in the northern core area (W-834-B2 and W-834-B3) may not be fully capturing some portions of highest VOC concentrations in that area. In the leachfield area, the extraction wellfield captures portions of the VOCs in ground water; however, the highest concentrations (in the vicinity of monitoring well W-834-2113) are not fully captured.

TBOS/TKEBS is found exclusively in the core area. The maximum TBOS/TKEBS ground water concentration in the Tpsg HSU in the core area has decreased from a historic maximum of 7,300,000 μ g/L (W-834-D3, 1995) to a first semester 2011 maximum of 4,800 μ g/L (W-834-D3, February). The maximum TBOS/TKEBs concentration in the core area shown on Figure 9 (first semester of 2010) is 140,000 μ g/L in W-834-D3. TBOS/TKEBS concentrations vary from

one sampling event to the next due to varying amounts of free-phase TBOS/TKEBS in the subsurface. Because TBOS/TKEBS concentrations in Tpsg HSU wells in the leachfield and distal areas have historically been below reporting limits, sampling for TBOS/TKEBS in the leachfield and distal areas under the new (2009) Compliance Monitoring Plan was changed to a biennial frequency, with approximately half the wells to be sampled during even numbered years and half to be sampled during odd numbered years. TBOS/TKEBS concentrations in the Tpsg HSU were below reporting limits in those leachfield and distal area wells sampled during first semester 2011. Similarly, as shown on Figure 9, TBOS/TKEBS concentrations in the Tpsg HSU were below reporting limits in those leachfield and distal area wells sampled during first semester 2010.

The maximum nitrate ground water concentration in the Tpsg HSU in the core area has decreased from a historic maximum of 270 mg/L (W-834-D15, 2000) to a first semester 2011 maximum of 150 mg/L (W-834-J1, March). The maximum nitrate concentration in the core area shown on Figure 11 (first semester of 2010) is 140 mg/L in W-834-J1. In the leachfield area, nitrate in the Tpsg HSU has decreased from a historical maximum of 749 mg/L (W-834-K1A, 2000) to a first semester 2011 maximum concentration of 120 mg/L (W-834-S1, March). The maximum total VOC concentration in the leachfield area shown on Figure 11 (first semester of 2010) is 110 mg/L in monitoring wells W-834-S1 and W-834-S12A. In the distal area, nitrate in the Tpsg HSU has decreased from a historical maximum of 480 mg/L (W-834-S6, 1997) to a first semester 2011 maximum concentration of 300 mg/L (W-834-M1, February). The maximum nitrate concentration in the distal area shown on Figure 11 (first semester of 2010) is 290 mg/L in W-834-M1. Although both natural (soil) and anthropogenic sources contribute to the nitrate in the perched ground water, the anthropogenic sources are likely the most significant.

As shown on Figure 16, the ground water and soil vapor extraction and treatment system has removed 43 kg and 320 kg of VOCs, respectively as of the end of 2010. By the end of 2010, the ground water extraction and treatment system has removed 240 kg of nitrate and 9.5 kg of TBOS/TKEBs. In the future, DOE/LLNL will continue to conduct rebound testing to assess source area cleanup performance.

7.5.2.2. Remediation Progress in the Tps-Tnsc₂ HSU

TCE, cis-1,2-DCE, chloroform, PCE, and 1,1,1-TCA are the VOC contaminants of concern in Building 834 OU ground water. In the Tps-Tnsc₂ HSU, chloroform and 1,1,1-TCA have not been detected above their cleanup standards of 80 μ g/L (THMs) and 200 μ g/L, respectively. TCE has decreased from a historical maximum concentration of 250,000 μ g/L (W-834-A1, 2001) to a first semester 2011 maximum of 210,000 μ g/L (W-834-A1, February). The cleanup standard (state and federal MCL) for TCE is 5 μ g/L. Cis-1,2-DCE has decreased from a historical maximum concentration of 11,000 μ g/L (W-834-U1, 2001) to a current maximum of 2,800 μ g/L (W-834-U1, February). The cleanup standard (state MCL) for cis-1,2-DCE is 6 μ g/L. PCE has decreased from a historical maximum concentration of 7,900 μ g/L (W-834-A1, 2001) to a current maximum concentration of 880 μ g/L (W-834-A1, February). The cleanup standard (state and federal MCL) for PCE is 5 μ g/L.

The Tps-Tnsc₂ HSU perching horizon exhibits the highest total VOC ground water concentrations within the Building 834 OU. Figure 20 shows long-term VOC trends in all wells screened in this HSU throughout the Building 834 OU. As shown, the highest total VOC concentrations have consistently been detected in core area monitoring wells W-834-A1 and

W-834-U1, both of which have exhibited fairly stable VOC trends. These two wells were installed in 2000. The current (first semester 2011) maximum total VOC concentration in the Tps-Tnsc₂ HSU in the core area is 212,380 µg/L in well W-834-A1 (February 2011). The maximum total VOC concentration in the core area shown on Figure 8 (second semester of 2010) is 180,000 µg/L in W-834-A1. As shown on Figure 21, well W-834-D10 exhibited the previous historical maximum total VOC concentration in the core area at 27,208 µg/L (1996) prior to the installation of W-834-A1 and W-834-U1. Remediation efforts in the overlying Tpsg HSU in the core area have not significantly reduced VOC concentrations in ground water in the low-permeability sediments of the Tps-Tnsc₂ HSU clay/claystone perching horizon due to the extremely low yield from this HSU. VOCs in the Tps-Tnsc₂ clay likely act as a long-term source for diffusive flux into the overlying Tpsg HSU, significantly extending ground water Tps-Tnsc₂ HSU well W-834-2001 was installed in 2003 and ground water cleanup time. extraction from this well began in 2007. As shown in Figure 21, this well (dashed line) shows a general decreasing VOC trend from pre-remediation levels. This well is screened in the very shallow portion of the Tps-Tnsc₂ HSU, and extraction from this well does not affect deeper portions of the HSU, including previously mentioned high concentration wells W-834-A1 and W-834-U1. Well W-834-A1 will continue to be monitored closely. If VOC concentrations remain stable or increase over time, installation of an extraction well in the vicinity of this well may be considered.

In the leachfield area, the Tps-Tnsc₂ HSU is monitored by wells W-834-S8 and W-834-S9. As shown on Figure 21, both of these wells have exhibited slightly decreasing to stable trends since monitoring began in 1989. The historic maximum total VOC concentration in the Tps-Tnsc₂ HSU in the leachfield area is 16,000 μ g/L (W-834-S8, 1992). The current (first semester 2011) total VOC maximum concentration is 2,790 μ g/L in well W-834-S8. The maximum total VOC concentration shown on Figure 8 (second semester of 2010) is 4,100 μ g/L in well W-834-S8. No active remediation is currently occurring in the Tps-Tnsc₂ HSU in the leachfield area. VOC concentrations in the two wells screened the Tps-Tnsc₂ HSU in this area will continue to be closely monitored.

In the distal area, the Tps-Tnsc₂ HSU is monitored by only one well, W-834-2119, which was installed in 2007. As shown on Figure 21, this well has exhibited a generally stable VOC trend. The current (first semester 2011) total VOC concentration in this well is 11,500 μ g/L. The total VOC concentration in this well shown on Figure 8 (second semester of 2010) is 16,000 μ g/L (August 2010), slightly above the historic maximum for this well of 15,000 μ g/L (2007). As described in detail in Appendix A, well W-834-2119 was used as a Tps-Tnsc₂ HSU compliance monitoring well for the T2 Area enhanced bioremediation treatability study. This well will continue to be closely monitored.

TBOS/TKEBs within the Tps-Tnsc₂ HSU is found exclusively in the core area and is significantly lower than in the overlying Tpsg HSU. The maximum TBOS/TKEBS ground water concentration in the Tps-Tnsc₂ HSU in the core area has decreased from a historic maximum of 67 μ g/L (W-834-1711, 2003) to a first semester 2011 maximum of 13 μ g/L (W-834-1711, February). The maximum TBOS/TKEBs concentration in the core area shown on Figure 10 (first semester of 2010) is 22 μ g/L in well W-834-1711. Because TBOS/TKEBS concentrations in Tps-Tnsc₂ HSU wells in the leachfield and distal areas have historically been below reporting limits, sampling for TBOS/TKEBS in the leachfield and distal areas under the new (2009) Compliance Monitoring Plan was changed to a biennial frequency, with approximately half the

wells to be sampled during even numbered years and half to be sampled during odd numbered years. TBOS/TKEBS concentrations in the Tps-Tnsc₂ HSU were below reporting limits in those leachfield and distal area wells sampled during first semester 2011. Similarly, as shown on Figure 10, TBOS/TKEBS concentrations in the Tps-Tnsc₂ HSU were below reporting limits in those leachfield and distal area wells sampled during first semester 2010.

The maximum nitrate ground water concentration in the Tps-Tnsc₂ HSU in the core area has decreased from a historic maximum of 98 mg/L (W-834-1711, 2006) to a first semester 2011 maximum of 90 mg/L (W-834-1711, February). The maximum nitrate concentration in the core area shown on Figure 12 (first semester of 2010) is 34 mg/L in W-834-2001. In the leachfield area, the historical maximum nitrate concentration in the Tps-Tnsc₂ HSU is the first semester 2010 result of 150 mg/L in W-834-S8 as shown on Figure 12. The current (first semester 2011) maximum nitrate concentration in the leachfield area is 100 mg/L (W-834-S8, February). In the distal area, nitrate in the Tps-Tnsc₂ HSU has decreased from a historical maximum of 110 mg/L (W-834-2119, 2006) to a first semester 2011 maximum concentration of 85 mg/L (W-834-2119, February). The maximum nitrate concentration in the distal area shown on Figure 12 (first semester 2011 maximum concentration of 85 mg/L (W-834-2119, February).

7.5.3. Risk Mitigation Remediation Progress

This section summarizes the results the annual risk re-evaluations conducted for the Building 834 OU to assess the progress of the remediation effort in mitigating VOC inhalation risk to onsite workers in indoor and outdoor air at Building 834D. The risks from Building 834 COCs were summarized in Section 3.5 and described in more detail in the Final Site-Wide ROD.

The risks associated with VOCs in subsurface soil at Building 834D were re-evaluated every year since 2003 as part of the Risk and Hazard Management Program and reported in the annual Compliance Monitoring Reports. Soil vapor extraction at Building 834 has contributed to reducing the human health risk due to inhalation of VOC vapors outside Building 834D to a level that is no longer of concern (an excess cancer risk of less than 10^{-6}). As presented in the 2003 and 2004 Annual Compliance Monitoring Reports (Dibley et al., 2004a and 2005a), the VOC inhalation risk to onsite workers in outdoor air at Building 834D was below 10^{-6} and the hazard index was below 1 for two sequential years and is no longer a concern. Although Building 834D indoor air continues to present an unacceptable risk (greater than 10^{-6}) to onsite workers, the risk evaluations conducted indicate both risk and hazard are being reduced. The excess cancer risk to onsite workers from VOC vapors volatilizing from the subsurface and migrating into indoor air at Building 834D has been reduced from 1×10^{-3} to 5.1×10^{-5} and the non-cancer hazard has been reduced to below 1. Building 834D continues to be used only for storage and institutional controls are in place to prevent human exposure.

The results of the ecological survey program conducted in 2004 and reported in the First Semester 2004 Compliance Monitoring Report (Dibley, 2004b) indicated that burrow air did not contain VOCs at concentrations that would result in a hazard index or quotient greater than 1.

In addition, surface soil sampling and analysis for cadmium conducted in 2003 indicated that the ecological hazard associated with cadmium in surface soil at Building 834 identified in the baseline ecological assessment (Webster-Scholten 1994) was no longer present. The baseline ecological hazard was based on a detection of cadmium in one surface soil sample. In 2003, 24 additional surface soil samples were conducted at Building 834. All cadmium concentrations

in these surface soil samples were below the reporting limit, including samples collected near the location where cadmium had previously been detected. Therefore cadmium was deleted from the list of ecological COCs and will no longer be evaluated and reported. Details of the 2003 soil sampling and cadmium analysis were presented in the 2003 Annual Compliance Monitoring Report (Dibley, 2004a).

No newly unidentified unacceptable ecological risk or hazard has been identified in the Building 834 OU. No information was identified during this review to question the ecological protectiveness of the remedy.

7.5.4. New Sources, Releases, or Contaminants

Ground water and soil vapor data indicate there are no new sources, releases, or contaminants in the Building 834 OU.

In 1999 through 2001, ground water samples were collected for perchlorate analysis to determine if this constituent was present in Building 834 ground water. Perchlorate was detected in ground water samples collected from two wells (W-834-T4A and W-834-T7A) in the Building 834 OU at concentrations above the method reporting limit of 4 μ g/L. In 2005, perchlorate was detected in ground water samples collected from four newly installed wells (W-834-1711, W-834-2117, W-834-2118, and W-834-2119) at concentrations ranging from 4.7 to 28 μ g/L. However, perchlorate was not detected in a verification sample that was immediately collected from one of these wells (W-834-2119).

As part of the perchlorate evaluation in 2007, DOE/LLNL did not attempt to collect perchlorate samples from 36 of the 52 total wells, due to either previous perchlorate nondetections in these wells, or in one case (W-834-T7A), a previous very low concentration $(4.5 \,\mu\text{g/L})$. Of the 29 remaining wells where sampling was attempted for perchlorate in 2007, 13 were dry and sampling has not been attempted for perchlorate since 2007 due to dry conditions. Of the remaining 16 wells that were actually sampled for perchlorate in 2007, only two (W-834-2118 and W-834-S7) yielded detectable perchlorate concentrations. As reported in the 2007 Annual Compliance Monitoring Report, well W-834-2118 yielded a concentration of 4 µg/L (August 2007) and W-834-S7 yielded concentrations of 8.8 µg/L (March 2007) and 9.9 µg/L (August 2007). Since 2007, perchlorate samples have been collected semi-annually from these two wells. Perchlorate has been detected once at a concentration above the 6 μ g/L cleanup standard in well W-834-2118 (6.4 µg/L in June 2006). Current perchlorate concentrations in this well are slightly above the 4 µg/L reporting limit (4.9 µg/L in February 2011). From 2007 to 2009, perchlorate was detected in well W-834-S7 at concentrations ranging from 8.8 to 11 µg/L. DOE/LLNL has been unable to collect samples for perchlorate analysis in well W-834-S7 since 2009 due to insufficient water in the well. Perchlorate will continue to be sampled semi-annually from these two wells to determine if perchlorate is consistently present above the cleanup standard.

7.5.5. New Technology Assessment

As discussed in Section 2, several innovative technologies have been tested in the Building 834 OU to determine if they were more effective in VOC cleanup than the pump-and-treat technology. The technologies included electron acceleration, ultraviolet light/peroxidation, electrical soil heating, surfactant injection/extraction (push-pull), and potassium permanganate injection. These innovative technologies were screened out in the Interim Site-Wide Feasibility

Study based on cost, effectiveness, and/or the creation of additional problems such as toxic byproducts.

The feasibility of implementing an *in situ* enhanced bioremediation technology was evaluated in the T2 portion of the distal area from 2005 to the present time. As discussed in detail in Appendix A, the objective of this test was to assess the performance of passive *in situ* bioremediation of TCE at concentrations greater than 10,000 μ g/L in the low-yielding Tpsg HSU in this area. The long-term test was conducted in various phases and involved tracer testing, nutrient and bacteria injection, and long-term performance monitoring. The primary recommendation from Appendix A is to assess the cost-benefit of expanding *in situ* bioremediation of Tpsg HSU ground water in the T2 distal area by implementing a re-circulation cell whereby closely spaced biostimulation/bioaugmentation injection and extraction well pairs are used to deliver and distribute reagents in the subsurface to promote biotransformation of TCE to benign end products.

If the use of recirculation cells for *in situ* bioremediation is found to be cost-effective, an evaluation of the cost/benefit of using horizontal biostimulation wells with long screens at the Tpsg/Tps clay contact, and/or enhancing permeability using pneumatic or hydraulic fracturing in vertical or horizontal wells to further improve distribution of reagents and microbial populations in the target zone is recommended for consideration in the future.

8. Technical Assessment

The protectiveness of the interim remedy was assessed by determining if:

- 1. The interim remedy is functioning as intended at the time of the decision documents.
- 2. The assumptions used in the decision-making process are still valid.
- 3. Any additional information has been identified that would call the protectiveness of the interim remedy into question.

This Five-Year Review determined that the remedy for the Building 834 OU is protective, based on the following:

- 1. The remedy was determined to be functioning as intended at the time of the decision documents because:
 - System operation procedures are consistent with requirements.
 - No early indicators of potential interim remedy failure were identified.
 - Costs have generally been within budget, except when extra costs were incurred to address unanticipated problems or regulatory requests.
 - The remedy is functioning as intended. Ground water and soil vapor extraction are reducing contaminant concentrations in the subsurface. The maximum VOC concentrations in ground water in the perched Tpsg HSU have decreased by approximately two orders of magnitude, although high concentrations remain in the underlying low-permeability Tps-Tnsc₂ HSU. Expansion of dual-phase extraction in the Tps-Tnsc₂ HSU may be considered in the future if needed to assist with long-term cleanup in this HSU. Estimates of dissolved phase VOC mass prior to the start of ground water remediation in 1995 ranged from 65 kg to 120 kg. As of the end of

2010, DOE/LLNL have removed approximately 43 kg of VOCs from ground water, representing 36 to 66% of the mass of dissolved phase VOCs that were present prior to remediation. As of the end of 2010, DOE/LLNL have removed approximately 322 kg of VOCs from soil vapor, indicating that soil vapor extraction is much more effective than ground water extraction in removing contaminants from the subsurface.

- Ground water and vapor treatment systems are performing as designed and will continue to be operated and optimized. Examples of types of optimization that may be considered include installing new extraction wells, adding higher capacity pumps to maximize yield and to increase hydraulic capture, and upgrading the treatment facilities to accommodate increased flow, where appropriate.
- 2. The assumptions used in the decision-making process was determined to still be valid because:
 - On April 19, 2003, the California Code of Regulations, Title 22, Section 67391.1 was adopted that contains requirements for imposing legal limitations on future site uses and activities through a land use covenant. However, there is no impact on the protectiveness of the remedy related to this new requirement for a land use covenant at the time of property transfer. In addition, the State of California enacted a MCL for perchlorate on October 18, 2007. These changes occurred after the 2002 Interim Site-Wide ROD, but prior to the 2008 Final Site-Wide ROD. There have been no changes in location-, chemical-, or action-specific ARARs or to-be-considered requirements since the 2008 Final Site-Wide ROD for Site 300 was signed, nor have there been changes in exposure pathways, toxicity, and other contaminant characteristics.
 - There have been no changes in land, building, or water use in the Building 834 OU since the Final Site-Wide ROD for Site 300 was signed.
 - All required institutional controls are in place and no current or planned changes in land use at the site suggest that they are not or would not be effective.
 - Ground water and vapor treatment systems are performing as designed.
- 3. No additional information was identified that would call the protectiveness of the remedy into question:
 - The Health and Safety Plan and Site-Wide Contingency Plan are in place, sufficient to control risks, and properly implemented.
 - There have been no changes in risk assessment methodologies that could call the protectiveness of the interim remedy into question.
 - No new or previously unidentified unacceptable risk or hazard to human health or ecological receptors has been identified in annual risk re-evaluations or in ecological reviews.
 - No unanticipated events (i.e., natural disasters, new contaminants discovered, etc.) occurred that would call the protectiveness of the remedy into question.
 - No additional information has been identified that would call the protectiveness of the interim remedy into question.
 - There are no byproducts of the remedy.

9. Deficiencies

No deficiencies in the remedy were identified during this evaluation. However, the length of time necessary to achieve ground water cleanup standards using pump and treat technologies may be long due to: (1) low well yields resulting from the recharge-limited nature of the Tpsg HSU, (2) VOCs that will likely continue to diffuse from the low permeability Tps-Tnsc₂ HSU into perched ground water in the overlying Tpsg HSU, and (3) the limited ability of pump and treat technology to remove VOCs from low-permeability sediments in the Tps HSU.

Alternative remedial technologies, such as bioremediation, will continue to be evaluated in the T2 distal area to improve the long-term performance of the remedy.

There are no unresolved issues related to cleanup in the Building 834 OU.

10. Recommendations and Follow-Up Actions

The following recommendations to be carried out by the DOE were developed during the review process:

- 1. Assess the cost-benefit of expanding *in situ* bioremediation at T2 by implementing a recirculation cell with biostimulation/bioaugmentation injection wells and extraction wells to distribute sodium or ethyl lactate and dechlorinating bacteria to further promote biotransformation of trichloroethene to ethene.
- 2. Monitor Building 834 COCs including VOCs (TCE, cis-1,2-DCE, chloroform, PCE, and 1,1,1-TCA) TBOS/TKEBS, and nitrate concentrations in Tps-Tnsc₂ HSU monitoring wells W-834-A1 and -2119 during the next five years. Additional actions, including installation of extraction wells in the vicinity of these wells, may be considered if these wells exhibit increasing VOC trends.
- 3. Monitor COC concentrations in wells W-834-B4 and W-834-C5 during the next five years. Additional actions, including installation of extraction wells in the vicinity of these wells, may be considered if these wells exhibit increasing VOC trends.
- 4. Monitor COC concentrations in well W-834-2113 during the next five years. Additional actions, including conversion of this well to an extraction well, installation of an extraction well in the vicinity of W-834-2113, or implementing *in situ* bioremediation in this area, may be considered if this well exhibits stable or increasing VOC trends.
- 5. Evaluate the implications of the September 28, 2011 change to EPA's TCE toxicity value for the TCE inhalation risk at the Building 834 OU which will be discussed in the next five-year review report for the Building 834 OU that will encompass the time period (July 2011 to June 2016) during which this change occurred.

No other follow-up actions were identified related to this Five-Year Review.

DOE will: (1) estimate costs and the timeframe necessary to accomplish the new work scope; (2) prioritize new work scope and present these priorities to the regulatory agencies; (3) incorporate the new work scope into upcoming fiscal year budget requests; and (4) develop a schedule for implementing the work.

In addition, DOE/LLNL will continue to evaluate other remedial technologies that could shorten cleanup time, especially those that will facilitate remediation of the low-permeability sediments. However, even if these technologies are implemented, it may not be possible to fully remediate volatile organic compounds in the low-permeability sediments. As a result, it may not be technically or economically feasible to achieve even the 5 μ g/L TCE MCL in ground water at the Building 834 OU. Because the perched Tpsg HSU at Building 834: (1) is not used as a source of water due to poor water quality and low well yield, (2) is isolated from the underlying regional water-supply aquifer (lower Tnbs1 HSU), and (3) water in this HSU cannot migrate laterally outside the Building 834 area, DOE may submit a Technical/Economic Impracticability Waiver and/or request approval of a Containment Zone for ground water in the Building 834 OU in the future.

11. Protectiveness Statement

The remedy at the Building 834 OU is protective of human health and the environment for the site's industrial land use. The remedy protects human health because exposure pathways that could result in unacceptable risk to onsite workers are being controlled by the implementation of institutional controls, the Health and Safety Plan, and the Contingency Plan.

The cleanup standards for Building 834 OU ground water are drinking water standards. Because drinking water standards do not differentiate between industrial and residential use, the ground water cleanup remedy will be protective under any land use scenario.

The cleanup standards for VOCs in subsurface soil are to reduce concentrations to mitigate risk to onsite workers and prevent further impacts to ground water to the extent technically and economically feasible. Because some VOCs may remain in subsurface soil following the achievement of these cleanup standards, a land use control prohibits the transfer of lands with unmitigated contamination that could cause potential harm under residential or unrestricted land use. This prohibition is included in the Final Site-Wide ROD. This prohibition will remain in place until and unless a risk assessment is performed in accordance with current U.S. EPA risk assessment guidance and is agreed by the DOE, the EPA, the DTSC, and RWQCB as adequately showing no unacceptable risk for residential or unrestricted land use.

12. Next Review

The next statutory review will be conducted within five years of the signature date of this report (2017).

13. References

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14. Acronyms and Abbreviations

1,1,1 - TCA	1,1,1-Trichloroethane
ARARs	Applicable or relevant and appropriate requirements
ATA	Advanced Test Accelerator
bgs	Below ground surface
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
COC	Contaminant of concern
CTR	California Toxics Rule
DCE	Dichloroethylene
DNAPL	Dense non-aqueous phase liquid
DOE	Department of Energy
DTSC	Department of Toxic Substances Control
EPA	Environmental Protection Agency
ERD	Environmental Restoration Department
ft	Feet
GAC	Granular activated carbon
gpm	Gallons per minute
GSA	General Services Area
GWTS	Ground water extraction and treatment system
HE	High explosives
HMX	High-Melting Explosive
HSU	Hydrostratigraphic unit
kg	Kilogram
LLNL	Lawrence Livermore National Laboratory
LLNS	Lawrence Livermore National Security
LNAPL	Light non-aqueous phase liquid
MCL	Maximum contaminant level
mg/kg	Milligrams per kilograms
mg/L	Milligrams per liter
MNA	Monitored natural attenuation
O&M	Operation and maintenance
OU	Operable unit
PCBs	Polychlorinated biphenyls
PCE	Tetrachloroethylene
pCi/L	PicoCuries per liter
$ppm_{v\!/\!v}$	Parts per million on a volume per volume basis
RAOs	Remedial Action Objectives
RCRA	Resource Conservation and Recovery Act
RDX	Research Department explosive

Remedial Investigation/Feasibility Study
Record of Decision
Remedial Project Managers
Regional Water Quality Control Board
Superfund Amendment Reauthorization Act
Standard cubic flow per minute
Soil vapor extraction and treat system
Tetrabutyl orthosilicate/ Tetrakis (2-ethylbutyl) silane
Trichloroethane
Trichloroethylene
Total Dissolved Solids
Total trihalomethanes
Tertiary Neroly Lower Blue Sandstone
Tertiary Neroly Upper Blue Sandstone
Tertiary Neroly Lower Siltstone/Claystone
Tertiary Neroly Upper Siltstone/Claystone
Tertiary Pliocene nonmarine sediments
Tertiary Pliocene sand and gravel
United States
Volatile organic compounds
Cubic yards
Micrograms per liter

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Figure 3. Building 834 Operable Unit site map showing piezometers and monitoring, extraction, and guard wells, and treatment facilities.



Figure 4. Hydrogeologic cross-section of the Building 834 Operable Unit.



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Figure 5. Building 834 Operable Unit ground water potentiometric surface map for the Tpsg perched water-bearing zone.

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Figure 6. Building 834 Operable Unit map showing ground water elevations for the Tps-Tnsc₂ hydrostratigraphic unit.

Five-Year Review for the Building 834 OU at LLNL Site 300



Figure 7. Building 834 Operable Unit total volatile organic compound (VOC) isoconcentration contour map for the Tpsg perched water-bearing zone.



Figure 8. Building 834 Operable Unit map showing total volatile organic compound (VOC) concentrations for the Tps-Tnsc₂ hydrostratigraphic unit.
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Figure 9. Building 834 Operable Unit map showing TBOS/TKEBS concentrations for the Tpsg perched water-bearing zone.



Figure 10. Building 834 Operable Unit map showing TBOS/TKEBS concentrations for the Tps-Tnsc₂ hydrostratigraphic unit.

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Figure 11. Building 834 Operable Unit map showing nitrate concentrations for the Tpsg perched water-bearing zone.



Figure 12. Building 834 Operable Unit map showing nitrate concentrations for the Tps-Tnsc₂ hydrostratigraphic unit.



Figure 13. Building 834 Operable Unit institutional/land use controls.



Figure 14. Building 834 Operable Unit soil vapor extraction and treatment system: Time series plots of monthly facility flow and trichloroethene (TCE) vapor concentrations in facility influent and core area vapor extraction wells (a) W-834-B2, -B3, and -J1; (b) W-834-D6, -D7, and -D12; and (c) W-834-D4, -D13, and -2001.







Figure 16. Cumulative mass of total volatile organic compound (TVOCs) removed from ground water and soil vapor



Figure 17. Building 834 Operable Unit ground water extraction and treatment system: Time-series plots of monthly facility flow and total volatile organic compound (TVOC) concentrations in Tpsg HSU extraction and monitoring wells in a) the northern core area and b) the southern core area.



Figure 18. Building 834 Operable Unit ground water extraction and treatment system: Time-series plots of monthly facility flow and total volatile organic compound (TVOC) concentrations in Tpsg HSU extraction and monitoring wells in a) the west-central core area and b) the east-central core area.



Figure 19. Building 834 Operable Unit ground water extraction and treatment system: Time-series plots of monthly facility flow and total volatile organic compound (TVOC) concentrations in Tpsg HSU extraction and monitoring wells in the leachfield area.

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Figure 20. Comparison of the distribution of total volatile organic compounds (TVOCs) in the Tpsg perched water-bearing zone at the Building 834 Operable Unit in second semester 2005 and second semester 2010.





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ground water and soil vapor in the Building 834 core, leachfield, and distal areas.

Fiscal Year	Annual Budget	Actual Annual Cost	Cost Variance ^a
2007	\$393,633	\$391,821	\$1,812
2008	\$429,173	\$359,912	\$69,261
2009	\$465,200	\$291,597	\$173,603
2010	\$430,862	\$297,223	\$133,639
2011	\$417,150	\$366,658 ^b	\$50,492

Table 1. Actual annual costs for the Building 834 Operable Unit for fiscal years 2007 through 2011.

Notes:

The Building 834 Operable Unit was consistently under budget due to lower than expected operations, maintenance, and optimization costs. Actual cost as of April 2011 were projected (estimate at completion) to September 2011 (end of fiscal year). a

b

Table 2. Description of institutional/land use controls for the Building 834 Operable Unit.

Institutional/land use control performance objective and duration	Risk necessitating institutional/land use control	Institutional/land use controls and implementation mechanism
Prevent water-supply use/consumption of contaminated groundwater until ground water cleanup	VOCs and nitrate concentrations in ground water exceeding drinking water standards.	There are no existing or planned water-supply wells in the Building 834 Operable Unit. Any proposed well drilling activities would be submitted to the LLNL Work Induction Board, and are reviewed by LLNL Environmental Restoration Department to ensure that new water-supply wells are not located in areas of ground water contamination.
standards are met.		Prohibitions on drilling water-supply wells in areas of ground water contamination will be incorporated into the LLNL Site 300 Integrated Strategic Plan or other appropriate institutional planning documents.
		Contamination is limited to onsite ground water and modeling indicates the plumes will not migrate offsite. Therefore, land use controls are not needed to prevent offsite water-supply use/consumption of contaminated ground water.
Control excavation activities to prevent onsite worker exposure to VOCs in subsurface soil until it can be verified that concentrations do not pose an exposure risk to onsite workers.	Potential exposure to VOCs at depth in subsurface soil at the Building 834 Complex ^a .	All proposed excavation activities must be cleared through the LLNL Work Induction Board and require an excavation permit. The Work Induction Board coordinates with the LLNL Environmental Restoration Department to identify if there is a potential for exposure to contaminants in the proposed construction areas. If a potential for contaminant exposure is identified, the LLNL Environmental Health and Safety personnel ensures that hazards are adequately evaluated and the necessary controls are identified and implemented prior to the start of work. The Work Induction Board including the LLNL Environmental Analyst will also work with the Program proposing the construction project to determine if the work plans can be modified to move construction activities outside of areas of contamination. Controls for excavation activities will be incorporated into the LLNL Site 300 Integrated Strategic Plan or other appropriate institutional planning documents.
Maintain building occupancy restriction to prevent onsite worker inhalation exposure to VOCs inside Building 834D until annual risk re-evaluation indicates that the risk is less than 10 ⁻⁶ .	A pre-remediation risk of 1×10^{-3} was identified for onsite workers from inhalation of VOCs volatilizing from subsurface soil into ambient air inside Building 834D.	Building 834D is not currently occupied. Warning signs are in place and will be maintained prohibiting full time occupancy without notification and authorization by LLNL Site 300 Management. Any significant changes in activities conducted in Building 834D must be cleared through LLNL Work Induction Board. The Work Induction Board coordinates with the LLNL Environmental Restoration Department to identify if there is a potential for exposure to contaminants as a result of the proposed building usage. If a potential for contaminant exposure is identified as a result of the changes in building use, the LLNL Environmental Health and Safety personnel will be notified and determine any necessary engineered control requirements to prevent

Table 2. Description of institutional/land use controls for the Building 834 Operable Unit. (Continued)

Institutional/land use control performance objective and duration	Risk necessitating institutional/land use control	Institutional/land use controls and implementation mechanism
Building occupancy restrictions (continued)		exposure. If fulltime building occupancy is proposed, engineering controls will be implemented to prevent onsite worker exposure that could migrate from the subsurface into the building until the inhalation risk was mitigated through remediation. This building occupancy restriction will be incorporated into the LLNL Site 300 Integrated Strategic Plan or other appropriate institutional planning documents.
		DOE will conduct annual risk re-evaluations to determine when the tritium inhalation risk inside Building 834D has been mitigated. The risk re-evaluation results will be reported in the Annual Site-Wide Compliance Monitoring Reports.
		The baseline risk assessment also identified a pre-remediation risk of 6×10^{-4} for onsite workers continuously inhaling VOC vapors volatilizing from the vadose zone into outdoor air in the vicinity of Building 834D over a 25-year period. However this risk has been successfully mitigated through ground water and soil vapor extraction and treatment, therefore institutional/land use controls are no longer needed to prevent onsite worker exposure to VOCs in outdoor air.
Prohibit transfer of lands with unmitigated contamination that could cause potential harm under residential or unrestricted land use.	Potential exposure to contaminated waste and/or environmental media.	The Site 300 Federal Facility Agreement contains provisions that assure that DOE will not transfer lands with unmitigated contamination that could cause potential harm. In the event that the Site 300 property is transferred in the future, DOE will execute a land use covenant at the time of transfer in compliance with Title 22 California Code of Regulations, Division 4.5, Chapter 39, Section 67391.1.
		Development will be restricted to industrial land usage. These restrictions will remain in place until and unless a risk assessment is performed in accordance with then current U.S. EPA risk assessment guidance and is agreed by the DOE, U.S. EPA, DTSC, and the RWQCB as adequately showing no unacceptable risk for residential or unrestricted land use. These restrictions will be incorporated into the LLNL Site 300 Integrated Strategic Plan or other appropriate institutional planning document.

Notes appear on the following page.

Table 2. Description of institutional/land use controls for the Building 834 Operable Unit. (Continued)

Notes:

- **DOE** = United States Department of Energy.
- DTSC = California Department of Toxic Substances Control.
- LLNL = Lawrence Livermore National Laboratory.
- **RWQCB = California Regional Water Quality Control Board.**
- U.S. EPA = United States Environmental Protection Agency.
 - **VOCs** = Volatile organic compounds.

^a Risk for onsite worker exposure to VOCs at depth in subsurface soil could not be re-calculated as there are no new subsurface soil data. Land use controls based on the potential exposure to VOCs in subsurface soil during ground-breaking construction activities conservatively assume that the VOCs in subsurface soil may pose a risk to human health.

Location	Number of Perchlorate Samples Collected (Date Range)	Range of Perchlorate Concentrations (µg/L)	Comments
W-834-1709	5 (2005-2009)	All < 4	Discontinued sampling due to history of non- detects.
W-834-1711	2 (2005-2006)	28 and < 4	Discontinued sampling due to non-detect in 2006.
W-834-1824	1 (2007)	< 4	Not re-sampled due to non-detect.
W-834-1825	1 (2007)	< 4	Not re-sampled due to non-detect.
W-834-1833	1 (2007)	< 4	Not re-sampled due to non-detect.
W-834-2001	4 (2005-2008)	All < 4	Discontinued sampling due to history of non- detects
W-834-2113	1 (2005)	< 4	Not re-sampled due to non-detect.
W-834-2117	6 (2005-2006)	7.8 in 2005; rest < 4	Discontinued sampling due to 5 successive non- detects after first detection.
W-834-2118	15 (2005-2011)	11 to < 4	Continue sampling semiannually due to continued detections.
W-834-2119	5 (2005-2007)	4.7 in 2005; rest < 4	Discontinued sampling due to 4 successive non- detects after first detection.
W-834-A1	1 (2000)	< 4	Not re-sampled due to non-detect.
W-834-A2	0	NA	Sample attempted in 2007, but dry.
W-834-B2	1 (2007)	< 4	Not re-sampled due to non-detect.
W-834-B3	1 (2007)	< 4	Not re-sampled due to non-detect.
W-834-B4	1 (2001)	< 4	Not re-sampled due to non-detect.
W-834-C2	0	NA	Sample attempted in 2007, but dry.
W-834-C4	1 (2000)	< 4	Not re-sampled due to non-detect.
W-834-C5	1 (2000)	< 4	Not re-sampled due to non-detect.
W-834-D10	0	NA	Sample attempted in 2007, but dry.
W-834-D11	2 (2007)	Both < 4	Not re-sampled due to non-detects.
W-834-D12	1 (2007)	< 4	Not re-sampled due to non-detect.
W-834-D13	1 (2007)	< 4	Not re-sampled due to non-detect.
W-834-D14	1 (1999)	< 4	Not re-sampled due to non-detect.
W-834-D15	1 (2001)	< 4	Not re-sampled due to non-detect.
W-834-D16	0	NA	Sample attempted in 2007, but dry.

Table 3.	Summary	of perchlorate	sampling and	l analysis :	results for	Building 834 (Operable
Unit well	S.						

Location	Number of Perchlorate Samples Collected (Date Range)	Range of Perchlorate Concentrations (µg/L)	Comments
W-834-D17	1 (2000)	< 4	Not re-sampled due to non-detect.
W-834-D18	1 (2000)	< 4	Not re-sampled due to non-detect.
W-834-D2	0	NA	Sample attempted in 2007, but dry.
W-834-D3	1 (1999)	< 4	Not re-sampled due to non-detect.
W-834-D4	1 (1999)	< 4	Not re-sampled due to non-detect.
W-834-D5	2 (1999)	Both < 4	Not re-sampled due to non-detects.
W-834-D6	1 (1999)	< 4	Not re-sampled due to non-detect.
W-834-D7	1 (1999)	< 4	Not re-sampled due to non-detect.
W-834-D9A	0	NA	Sample attempted in 2007, but dry.
W-834-G3	0	NA	Sample attempted in 2007, but dry.
W-834-H2	0	NA	Sample attempted in 2007, but dry.
W-834-J1	1 (1999)	< 4	Not re-sampled due to non-detect.
W-834-J2	1 (2007)	< 4	Not re-sampled due to non-detect.
W-834-J3	1 (2000)	< 4	Not re-sampled due to non-detect.
W-834-K1A	0	NA	Sample attempted in 2007, but dry.
W-834-M1	2 (1999)	Both < 8	Not re-sampled due to non-detects.
W-834-M2	1 (1999)	< 4	Not re-sampled due to non-detect.
W-834-81	1 (1999)	< 4	Not re-sampled due to non-detect.
W-834-S10	0	NA	Sample attempted in 2007, but dry.
W-834-S12A	1 (2007)	< 4	Not re-sampled due to non-detect.
W-834-813	2 (2000 & 2001)	Both < 4	Not re-sampled due to non-detect.
W-834-84	1 (1999)	< 4	Not re-sampled due to non-detect.
W-834-85	1 (1999)	< 4	Not re-sampled due to non-detect.
W-834-S6	1 (1999)	< 4	Not re-sampled due to non-detect.
W-834-S7	6 (2007-2009)	8.8 to 11	Continue sampling semiannually due to continued detections.
W-834-S8	1 (1999)	< 4	Not re-sampled due to non-detect.
W-834-S9	1 (1999)	< 4	Not re-sampled due to non-detect.
W-834-T1	1 (1999)	< 4	Not re-sampled due to non-detect.
W-834-T11	0	NA	Sample attempted in 2007, but dry.

Table 3. Summary of perchlorate	sampling and analysis	s results for Building	834 Operable
Unit wells. (Continued)			

Location	Number of Perchlorate Samples Collected (Date Range)	Range of Perchlorate Concentrations (µg/L)	Comments
W-834-T2	1 (1999)	< 4	Not re-sampled due to non-detect.
W-834-T2A	1 (2007)	< 4	Not re-sampled due to non-detect.
W-834-T2B	1 (1999)	< 4	Not re-sampled due to non-detect.
W-834-T2C	1 (1999)	< 4	Not re-sampled due to non-detect.
W-834-T2D	1 (1999)	< 4	Not re-sampled due to non-detect.
W-834-T3	1 (1999)	< 4	Not re-sampled due to non-detect.
W-834-T5	3 (1999)	All < 4	Not re-sampled due to non-detect.
W-834-T7A	1 (1999)	4.5	Not re-sampled due most likely to low initial concentration.
W-834-T8A	0	NA	Sample attempted in 2007, but dry.
W-834-T9	0	NA	Sample attempted in 2007, but dry.
W-834-U1	1 (2000)	< 4	Not re-sampled due to non-detect.

Table 3. Summary of perchlorate sampling and analysis results for Building 834 Opera	ble
Unit wells. (Continued)	

Notes:

μg/L = Micrograms per liter.

NA = Not Applicable.

Table 4. Summary of pre-remediation and current contaminant of concern concentrations in ground water and soil vapor in the Building 834 core, leachfield, and distal areas.

Sub Area (HSU)	Maximum Total VOC Concentration in Ground Water (µg/L)		Maximum TBOS/TKEBS Concentration in Ground Water (µg/L)		Maximum Nitrate Concentration in Ground Water (mg/L)		Maximum TCE Concentration in Soil Vapor (ppm _v)	
	Pre- remediation	Current	Pre- remediation	Current	Pre- remediation ^a	Current	Pre- remediation	Current
Core Area (Tpsg)	1,060,000	19,383	7,300,000	4,800	270	150	3,200	3.6
Core Area (Tps-Tnsc ₂)	250,767 ^b	212,380	67	13	98	90	30 ^d	30 [°]
Leachfield Area (Tpsg)	179,200	12,000	< 10	< 10	749	120	710	6
Leachfield Area (Tps-Tnsc ₂)	16,000	2,790	< 10	< 10	150	100	NA	NA
Distal Area (Tpsg)	86,000	11,052	28 ^d	< 10	480	300	NA	NA
Distal Area (Tpsg-Tnsc ₂)	16,000 ^e	11,500	10 ^b	< 10	110	85	NA	NA

Notes:

- HSU = Hydrostratigraphic unit.
- $\mu g/L =$ Micrograms per liter.
- mg/L = Milligrams per liter.
- NA = Not Applicable (No vapor samples collected).
- ppm_v = Parts per million on a volume-to-volume basis.
- TBOS = Tetrabutyl orthosilicate.
- TKEBS = Tetrakis (2-ethylbutyl) silane.
 - **TCE = Trichloroethene.**
 - **VOC** = Volatile organic compound.

Table 4. Summary of pre-remediation and current contaminant of concern concentrations in ground water and soil vapor in the Building 834 core, leachfield, and distal areas. (Continued)

Notes (continued):

Core Area pre-remediation time period = prior to 1995 (ground water) and 1998 (soil vapor).

Leachfield pre-remediation time period = prior to 2004 (both ground water and soil vapor).

Distal Area pre-remediation time period = prior to 2005 (beginning of in situ bioremediation testing).

Current maximum concentrations represent first semester 2011.

^a Nitrate in ground water not actively remediated; instead, historical maximum shown.

^b Historical maximum shown (well showing current maximum (W-834-A1) was not installed during pre-remediation time period (pre-1995).

^c W-834-2001 is only vapor well in Tps-Tnsc2. Current concentration = historic high (no pre-1998 concentration).

^d TBOS/TKEBs in ground water not actively remediated in this subarea; instead, historical maximum shown.

^e Historical maximum shown (well showing current maximum, and only well monitoring this HSU, (W-834-2119) was not installed during pre-remediation (*in situ* bioremediation testing) time period (pre-2005).

Appendix A

T2 Enhanced Bioremediation Treatability Study

Appendix A

T2 Enhanced *In Situ* Bioremediation Treatability Study at the Building 834 Operable Unit at Lawrence Livermore National Laboratory (LLNL) Site 300

A-1. Introduction

While the existing ground water and soil vapor extraction and treatment system has been successful in reducing contaminant concentrations in the Building 834 Operable Unit (OU), the U.S. Department of Energy (DOE)/LLNL is continuing to evaluate innovative technologies to improve remediation of volatile organic compound (VOCs) in low-permeability sediments and expedite cleanup.

From January 2005 through June 2011, DOE/LLNL conducted multi-phase, longterm testing to evaluate the efficacy of enhanced *in situ* bioremediation technology to remediate VOC contamination in the T2 Distal Area of the Building 834 OU. This testing included:

- Laboratory microcosm study to assess biostimulation using different electron donors and bioaugmentation with a microbial consortium to mediate complete dechlorination of trichloroethene (TCE) to ethene (April 2005 to February 2006).
- *In situ* tracer testing to determine hydraulic parameters for *in situ* biostimulation/augmentation design (January to July 2005).
- *In situ* biostimulation to assess the transformation of reduction-oxidation (redox) conditions in the ground water from oxidizing to reducing conditions suitable for bioaugmentation (April 2007 to August 2008).
- *In situ* bioaugmentation with continued biostimulation to evaluate its effectiveness in reducing VOC concentrations through reductive dechlorination. (August to December 2008).
- Post-test monitoring to determine if VOC concentrations rebound after biostimulation/augmentation ceased (January 2009 to June 2011).

These tests and their results are discussed in Sections A-2 through A-5. The treatability study conclusions and recommendations are presented in Sections A-6 and A-7.

A-2. Microcosm Study

A laboratory microcosm study was conducted by Sirem using geologic materials and ground water from the Building 834 OU to assess:

1. Different electron donors such as corn syrup, HRCTM (a viscous, slow-release, lactic acid liquid), and ethanol, and

2. Bioaugmentation with KB-1TM, a natural, non-pathogenic microbial consortium containing microorganisms (Dehalococcoides) known to mediate complete dechlorination of TCE to ethene.

Groundwater and soil used in the microcosm study was collected from well W-834-2117 located upgradient of the treatment zone and completed in the Tpsg hydrostratigraphic unit (HSU). Microcosms were prepared under anaerobic conditions in an effort to simulate *in situ* conditions in the laboratory to the extent possible. The initial TCE concentration in each microcosm was set at 30 milligrams per liter (mg/L) to mimic concentrations in the treatment zone. A complete report of the methods and results is included as Attachment 1.

The main conclusions of the microcosm study are summarized as follows:

- The rate and extent of biodegradation of TCE is limited by the availability of nutrients (electron donors) and the absence of suitable strains of bacteria capable of complete dechlorination of TCE to ethene.
- Bioaugmentation was necessary in all treatments to achieve complete dechlorination because indigenous bacteria at the site are capable of only partial dechlorination of TCE to cis-1,2 dichloroethylene (DCE).
- Complete dechlorination of TCE is possible with corn syrup and bioaugmentation with KB-1, however it occurs at a slower rate than with HRCTM or ethanol as electron donors.
- Some methane production in the HRCTM and ethanol treatments occurred during vinyl chloride and/or ethene production, shortly after bioaugmentation with KB-1TM.

Based on the microcosm study results, sodium lactate (Na lactate) was selected as the most cost-effective electron donor for the *in situ* bioremediation study at Building 834. Na lactate is the main ingredient in the relatively expensive proprietary product, HRCTM. Ethanol was not selected due to safety concerns regarding storing a flammable liquid at an explosives test facility during the hot summer months. Corn syrup was not selected because the biotransformation kinetics was found to be slower than HRCTM or ethanol.

A-3. *In Situ* Tracer and Bioremediation Test Area Hydrogeology and Contaminant Conditions

The *in situ* tracer test and subsequent biostimulation/bioaugmentation test were conducted in the Distal Area (T2) portion of the Building 834 OU, located about 800 feet (ft) south of the 834 Core Area and about 600 ft south of the Building 834 Leachfield area (Figure A-1). The hydrogeology and contaminant conditions in the T2 test area are discussed in Sections A-3.1 and A-3.2, respectively.

A-3.1. Hydrogeology of the T2 Test Area

The primary geologic units in the T2 *in situ* tracer and biostimulation/bioaugmentation test area are shown in Figure A-2. This photo was taken in a gully just west of the test area. It shows the target HSU (Tpsg), which is comprised mainly of hard, calcium carbonate-cemented, low permeability gravels, with some well-sorted, medium-grained, permeable sand lenses. The cemented gravels are so indurated

that rotary drilling methods are required to install wells in this HSU. Auger and direct push methods, such as cone penetrometer or geoprobe, have been attempted in the past but could not penetrate the Tpsg cemented gravels. The underlying Tps clay is comprised of low permeability, mostly smectite clay. It serves as a perching horizon for shallow ground water that is a combination of natural rainfall recharge and some residual component of process water discharged to the subsurface during past technical operations (e.g., 834 septic system leachfield).

Perched ground water in the Tpsg HSU is spatially and temporally variable depending on Building 834 Core and Leachfield extraction wellfield pumping, limited seasonal rainfall recharge, and evapotranspiration along the surrounding hillslope where the Tpsg and Tps clay crop out. With the exception of discrete permeable zones in the form of fractures or sand lenses shown in Figure A-2, the geologic materials in the test area exhibit very low hydraulic conductivity. Slug tests performed in Tpsg HSU wells indicate hydraulic conductivities ranging from 10^{-4} to 10^{-6} centimeters per second (cm/sec). Porosity and hydraulic conductivity data for the main geologic units in the T2 test area are summarized in Table A-1.

HSU	Estimated Porosity (%)	Hydraulic Conductivity (cm/sec)		
Tpsg				
cemented gravel matrix	< 10	$\leq 10^{-6}$		
sand lens	20 to 30	10^{-3} to 10^{-4}		
fractured gravel	unknown	unknown		
Bulk	20 (tracer test)	10^{-4} to 10^{-6} (slug tests)		
Tps clay				
clay matrix	20 to 40	$\leq 10^{-6}$		
fractured clay	unknown	unknown		
Bulk	unknown	10^{-6} (slug tests)		

 Table A-1. Summary of estimated porosity and hydraulic conductivity for Tpsg and

 Tps clay in the T2 Treatability Test Area.

Beneath the Tps Clay perching horizon is about 275 ft of mostly unsaturated interbedded sandstone, siltstone and claystone bedrock of the Neroly Formation. Deep ground water beneath the T2 test area is encountered in the regional Lower Tnbs₁ HSU at a depth of over 300 ft. Ground water in the Lower Tnbs₁ HSU is monitored in well W-834-T1 within the T2 test area and W-834-T3 just south of the test area. To date, these wells have been devoid of anthropogenic contaminants.

A map showing the test area, treatment zone, injection, bioaugmentation, performance monitoring, compliance, and background wells is presented in Figure A-3. The test site is located along a broad ridge between two gullies. A simplified, north-south cross-section through the test area is presented in Figure A-4. During rainfall events, surface runoff tends to flow toward these adjacent gullies and the cemented Tpsg gravel is so impermeable that it significantly limits direct infiltration. The long-term hydrographs for Tpsg wells that were installed back in the mid-1980s in this area (W-834-T2, W-834-T2A, and W-834-T2D) exhibit < 0.5 to 1.5 ft of rise during an average rainfall seasonal (9 to 10 inches of rain). During the 1998 El Niño, water levels

in these wells increased by about 4 ft in response to the 20+ inches of rain that fell that year.

A-3.2. Pre-Test Contaminant Conditions in the T2 Test Area

Ground water monitor wells were installed in the T2 area during three phases. The initial phase in 1988 included the installation of some of the first Tpsg monitor wells in the Distal Area (W-834-T2, W-834-T2A, W-834-T2B, W-834-T2C, W-834-T2D and W-834-T9). The second phase in 2002 included the installation of Tpsg wells W-834-1824, W-834-1825, and W-834-1833. The third phase in 2005 included the installation of Tpsg well W-834-2117 located upgradient of the T2 area and Tpsg well W-834-2118 and Tps clay well W-834-2119 located downgradient of the T2 area (Figure A-1). During the installation of these wells, a total of 109 soil samples were collected primarily from the Tpsg and Tps clay HSUs and analyzed for VOCs. In general, VOC soil concentrations were low (<1.5 milligrams per kilograms [mg/kg]) relative to the high TCE concentrations (> 200 mg/kg) detected in the 834 Core and Leachfield areas. Most of the TCE with concentrations above 0.1 mg/kg in the T2 area was detected in the 38 to 40 foot range near the contact between the Tpsg and the Tps clay. A maximum TCE soil concentration of 1.2 mg/kg was detected in the Tps clay at 40.5 feet in W-834-1833.

The historical maximum dissolved total VOC (mainly TCE) concentration in the T2 test area was 86,000 micrograms per liter (μ g/L) in W-834-T2A (June 1988). Since 1988, total VOC concentrations in these wells initially exhibited an increasing trend until the early 1990s. Since then they have exhibited a gradually decreasing trend until the present. Prior to the start of this test in early 2005, total VOC concentrations in the T2 test area ranged from 12,000 to 30,000 μ g/L. Prior to the start of biostimulation in early 2007, total VOC concentrations ranged up to 15,000 μ g/L.

Prior to *in situ* test in the T2 area, only sporadic detections of cis-1,2 DCE were detected in any of the test area wells up to a maximum concentration of 2,600 μ g/L (W-834-T2A March, 1999). Vinyl chloride was never detected in any of the long-term monitor wells in the test area down to reporting limits as low as 0.5 μ g/L. In 2002, three new wells were added in the test area (W-834-1824, W-834-1825, and W-834-1833) along a north-south transect in anticipation of the treatability studies. All three wells were screened near the base of the Tpsg HSU and contained TCE at concentrations ranging from 15,000 to 25,000 μ g/L, cis-1,2 DCE up to about 40 μ g/L, and no vinyl chloride above 0.5 μ g/L in their initial samples. The initial static water levels in these wells were 3 to 4 ft above the screen bottom located at the contact between the Tpsg and the underlying Tps clay perching horizon.

A-4. Tracer Test

Prior to conducting the *in situ* bioremediation treatability study, a tracer test was conducted to determine hydraulic parameters to design the biostimulation phase involving the injection of Na lactate injection into Building 834 ground water. The primary objectives of the tracer test were to determine the:

- Steady-state injection rate.
- Zone-of-influence from a single injection well.

- Transit time from the injection well to observation well(s).
- The extent of tracer/ground water mixing.

As discussed in Section A-3, the tracer test was conducted in the same area as the subsequent biostimulation/bioaugmentation test (Distal Area portion of the Building 834 OU).

The tracer test was conducted from January to July 2005. The following parameters were monitored during the tracer test to assess migration of the tracer in the Tpsg waterbearing zone:

- Ground water levels.
- Specific conductance.
- Stable isotopes of water (delta deuterium [D] and delta oxygen-18 [O-18]).

Hetch Hetchy water was selected as a conservative tracer for the test because it is distinctly different both chemically and isotopically from Building 834 ground water. For example, Building 834 ground water has an isotopic signature of delta D = -40 to -45 per mil (parts per 1,000) and delta O-18 = -3 to -4 per mil, and specific conductance of 1,100 to 1,300 μ S (microseimens) Hetch Hetchy water, which is primarily Sierra Nevada snowmelt water, contains a distinctly different isotopic signature (delta D = -104 per mil and delta O-18 = -14 per mil) and a much lower specific conductance (~100 μ S) due to significantly lower total dissolved solids (TDS).

During the tracer test, well W-834-1824 was used as the tracer injection well and wells W-834-T2, W-834-T2A, W-834-T2D, W-834-1825, and W-834-1833 were used to monitor for the presence of the tracer. The injection well and all five monitor wells are completed in the Tpsg HSU.

From January 18 to July 26 of 2005, more than 24,000 liters (L) (6,250 gallons) of Hetch Hetchy tracer water were injected into Tpsg HSU well W-834-1824 under a sustained head of approximately 15 ft (5 meters) above the static water table. This constant head was maintained using a float switch that allowed Hetch Hetchy water to enter the injection well under a gravity feed from a nearby tank whenever the water level dropped below the switch. As shown in Figure A-5(a), the injection flow rate stabilized at about 26 gallons (\sim 100 L) per day after about one month of injection.

An immediate (<1 hour) water level response was measured in all nearby performance monitor wells at the onset of Hetch Hetchy tracer injection into W-834-1824, indicating a direct hydraulic connection between these wells. Although all nearby wells exhibited an immediate hydraulic response, the transit time for the tracer to arrive at the nearest downgradient performance monitor well W-834-T2 was 3 to 4 months (Figure A-6). During the tracer test, a total of 6,312 gallons (~ 25,000 L) of Hetch Hetchy tracer was injected into well W-834-1824. The stabilized injection rate was determined to be about 100 L per day with a tracer velocity of about 0.1 meters per day under an injection head of 10 ft (~ 3.3 meters) above static water levels (Figure A-6).

Samples were collected for isotopic analysis on a monthly basis from key performance wells during the tracer test. The isotope data were used to assess: (1) the migration of the tracer in Tpsg HSU ground water, and (2) Hetch Hetchy tracer/ground water mixing to evaluate the reduction in TCE concentrations due to dilution.

Based on analysis of stable isotopes of water in samples collected from the performance monitor wells during the tracer test, tracer was detected in three of the five performance monitor wells W-834-T2, W-834-1825, and W-834-1833. As shown in Figure A-6, the greatest percentage (25%) of tracer was detected in the nearest downgradient well W-834-T2, while 12% of tracer was detected in W-834-1825. The 5% tracer estimated in well W-834-1833 is within the overall uncertainty of this test, so it is not conclusive that tracer water reached this location. Salinity decreased in the nearest performance well W-834-T2, while the salinity increased or remained constant in the other wells. Salinity increases suggest the presence of residual salts in the vadose zone, possibly from previous El Niño high water levels. The presence of vadose zone salts precluded the use of specific conductance only as a tracer indicator.

Based on tracer test results, it was concluded that the T2 treatment zone could be influenced via passive injection into a single well, although the injection rate would be slow and the transit times would be relatively long (months). In addition to water levels, specific conductance, and stable isotopes of water, TCE was monitored during the tracer test to further assess dilution related to the injection of tracer water. As expected, significant decreases in TCE were observed in the injection well W-834-1824 and, to a lesser extent, in wells W-834-T2 and W-834-1825 due to tracer injection; whereas little to no tracer or dilution of TCE were observed in wells W-834-1833, W-834-T2A, or W-834-T2D.

The porosity of the Tpsg HSU in the treatment area was estimated to be about 0.20 based on the volume of Hetch Hetchy water injected (6,312 gallons = 843 cubic feet [ft³]) during the tracer test divided by the total volume of Tpsg HSU (3,885 ft³) in the vicinity of well W-834-1824 that was impacted by the injected water. This is considered a rough bulk porosity estimate to be used for approximate dissolved mass estimation purposes. Given the T2 site hydrogeology, the bulk of ground water storage and flow within the treatment zone resides in the permeable sand lenses and open fractures depicted in Figure A-2.

A-5. *In Situ* Bioremediation Treatability Study

The primary objective of the pilot-scale treatability study was to assess the performance of enhanced *in situ* bioremediation of TCE at concentrations greater than 10,000 μ g/L in a heterogeneous, anisotropic, dual porosity/permeability water-bearing zone typical of contaminant source areas at Site 300 (Figure A-2).

The *in situ* bioremediation test consisted of 2 phases:

- 1. Biostimulation to assess the transformation of redox conditions in the ground water from oxidizing to reducing conditions suitable for bioaugmentation.
- 2. Bioaugmentation with continued biostimulation to evaluate its effectiveness in reducing VOC concentrations through reductive dechlorination.

This test was conducted in a passive mode by injecting nutrients (i.e., biostimulation) and bacteria (i.e., bioaugmentation) into individual wells without the aid of extraction or re-circulation wells to facilitate detailed performance monitoring, assess technical feasibility, and collect data to design a larger scale cleanup effort.

Bioaugmentation was necessary because prior studies of the microbial community in the shallow ground water beneath the Building 834 OU indicate that indigenous bacteria capable of dechlorination beyond cis-1,2 DCE are not present. For example, a study of ground water samples from the 834 OU by Miller et al. (2007) based on denaturing gradient electrophoresis (DGGE) and quantitative PCR, concluded that:

- 1. The bacterial community is closely related to ground water chemistry;
- 2. The Core area, where TCE is comingled with the silicon oil tetrakis (2-ethylbutoxy) silane (TKEBS) and diesel, is distinctly different than the T2 area and downgradient clean ground water;
- 3. A bacteria closely related to the TCE-dechlorinating, dichloroetheneaccumulating genus Dehalobacter is present in both the Core and T2 areas; and
- 4. The TCE-dechlorinating, ethene-producing species Dehalococcoides ethenothegenes was not detectable in any of the samples.

In addition, only sporadic trace levels of vinyl chloride and no ethene, that would indicate complete dechlorination of TCE is occurring, had been detected in ground water at the 834 OU prior to this treatability study.

Multiple data sets, including the Hetch Hetchy tracer test results, the analysis of dechlorination by-products in the form of light hydrocarbons (LHCs) and available nutrients in the form of volatile fatty acids (VFAs), and analysis of microbial deoxyribonucleic acid (DNA) extracted from ground water, were used to rigorously assess performance and attempt to distinguish the relative contributions of biotic and abiotic processes to the overall VOC mass reduction observed within the treatment zone during the test.

In accordance with Central Valley Regional Water Quality Control Board guidance for *In Situ* Groundwater Cleanup projects (WDR-R5-2008-0149), a treatment zone within the Tpsg HSU was defined in advance of the test (Figure A-3). As shown in Figure A-3, the T2 test area includes a treatment zone that encompasses injection well W-834-1824 and nearby Tpsg performance monitor wells W-834-T2, W-834-1825, W-834-T2A, and W-834-T2D. In addition, both lateral and vertical compliance wells were used to monitor any potential negative water quality impacts downgradient of the treatment zone in the same HSU (lateral compliance well) and beneath the Tpsg in underlying HSUs such as the Tps Clay perching horizon and the deeper regional aquifer, Lower Tnbs₁ HSU (vertical compliance well). Upgradient Tpsg monitor well W-834-2117 was used to assess background trends in water levels and ground water chemistry due to abiotic processes such as volatilization and upgradient pumping from the 834 Leachfield area extraction wells. The final assessment of *in situ* biotreatment performance, presented in Section A-5.4, takes these background trends into consideration.

Performance monitoring conducted during the *in situ* bioremediation test is discussed in Section A-5.1. The biostimulation and bioaugmentation test phases are discussed in Sections A-5.2 and A-5.3, respectively. The bioremediation test results are presented in Section A-5.4.

A-5.1. Performance Monitoring

In situ performance monitoring of test wells was conducted using water level transducers and YSITM downhole sensors (Figure A-3) during both the biostimulation and bioaugmentation phases of the treatability study.

Performance wells W-834-T2, W-834-1833, W-834-T2A, and W-834-T2D, injection well W-834-1824 and bioaugmentation well W-834-1825 were outfitted with water level transducers to monitor water levels at frequencies ranging from 1 to 6 hours throughout the test. In addition, wells W-834-T2, W-834-T2A, W-834-1825, and W-834-1833 were outfitted with YSI *in situ* probes to monitor dissolved oxygen (DO), oxidation-reduction potential (ORP), and specific conductance (SC). The DO, ORP, and SC data were recorded using a data logger and the data were periodically retrieved to assess ongoing operations and performance. The *in situ* sensor data were used to monitor redox conditions in response to Na lactate injection to determine if and when conditions were suitable for bioaugmentation. A hand-held Ultrameter was used to verify SC and ORP readings whenever ground water samples were collected. In general, there was good agreement between the YSITM sensors and the Ultrameter readings.

Ground water samples were collected using a bailer from all performance and compliance monitor wells on a quarterly basis and analyzed for VOCs by EPA Method 601. Light hydrocarbon (LHC) samples were collected from key performance wells (W-834-T2, and W-834-1833 and bioaugmentation well W-834-1825) to identify the presence of ethene, the TCE biotransformation end product, and volatile fatty acid (VFA) samples were collected to assess the extent of nutrients available for TCE biotransformation.

Samples were also periodically collected for isotopic analysis from key performance wells during the biotreatability study. The isotope data were used to assess Hetch Hetchy tracer/ground water mixing to assess the reduction in TCE concentration due to dilution.

Post-test monitoring was conducted in the T2 performance wells and bioaugmentation well W-834-1825 for a period of 2.5 years after biostimulation ceased in December 2008 to assess the extent of VOC rebound following the decline of available nutrients within the treatment zone. These trends are the best indicators of long-term dissolved and adsorbed (soil) phase VOC remediation effectiveness.

A-5.2. Biostimulation Phase of Treatability Study

The biostimulation phase of the test was conducted from April 2007 to December 2008, a period of average to below average rainfall. During this time about 45,000 L (11,400 gallons) and about 700 L (180 gallons) of 60% pure Na lactate were injected into well W-834-1824 in a series of 20 L (5 gallon) slugs every two weeks. Following each slug injection, the water level in the injection well was maintained at about 23 ft (7 meters) above static levels using Hetch Hetchy tracer water to enhance Na lactate injection. As shown in Figure A-5(b), an injection rate of 60 gallons (about 240 L) per day was achieved during the initial biostimulation phase of the test. However, this rate decreased significantly to only 8 gallons (about 32 L) per day after January 2008. The initial higher rate of injection is related to the fact that the injection head was maintained at a higher level (23 ft [7 meters]). The significant decrease in injection rate is most likely due to some "biofouling" in the vicinity of the injection well screen.

The objectives of the biostimulation phase were to transform the redox conditions in ground water from oxygen-rich, oxidizing conditions (DO = 7 milligrams per liter [mg/L]; ORP > +100 millivolt [mV]) to oxygen-depleted, reducing conditions (DO < 3 mg/L; ORP < -200 mV) suitable for bioaugmentation and to initiate and sustain reductive dechlorination. By September 2007, Hetch Hetchy tracer was detected at significant levels in wells W-834-1825 and W-834-T2 and by November 2007, cis-1,2 DCE concentrations increased in wells W-834-1825 and W-834-T2, and to a lesser extent in W-834-1833. However, redox conditions in these wells remained aerobic (i.e., positive ORP) and DO above 3 mg/L persisted suggesting that most of the Na lactate was being consumed in the immediate vicinity of well W-834-1824 to convert TCE to cis-1,2 DCE. Na lactate injection continued and by early July 2008 ground water in the treatment zone became anoxic (DO < 3 mg/L) and ORP fell below -200 mV, thereby indicating conditions suitable for bioaugmentation. After injection of 140 gallons (530 L) of Na lactate into W-834-1824 between April 2007 and July 2008, the ground water in the treatment zone had reached the redox conditions suitable for bioaugmentation. The Phase 2 bioaugmentation phase of the treatability study was initiated in August 2008 as discussed in Section A-5.3.

It should be noted that an unintended carbon source in the form of a rodent entered injection well W-834-1824 on July 27, 2005, one day after the end of the tracer test. This was discovered after a foul odor was detected emanating from the well and later confirmed by the water level response of the rodent arriving at the water table recorded by the water level transducers and the skeletal remains that were later removed using a bailer. A significant rise in cis-1,2-DCE, a negative ORP, and decreases in nitrate and sulfate were observed in this well following this event. However, vinyl chloride was not detected and no significant increase in iron or manganese was observed. These trends indicate that the decaying rodent served as a probable electron source for partial biodegradation of TCE to cis-1,2 DCE. No significant chemical changes were observed in other T2 Area wells during this time.

A-5.3. Bioaugmentation

The bioaugmentation phase of the treatability study was conducted from August 2008 to December 2008. During this phase, biostimulation was continued to maintain the reducing conditions in ground water favorable to bacterial dechlorination.

On August 5, 2008, the contractor Sirem injected a 10 liter slurry into well W-834-1825 that contained a consortium of dechlorinating bacteria (KB-1TM) including Dehalococcoides (Dhc) that is capable of complete dechlorinating TCE to the ethene dechlorination end product. In preparation for bioaugmentation, 4 liters (1 gallon) of Na lactate were added to W-834-1825 in July 2008 and an additional 500 milliliters (0.125 gallons) were added following bioaugmentation to ensure that adequate levels of electron donor were present to promote bacterial dechlorination. Periodic Na lactate injection continued in well W-834-1825 was displaced with Argon gas prior to bioaugmentation to minimize any chance that the KB-1 bacteria would come in contact with an oxygen atmosphere. The total VOC concentration and hydrographs for wells in the treatment zone during biostimulation and bioaugmentation are presented in Figures A-7 and A-8, respectively.

A ground water sample was collected months later in November 2008 from well W-834-1825 and submitted to Sirem for Gene-Trac analysis (Attachment 2). This analysis determined the microbial population in the ground water sample and specific proportion of Dhc present based on quantification of 16S ribosomal ribonucleic acid (rRNA) in the extracted DNA. The results indicate a microbial population of $10^{10}/L$ (gene copies per liter) with a range of 18 to 44% Dhc. According to Sirem, values at or above 10^7 gene copies per liter indicate high concentrations of Dhc often associated with high rates of dechlorination and ethene production. Test results exceeding $10^9/L$ are rarely observed. This result indicated that bioaugmentation was successful and that four months after bioaugmentation, the microbial population, including Dhc, appeared to be thriving.

In 2009 ground water samples were collected from wells W-834-1825 and W-834-T2 in May, August, and December and from well W-834-1833 in December for DNA analysis using Polymerase Chain Reaction (PCR) of 16S rRNA for comparison with TCE degradation genes from KB-1. The analysis was performed by the Biosciences and Biotechnology laboratory at LLNL. The following conclusions were made from this analysis:

- 1. Bacterial genomic DNA isolated from the KB-1 consortium and wells W-834-1825 and W-834-T2 yielded Dehalococcoides-specific 16S rRNA gene sequences from PCR.
- 2. The DNA also yielded Dehalococcoides-specific reductive dehalogenase (rdh) gene sequences.
- 3. DNA from well W-834-1833 did not yield gene products from either Universal 16S rRNA, Dehalo.-16S rRNA, nor any of the Dehalococcoides-specific rdh primer sets.

This analysis conclusively demonstrated that Dhc injected into well W-834-1825 was discovered in well W-834-T2. The hydraulic and/or biotic processes by which Dhc migrated from well W-834-1825 to well W-834-T2 are not clear. As shown in Figure A-8, the water level in well W-834-1825 rose above the water level in well W-834-T2 during the bioaugmentation event. During this short-term event, the local hydraulic gradient would have reversed from its normal direction. Additionally, at this time, the path between these wells would presumably have been enriched in nutrients due to the injection of Na lactate.

A-5.4. Performance Summary

The main focus of the treatability study was to rigorously assess the performance of *in situ* bioremediation in a typical Site 300 VOC source area, and to evaluate the efficacy of enhanced *in situ* bioremediation technology to remediate VOC contamination in the Building 834 OU. To this end, a broad range of performance parameters were monitored during and after the injection of Na lactate and the introduction of dechlorinating bacteria into the target Tpsg HSU. The spatial and temporal variation in dissolved VOC mass in the treatment zone observed during the test can be attributed to multiple biotic and abiotic processes, which are difficult to differentiate and quantify. Among the abiotic processes are:

• Volatilization.

- Diffusion into fine-grained materials.
- Adsorption onto mineral surfaces.
- Displacement into adjacent geologic units such as the underlying Tps clay.

Additionally, a general background trend of declining VOC concentrations was exhibited in wells W-834-2117 and W-834-1833. This trend is due to the abiotic processes mentioned and, in part, to hydraulic capture of TCE via upgradient pumping in the Building 834 Leachfield area. In other words, dissolved TCE is decreasing over time apart from any reduction attributable to *in situ* bioremediation and must be taken into account when conducting any technically defensible performance assessment.

This section summarizes trends in performance data collected during the treatability study and how these trends relate to the overall performance of *in situ* bioremediation. This test was designed to assess performance rather than optimize cleanup. The information collected during this test can be used for full-scale implementation design to maximize cleanup. A summary of all performance data is presented in Attachment 3. For each well, the trend of each performance parameter is summarized as follows: (1) overall, (2) tracer test, (3) biostimulation phase, (4) post-bioaugmentation phase, and (5) pre-test/post test results.

Time-series plots of total VOC concentrations in the key treatment zone wells (W-834-T2, W-834-1824, W-834-1825, and W-834-1833), upgradient "background well" W-834-2117, and downgradient well W-834-2118 during the test are presented in Figure A-7. These time-series plots show an overall declining trend in the background well, a steep decline in VOCs in wells W-834-T2 and W-834-1825 following the bioaugmentation, and the rebound in VOCs in well W-834-T2 about 1 year after bioaugmentation.

Detailed hydrographs for all test wells during 2008 are presented in Figure A-8. These hydrographs indicate that water levels in all wells rose 1 to 2 ft in response to rainfall events in early 2008, and that the water level in well W-834-1825 temporarily rose above well W-834-T2 during the bioaugmentation event when a 10 L slurry was injected into that well. ORP, nitrate, sulfate and VFA time-series plots for wells W-834-T2, W-834-1825, and W-834-1833 are presented in Figure A-9. These plots demonstrate how the redox conditions changed in the treatment zone from oxidizing to nitrate- and sulfate-reducing conditions, especially in wells W-834-T2 and W-834-1825 prior to bioaugmentation. The VFA plots show the extent of nutrients present in these wells during the test. (Note the significant difference in VFA scale between the three wells presented in Figure A-9.) Well W-834-1833 exhibited very little evidence of any impact during the test related to Hetch Hetchy tracer or Na lactate injection.

The response in wells W-834-1825 and W-834-T2 to biostimulation and bioaugmentation in terms of VOC breakdown products (i.e., cis-1,2-DCE, vinyl chloride, and ethene) is presented in Figure A-10. This time-series plot is presented in moles/Liter (not μ g/L) to show a true stoichiometric comparison between TCE levels and biotransformation breakdown products. It is evident from the plot presented in Figure A-10 that wells W-834-T2 and W-834-1825 responded similarly to biostimulation, but very differently to bioaugmentation. After bioaugmentation, TCE and cis-1-2-DCE concentrations in well W-834-1825 decreased significantly, and vinyl chloride and ethene
were detected at low levels for the first time and continue to remain low to the present. In well W-834-T2, ethene increased to much higher levels than in well W-834-1825 following bioaugmentation. Another significant difference is that TCE, cis-1,2-DCE, and vinyl chloride began rebounding in well W-834-T2 (total VOC=3,900 μ g/L) about one year after bioaugmentation, whereas little or no VOC rebound has been observed at well W-834-1825 (total VOC=24 μ g/L). Also, ethene levels continue to be higher in well W-834-T2 (410 μ g/L) than well W-834-1825 (32 μ g/L) indicating ongoing dechlorination of TCE in both wells.

Injection well W-834-1824 exhibited a significant decrease in TCE due primarily to injection of and dilution by Hetch Hetchy tracer water. However, some TCE breakdown products, including cis-1,2-DCE and some vinyl chloride, were detected following injection of Na lactate. Total VOC concentrations remained low (169 μ g/L) in the injection well and low concentrations of vinyl chloride (15 μ g/L) and ethene (2.6 μ g/L) continue to be detected, indicating some microbial breakdown of TCE.

Total VOC and TCE concentrations in performance monitoring wells W-834-T2A and W-834-T2D exhibited little to no change during this test. In fact, these wells exhibited very little evidence that they were impacted by any of the test activities. Similar results were obtained from well W-834-1833 in that there is little evidence that this well was impacted by the tracer or biotreatability studies even though a substantial volume of Hetch Hetchy tracer water was injected during the test. Figure A-7 also contains data from upgradient Tpsg "background" well W-834-2117. Data from this well was included to show background trends upgradient of the T2 test area, so that the performance of *in situ* bioremediation within the treatment zone can be interpreted in the context of these trends. Total VOC concentration in well W-834-2117 decreased by more than 50% from 20,000 μ g/L to about 8,000 μ g/L between 2005 and 2011. Similar declines in total VOC concentration were observed in downgradient performance wells W-834-1833, W-834-T2A and W-834-T2D (W-834-T2A and W-834-T2D are not shown on plot). Total VOC concentration in Tpsg downgradient well W-834-2118 and in Tps clay well W-834-2119 remained essentially unchanged throughout the test.

A series of Earth Vision plots were generated to visualize the spatial distribution of tracer fraction and various VOCs prior to, during, and after the biotreatability test (Figures A-11 through A-15). Some of these plots were also used to estimate dissolved VOC mass. Figure A-11 shows the distribution of tracer water (in % tracer fraction) and TCE (in μ g/L) at the end of the tracer test (July 2005) in the T2 Area. As can be seen, detectable tracer water is limited to the vicinity of wells W-834-1824, W-834-1825, and W-834-T2 with no tracer water detected in the furthest downgradient well W-834-1833. The extent of TCE at concentrations of less than 10,000 μ g/L at this time is due primarily to dilution and displacement of the TCE plume by injection of Hetch Hetchy tracer water. The extent of the Hetch Hetchy tracer was consistent with the treatment zone created by Na lactate injection and shown in the plots presented in Figures A-11 through A-15.

Figure A-12 shows the extent of TCE and cis-1,2-DCE at one month prior to any biostimulation with Na lactate (March 2007) and at two months prior to bioaugmentation (June 2008) after over a year of Na lactate injection. The decrease in TCE and the presence of cis-1,2-DCE in March 2007 is due mainly to two factors: (1) the inadvertent addition of an electron source (a rodent) that facilitated indigenous bacteria to transform

TCE to cis-1,2-DCE, and (2) some dilution from Hetch Hetchy tracer remaining after the tracer test. The June 2008 plots show further decrease in TCE and a significant increase in the extent and magnitude of cis-1,2-DCE. However, the highest concentration of cis-1,2-DCE shifted from well W-834-1824 in March 2007 to well W-834-1825 in June 2008. This is mainly due to the injection of Hetch Hetchy tracer into well W-834-1824 and the displacement of contaminated ground water toward the downgradient wells. Vinyl chloride and ethene are not shown for this time period because these constituents were not detected until after bioaugmentation ceased in August 2008.

Figure A-13 presents the extent of TCE reduction ($<10 \ \mu g/L$) and the extent of vinyl chloride and ethene seven months after bioaugmentation (March 2009). As shown in Figure A-13, the 1,500 $\mu g/L$ of ethene detected in well W-834-T2 is the maximum level of ethene detected in any well during the test. By December 2009 (16 months after bioaugmentation), TCE and cis-1,2-DCE in the treatment zone remained low, however, the maximum vinyl chloride concentration had shifted from well W-834-1825 to well W-834-T2 (Figure A-14). By August 2010, two years after bioaugmentation, the extent of TCE and cis-1,2-DCE had not changed significantly. However, the extent of vinyl chloride and ethene ($<10 \ \mu g/L$) had decreased slightly and remained higher at well W-834-T2 than in the other wells (Figure A-15). Based on the most recent data (March 2011), ethene remained at about the same level in all samples from wells at 410 $\mu g/L$ in well W-834-T2, 32 $\mu g/L$ in well W-834-1825, and 2.6 $\mu g/L$ in well W-834-1824.

During the three months following bioaugmentation, VFAs (lactic, butyric, propionic, pyruvic, and acetic acids) increased significantly in wells W-834-T2 and W-834-1825. These trends indicate that Na lactate was being utilized as an electron donor in the microbial breakdown of TCE. As expected, nutrient levels have decreased significantly since Na lactate injection ceased in December 2008. Nutrient levels remained below 1 mg/L throughout the test in well W-834-1833. The most recent VFA data suggest that some nutrients remain in the vicinity of well W-834-1825, but that the W-834-T2 well vicinity has been depleted. At this time, the overall decline in bioremediation performance is mainly due to the lack of available nutrients.

Figure A-16 presents a summary of data collected during this test including monthly rainfall, Hetch Hetchy tracer (45,600 L or 11,400 gallons) and Na Lactate (725 L or 184 gallons) injection volumes, injection rate, and specifies the time period for five VOC mass estimates that were made to assess overall performance:

- Pre-biostimulation (March 2007 and June 2008).
- Post-biostimulation and bioaugmentation (March and May 2009).
- Post-rebound (August 2010).

This plot shows the rainfall recharge conditions along with the volumes of Hetch Hetchy tracer and Na lactate injected during the test. The annual rainfall was generally below average during the period from 2007 to 2009 during the biostimulation phase of this test. After the above average rain during the month of January 2008, rainfall and Na lactate injection decreased significantly and water levels in the treatment zone declined throughout the remainder of the Na lactate injection period.

In addition to concentration trends in individual wells, the overall TCE mass reduction within the treatment zone was assessed. A 3-dimensional (3D) Earth Vision property model was created to estimate dissolved VOC mass in the Tpsg HSU for selected time periods during this test. The domain of the property model is 125 ft by 125 ft including the treatment zone and extending to the nearby extent of saturation to the southwest. The model contains two geologic layers: the Tpsg and the underlying Tps clay perching horizon. Control points were used to constrain the interpolation of the spatial data. A 3D property grid (x,y,z,p), with the property being dissolved VOC concentration, was generated using data from each well and a grid spacing (15 ft x 15 ft x 2.5 ft) that was determined after testing several grid spacings to determine the grid that best correlated to the spatial distribution of measured data. The top of the volume is a 2-dimensional (2D) surface based on ground water elevation data and the bottom is the 2D surface based on the elevation of the underlying Tps clay perching horizon. VOC concentrations at each well were vertically averaged over the saturated thickness and interpolated between wells using Earth Vision's proprietary, inverse-distance weighting algorithm.

Earth Vision volumetrics was used to roughly estimate dissolved mass of various VOCs for each time period using water level and chemical data assuming a porosity equal to 0.20. Dissolved VOC mass was estimated at two scales: (1) T2 domain (125 ft by 125 ft) which includes all injection, performance, and compliance wells and the surrounding area, and (2) treatment zone (50 ft by 50 ft) which is defined by the extent of tracer, Na lactate, and dechlorination byproducts. The treatment zone is contained within the T2 domain. It includes wells W-834-1824, W-834-1825, and W-834-T2 and extends up to, but does not include wells W-834-1833, W-834-T2A, and W-834-T2D.

Assuming a 20% bulk porosity estimated based on the tracer test, water volume varied from about 43,000 L (May 2009) to 83,000 L (August 2010) within the 125 ft x 125 ft T2 domain, and from about 21,000 L (March 2009) to 29,000 L (August 2010) within the 50 ft x 50 ft treatment zone during the test. This variation in water volume is due mainly to the magnitude and timing of rainfall recharge and the injection of Hetch Hetchy tracer and Na lactate, balanced by the amount of evapotranspiration of perched ground water taking place along the nearby hillside. About two pore volumes of Hetch Hetchy tracer water were injected into the 50 ft x 50 ft treatment zone during the 1.5-year biostimulation period. This volume of water was injected during a period of below average annual rainfall (Figure A-16). In fact, the injection rate declined to 32 L/day in January 2008 and water levels in all the T2 area wells began to decline after the March 2008 recharge event even though injection continued until December 2008 (Figure A-8). As mentioned above, the probable cause for these declining perched ground water levels is that evapotranspiration is occurring along the nearby hillside at a higher rate than is being recharged by injection. These temporal variations in water levels influence the volume of water in the T2 and treatment zone domains and therefore have some impact on the estimate of dissolved VOC mass.

VOC mass estimates at the two domain scales for the following time periods are presented in Table A-2: prior to the start of biostimulation (March 2007 and June 2008), after biostimulation and bioaugmentation (March and May 2009), and after two years of rebound (August 2010). The mass estimates shown in Table A-2, are considered rough

estimates of dissolved VOC mass in the Tpsg HSU. They do not reflect mass of VOCs in the underlying Tps Clay or adsorbed to mineral surfaces. At the start of Na lactate injection (April 2007) the estimated dissolved mass of VOCs in the Tpsg within the T2 domain (125 ft by 125 ft area) was about 660 grams (g), consisting mostly of TCE with minor DCE mainly in the treatment zone. At this time, about 149 g of TCE and some cis-1,2 DCE were present within the treatment zone. In June 2008, after about one year of Na lactate injection, the estimated dissolved mass of VOCs within the T2 domain was 478 grams, still consisting of mostly TCE (461 g) and the remainder consisting of cis-1,2-DCE. Within the treatment zone, the VOC mass was 93 g, of which 78 g was TCE. In 2009, after biostimulation and bioaugmentation, the estimated dissolved mass of VOCs had decreased to 181 g and 103 g in March and May 2009, respectively within the T2 domain and to about 20 g and 18.6 g within the treatment zone. Vinyl chloride was detected and, for the first time, significant amounts of ethene. As presented in the VOC mass estimate summary plot in Figure A-17, by May 2009 ethene was the dominant VOC within the treatment zone. By this time, dissolved VOC mass in the Tpsg within the treatment zone had decreased by 88% from March 2007, as a result of mainly biotic but also abiotic processes.

DATE	ТСЕ	cis-1,2 DCE	VC	Total VOCs	Ethene
March 2007	655/149.3	5.4/4.3	0.0/0.0	659.4/153.6	0.0/0.0
June 2008	461/78	17/15	0.0/0.0	478/93	0.0/0.0
March 2009	181/20.2	1.5/0.8	0.41/0.31	182.9/21.3	4.0/4.0
May 2009	103/18.6	0.85/0.51	0.18/0.11	104/19.2	4.6/4.6
August 2010	212/47	5.4/4	1.9/1.5	219.3/52.5	1.6/1.7

 Table A-2. VOC mass estimate summary table.

Note: All VOC mass in grams. The 1st entry is VOC mass in T2 domain; 2nd entry in the treatment zone. Total VOCs include TCE, cis-1,2 DCE, and VC.

Biotic transformation of TCE to ethene accounts for a significant portion of the observed VOC mass reduced, however, some of this reduction is attributable to abiotic processes. Although a significant effort was made to rigorously monitor performance during this treatability study, the relative contributions of biotic and abiotic processes to VOC reduction in the treatment zone is difficult to separate and quantify. The relative difference between abiotic versus biotic processes to the reduction of VOCs is clearly exhibited in Figure A-7 by the steep declining trends in the three treatment zone wells W-834-1824, W-834-1825 and W-834-T2, compared to background wells W-834-1833 and W-834-2117. Judging from the VOC decrease in "background" well W-834-2117 (about 30%), abiotic processes account for some portion of the observed VOC mass reduction within the treatment zone. Although ethene is conclusive evidence that TCE is being completely dechlorinated due to biotic processes, the amount of ethene (about 4.6 g May 2009) produced at any one time does not reflect the total decrease in dissolved VOC mass (130 g) due to biotic processes. Ethene is transient and is not conserved in the subsurface due to its volatility and susceptibility to further biotic breakdown.

One of the best measures of long-term performance is to monitor VOC concentration and mass during an extended rebound period during which the hydraulics are allowed to return to natural, unstressed conditions and no additional nutrients or dechlorinating bacteria are injected into the subsurface. As presented in Figures A-7 and A-15, significant VOC rebound was observed in the vicinity of well W-834-T2, whereas little to no rebound has been observed at wells W-834-1824 or W-834-1825. By August 2010, dissolved VOCs had rebounded to 12 g and ethene had decreased to 2 g, indicating some continued biotransformation two years after bioaugmentation, albeit at a decreased rate. The rebound in VOCs at well W-834-T2 is due to the depletion of nutrients in the vicinity of that well such that the flux of VOCs (mainly TCE) into the dissolved phase exceeds the biotransformation rate. In a fully implemented enhanced biotreatment project, this trend would be easily reversed by the addition of Na lactate and, if needed, additional bioaugmentation. In the vicinity of well W-834-1824, the lack of rebound can be partly attributed to a combination of biotic processes and abiotic processes (mainly the displacement and dilution of VOCs by Hetch Hetchy water injection). The lack of rebound at well W-834-1825 is most likely due to the fact that this is the well that was bioaugmented and therefore, the biotransformation of TCE in the dissolved and adsorbed phases in the vicinity of this well both was thorough and complete.

A-6. Conclusions

The following conclusions regarding the performance of enhanced *in situ* bioremediation at T2 are based on the integration of multiple data sets collected prior to and during the five-year T2 treatability study:

- Passive biostimulation using Na lactate and bioaugmentation using KB-1TM successfully transformed TCE to a benign end product, ethene, within a limited treatment zone (about 50 ft by 50 ft) that includes the vicinity of wells W-834-1824, W-834-1825, and W-834-T2.
- Vinyl chloride and ethene were not detected after biostimulation with Na lactate but prior to bioaugmentation with KB-1, indicating the lack of indigenous bacteria capable of complete dechlorination to ethene in the treatment zone. This is consistent with the results of the microcosm study and other data collected in the Building 834 OU.
- The persistence of ethene in well W-834-T2 seven months after bioaugmentation in well W-834-1825, located about 25 ft away, suggests that preferential pathways likely played a significant role in the distribution of Na lactate and KB-1TM bacteria. These pathways will dominate the performance of any *in situ* source area treatment technology and they cannot be easily identified in advance using conventional subsurface characterization methods or without significant hydraulic stress of the treatment zone;
- By mid-2009, dissolved VOC mass was reduced by about 88% from levels measured prior to biostimulation or bioaugmentation in March 2007. This reduction in dissolved VOCs is due mainly to biotic but also to abiotic processes such as volatilization and adsorption. The relative contributions of these two processes to the overall VOC mass reduction was difficult to quantify even

though multiple, independent hydraulic, chemical, and biological parameters were monitored, some in real time. Periodic rebound monitoring can be used to assess long-term performance.

- Declining levels of ethene and rebound of VOCs in well W-834-T2 two years after bioaugmentation and Na lactate injection, indicates a TCE flux into the dissolved phase that exceeds biotic and abiotic attenuation rates in the vicinity of that well. VOC rebound is most likely due to dissolution, desorption, and diffusion of TCE from geologic materials within the Tpsg and underlying Tps clay and the depletion of available nutrients and the microbial community, especially Dhc.
- Lack of any significant rebound at well W-834-1825 indicates that biotransformation of both dissolved and adsorbed phases in the vicinity of this well has been thorough and complete.
- Periodic injections of electron donor and possibly additional bioaugmentation in selected wells will be required to maintain and optimize effective long-term *in situ* bioremediation.
- Due to the limited zone of influence from a single well, any *in situ* source area treatment technology applied at Site 300 that uses reagent and/or bacteria injection, will require numerous, closely spaced wells (on the order of 50 to 100 ft apart) and the use of re-circulation cells.
- *In situ* bioremediation did not negatively impact ground water quality outside a fairly limited, pre-described treatment zone in the target HSU, Tpsg, or deeper HSUs, such as the Tps Clay or Lower Tnbs₁.

Section A-7 presents recommendations for a path forward based on the results and conclusions from this study.

A-7. Recommendations

The overall performance of any enhanced *in situ* bioremediation technology at the Building 834 T2 area or any of the other typical contaminant source area at Site 300 will be constrained by limited recharge and low permeability, anisotropic, heterogeneous geologic materials. The zone-of-influence from a single vertical well to deliver and distribute any reagent or microbial population into the subsurface is limited to a radius of a few tens of feet. Multiple, closely spaced (<50 ft) injection/extraction well pairs as recirculation cells are recommended especially in the highest concentration source areas to improve the delivery and distribution of reagents in the subsurface under these hydrogeologic conditions.

Given these constraints, it is recommended to assess the cost-benefit of expanding *in situ* bioremediation at T2 by implementing a re-circulation cell with multiple biostimulation/bioaugmentation injection wells and extraction wells. If the use of recirculation cells for *in situ* bioremediation is found to be cost-effective, an evaluation of the cost/benefit of using horizontal biostimulation wells with long screens at the Tpsg/Tps clay contact, and/or enhancing permeability using pneumatic or hydraulic fracturing in vertical or horizontal wells to further improve distribution of reagents and microbial populations in the target zone is recommended.

A-8. References

Miller, Todd, Mark, Franklin, and Halden, Rolf (2007), *Bacterial Community analysis of shallow groundwater undergoing sequential anaerobic and aerobic chloroethene biotransformation*, FEMS Microbial Ecol 60, 299-311.

A-9. Acronyms and Abbreviations

cm/sec	Centimeters per second
D	Deuterium
DCE	Dichloroethylene
DGGE	Denaturing gradient electrophoresis
Dhc	Dehalococcoides
DNA	Deoxyribonucleic acid
DO	Dissolved oxygen
DOE	Department of Energy
ft	Feet
ft ³	Cubic feet
g	Gram
HSU	Hydrostratigraphic unit
L	Liter
LHC	Light hydrocarbon
LLNL	Lawrence Livermore National Laboratory
mg/kg	Milligrams per kilograms
mg/L	Milligrams per liter
mV	Millivolts
O-18	Oxygen-18
ORP	Oxidation-reduction potential
OU	Operable unit
PCR	Polymerase chain reaction
rdh	Reductive dehalogenase
redox	Reduction-oxidation
rRNA	Ribosomal ribonucleic acid
SC	Specific conductance
TCE	Trichloroethylene
TDS	Total dissolved solids
TKEBS	Tetrakis (2-ethylbutoxy) silane
U.S.	United States
VC	Vinyl chloride
VFA	Volatile fatty acids
VOCs	Volatile organic compounds
μg/L	Micrograms per liter
μS	Microseimens

Appendix A

Figures

Appendix A

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Figure A-1. Building 834 Operable Unit site map showing piezometers and monitoring, extraction, and guard wells, and treatment facilities, and location of T2 Enhanced Biotreatability Test Area.



Figure A-2. Geology the T2 study area.



Figure A-3. T2 Treatability Test Well Field.



Figure A-4. North to south cross-section A-A' showing Tpsg and Tps Clay HSUs annotated with soil TCE results in mg/kg.





Figure A-5. Volume of water injected during tracer test and bioremediation test showing average injection rates.



Figure A-6. Hetch Hetchy water tracer fraction in T2 area wells (January 2005–August 2010).



Figure A-7. TVOC time-series plot (2006 to present).



Figure A-8. Hydrographs showing ground water elevations during lactate injection and bio-augmentation.



Figure A-9. Summary of performance data including time-series plots of ORP and volatile fatty acids (VFAs) for W-834-1825, -T2, and -1833.

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Figure A-11. Maximum extent of tracer (%) and TCE (ppb) at end of tracer test (July, 2005).



Figure A-12. TCE and cis-1,2-DCE concentrations a) 1 month prior to start of Na Lactate injection (March 2007) and b) 2 months prior to bioaugmentation (June 2008).



Figure A-13. TCE, cis-1,2-DCE, VC, and ethene concentrations 7 months after bioaugmentation (March 2009).



Figure A-14. TCE, cis-1,2-DCE, VC, and ethene concentrations 16 months after bioaugmentation (December, 2009).



Figure A-15. TCE, cis-1,2-DCE, VC, and ethene concentrations 24 months after bioaugmentation (August 2010).



Figure A-16. T2 Treatability Test Water Budget summary plot including monthly rainfall and volumes of H-H tracer and Na Lactate injected.



Jun-07

Sep-07

Dec-07

0.001 UIL Mar-07

Figure A-17. T2 Bio-treatability Test VOC Mass Estimate Summary Plot for a) T2 domain 125' x 125'; and b) Treatment zone 50 ' x 50'.

Dec-08

Mar-09

Jun-09

Sep-09

Dec-09

Mar-10

Jun-10

Sep-10

Jun-08

Mar-08

Sep-08

Attachment 1

Laboratory Biotreatability Study To Evaluate Biodegradation of Chlorinated Solvents in Groundwater

Prepared for:

Lawrence Livermore National Laboratory 7000 East Avenue Livermore, California 94551

LABORATORY BIOTREATABILITY STUDY TO EVALUATE BIODEGRADATION OF CHLORINATED SOLVENTS IN GROUNDWATER LAWRENCE LIVERMORE NATIONAL LABORATORY Livermore, California

Prepared by:



130 Research Lane, Suite 2 Guelph, Ontario N1G 5G3 SiREM Ref: TL0103

28 February 2006



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APPENDIX A: Henry's Law Calculation

APPENDIX B: SiREM Gene-Trac Report



LIST OF ABBREVIATIONS

cis-1,2-DCE	<i>cis</i> -1,2-dichloroethene
cells/L	cells per liter
COD	chemical oxygen demand
°C	degrees Celsius
°C/min	degrees Celsius per minute
Cr ³⁺	chromic ion
DHG	dissolved hydrocarbon gases
g/L	grams per liter
GC	gas chromatograph
HRC [™]	hydrogen release compound
IC	ion chromatograph
KB - 1™	KB - 1 [™] dechlorinator
LLNL	Lawrence Livermore National Laboratory
µg/L	micrograms per liter
μL	microliters
min	minutes
mg/L	milligrams per liter
mL	milliliters
mL/min	milliliters per minute
mM	millimolar
mmol/bottle	millimole per bottle
%	per cent
QL	quantitation limit
SIREM	SiREM Laboratories
TCE	trichloroethene
VOC	volatile organic compound
VC	vinyl chloride



1. INTRODUCTION

Lawrence Livermore National Laboratory (LLNL) retained SiREM Laboratories (SiREM) to perform a laboratory biotreatability study for volatile organic compounds (VOCs) in groundwater collected from an unspecified location (the Site). The purpose of the study was to assess natural attenuation, enhanced bioremediation, and bioaugmentation processes for the remediation of the target VOCs (namely trichloroethene [TCE] and its associated degradation products; *cis*-1,2-dichloroethene [*cis*-1,2-DCE] and vinyl chloride [VC]) at the Site.

Natural attenuation processes occur in situ and are mediated by indigenous microbial populations present at the Site. Enhanced anaerobic bioremediation can be achieved by stimulating the indigenous microbial populations through the addition of electron donors. Bioaugmentation is the process by which a microbial population known to promote complete reductive dechlorination is introduced to Site groundwater. KB-1TM Dechlorinator (KB-1TM) is a natural microbial consortium containing microorganisms (*Dehalococcoides*) known to be responsible for mediating the complete dechlorination of TCE, *cis*-1,2-DCE, and VC to ethene ^{1,2}. The culture is non-pathogenic according to biannual testing by an external laboratory (results available upon request).

Groundwater used in this study was collected by LLNL personnel from well 3X077-W-834-2117 on 1 February 2005 and was received by SiREM on 6 April 2005. Soil cores collected from location B-834-2117 on 1 February 2005 were received from LLNL on 6 April 2005. Microcosms were prepared under anaerobic conditions in an effort to simulate in situ Site conditions in the laboratory to the extent practicable. The remainder of this report is divided into three sections. Section 2 presents the experimental approach and methods, section 3 presents the results and discussion and section 4 presents conclusions of the microcosm study.

2. APPROACH AND METHODS

The following sections describe the approach and methods for microcosm construction and incubation (Section 2.1), and microcosm sampling and analysis (Section 2.2).

2.1 Microcosm Construction and Incubation

A total of 15 microcosms were constructed on 7 April 2005. Site soil and groundwater were placed in a disposable anaerobic glove bag with the materials required to construct the various treatment and control microcosms. The glove bag was purged with a carbon dioxide/nitrogen (20:80) gas mixture to create an anaerobic environment.



The soil was combined and mixed by hand to improve reproducibility between replicates. Microcosms were constructed by filling sterile 250 milliliter (mL) (nominal volume) screw cap Boston round clear glass bottles (Systems Plus, New Hamburg, Ontario) with 30 mL of homogenized soil and 180 mL of Site groundwater. The bottles were capped with Mininert[™] closures to allow repetitive sampling of the bottle with minimal VOC loss, and to allow nutrient amendment, as needed, throughout the incubation period. All controls and treatments were constructed in triplicate.

Anaerobic sterile control microcosms were constructed to quantify potential abiotic and experimental VOC losses from the microcosms. The sterile controls were constructed by autoclaving the Site soil once at 121 degrees Celsius (°C) and 15 pounds per square inch pressure for 45 to 60 minutes (min). After autoclaving, the control microcosms were returned to the anaerobic chamber, filled with 180 mL of Site groundwater and amended with 2.8 mL of 2.7 per cent (%) mercuric chloride (equal to a final liquid concentration of 0.05 %) and 0.5 mL of 5 % sodium azide (equal to a final liquid concentration of 0.017 %) to inhibit microbial activity.

All microcosms were sampled and incubated in an anaerobic chamber (Coy Laboratory Products, Grass Lake, MI) filled with approximately 80% nitrogen, 10% carbon dioxide, and 10% hydrogen (BOC gases). Hydrogen was present to scavenge low levels of oxygen via a palladium catalyst, and anaerobic conditions were verified by an open bottle of resazurin-containing mineral medium, which turns pink in color if oxygen is present. During quiescent incubation, all microcosms were covered to minimize photodegradation, and placed on their side to minimize VOC losses via the (submerged) Mininert[™] closure. Microcosms were incubated for a period of up to 238 days at 22°C (room temperature).

LLNL specified that the initial TCE concentration in all microcosms should be 30 milligrams per liter (mg/L) to mimic concentrations found at the Site. The initial TCE concentration measured in the prepared microcosms were not at target concentrations and on 7 April 2005 (Day - 6), all microcosms were amended with 3.0 microliters (μ L) of neat TCE (Sigma) to achieve the target concentration in the microcosms.

Three electron donor bioaugmented treatments (corn syrup, HRC[™], and ethanol) were evaluated in this biotreatability study. The corn syrup used was the BeeHive brand (ACH Food Company Inc., Memphis, TN), HRC[™] was obtained from Regenesis (San Clemente, CA), and anhydrous ethanol was obtained from Commercial Alcohols Inc. (Brampton, Ontario). Treatment microcosms were amended with electron donors at approximately twice the stoichiometric demand of the VOCs and selected inorganic compounds (i.e., nitrate and sulfate). As shown in Table 1, microcosms were amended



with either 393 μ L of an aqueous 75 grams per liter (g/L) corn syrup stock, 452 μ L of an aqueous 100 g/L hydrogen release compound (HRCTM) stock (HRCTM was assumed to be 100 % lactate by weight), or 28 μ L of neat ethanol on 13 April 2005 (Day 0). These volumes were calculated to give a concentration of 251 mg/L of donor in each microcosm on a chemical oxygen demand (COD) basis (Section 2.2.4). All microcosms were re-amended with 251 mg/L COD of their respective donors on 19-20 October 2005 (Days 189-190). Analysis of ethanol indicated that this donor was rapidly depleted in ethanol amended microcosms; hence, these microcosms were reamended several more times throughout the study (Table 2).

To assess the ability of bioaugmentation to improve the extent and rate of TCE dechlorination to ethene, two microcosms from each electron donor treatment were bioaugmented with KB-1[™] culture. One microcosm from each electron donor treatment was bioaugmented with a target *Dehalococcoides* concentration of 10⁶ cells per liter (cells/L) in the microcosm on 2 September 2005 (Day 142). To achieve this cell concentration, a 1 mL aliquot of a culture with a steady state concentration of approximately 10¹⁰ Dehalococcoides cells/L (determined by monthly Gene-Trac testing) was serially diluted twice in 9 mL of anaerobic mineral medium. Adding 1.8 mL of the diluted cell suspension to each 180 mL microcosm resulted in a four order-ofmagnitude reduction in Dehalococcoides concentrations compared to the parent culture. A second microcosm from each electron donor treatment was bioaugmented with a target *Dehalococcoides* concentration of 10⁸ cells/L in the microcosm on 19 October 2005 (Day 189). To achieve this cell concentration, 1.8 mL of the parent culture with 10¹⁰ Dehalococcoides cells/L was added to each microcosm without serial dilution as described above. The third microcosm from each electron donor treatment was not bioaugmented at any point in the study. Microcosms were not bioaugmented at time zero to allow for development of reducing conditions required by the KB-1[™] culture. Reducing conditions in these microcosms were obtained after the addition of the electron donor.

Table 2 summarizes the details of microcosm construction and amendments for the various treatment and control microcosms.

2.2 Microcosm Sampling and Analysis

2.2.1 Microcosm Sampling

Aqueous samples were collected from the control and treatment microcosms on a weekly to biweekly (i.e., every two weeks) basis for analysis of VOCs (TCE, *cis*-1,2-DCE, and VC), dissolved hydrocarbon gases (DHGs) (ethene, ethane, and methane), anions (sulfate, nitrate, nitrite, chloride, phosphate, bromide) and selected electron



donors (lactate and ethanol). Microcosms were sampled using gas-tight 1 mL Hamilton glass syringes. Separate sets of syringes were used for bioaugmented and non-bioaugmented treatments to reduce the potential for transfer of KB-1TM microorganisms to non-bioaugmented treatments. Syringes were cleaned with acidified water (pH ~2) and rinsed 10 times with deionized water between samples, to ensure that VOCs and microorganisms were not transferred between different samples or treatments. The analytical methods employed by SiREM are described below.

2.2.2 Analysis of VOCs, Dissolved Hydrocarbon Gases, and Ethanol

This section describes the methods used to quantify the chlorinated ethenes, DHGs, methanol and ethanol. The quantitation limits (QL) for the chlorinated ethenes, ethanes, and methanes and DHGs were typically 20 to 40 micrograms per liter (μ g/L) in the microcosm based on the lowest concentration standards that were included in the linear calibration trend. The QL for ethanol was 4 mg/L.

Aqueous VOC concentrations in the microcosms were measured using a Hewlett-Packard (Hewlett Packard 5890 series II Plus) gas chromatograph (GC) equipped with an auto sampler (Hewlett Packard 7684) programmed to heat each sample vial to 75°C for 45 min prior to headspace injection into a GSQ Plot column (0.53 millimeters x 30 meters, J&W) and a flame ionization detector. Sample vials were heated to ensure that all VOCs in the aqueous sample would partition to the headspace. The injector temperature was 200°C, and the detector temperature was 250°C. The oven temperature was programmed as follows: 35°C for 2 min, increase to 100°C at 50 degrees Celsius per minute (°C/min), then increase to 185°C at 25°C/min and hold at 185°C for 5.80 min. The carrier gas was helium at a flow rate of 11 milliliters per minute (mL/min).

After withdrawing a 0.25 mL sample (as described in section 2.2.1), the sample was injected into a 10 mL auto sampler vial containing 5.75 mL of acidified deionized water (pH ~2). The water was acidified to inhibit microbial activity between microcosm sampling and GC analysis. The vial was sealed with an inert TeflonTM-coated septum and aluminum crimp cap for automated injection of 3 mL of headspace onto the GC. One VOC standard was analyzed with each batch of samples to verify the yearly five-point calibration using methanolic stock solutions containing known concentrations of the target analytes. Calibration was performed using external standards that were purchased as standard solutions (Sigma). Known volumes of standard solutions were added to acidified water in auto sampler vials and analyzed as described above for microcosm samples. Data were integrated using Peak Simple Chromatography Data System Software (SRI, Inc.).


millimoles per bottle (Figures 1 to 5 and Table 3A) using Henry's Law as shown in Appendix A.

2.2.3 Analysis of Anions and Lactate

This section describes the methods to quantify anions and lactate.

Analysis was performed on a Dionex DX-600 ion chromatograph (IC) equipped with a Dionex AS-40 auto sampler and an AS18 column. The sample loop volume was 25 μ L. An isocratic separation was performed using 33 millimolar (mM) sodium hydroxide (reagent grade, Fisher) eluent for 13 minutes. One standard was analysed with each batch of samples to verify the yearly seven-point calibration using external standards of known concentrations. External standards were prepared gravimetrically using chemicals of the highest purity available (Sigma or Bioshop). Data were integrated using Dionex's Peaknet chromatography software. The QLs were as follows: 0.25 mg/L lactate, 0.03 mg/L chloride, 0.28 mg/L nitrite, 0.02 mg/L nitrate, 0.03 mg/L sulfate, 0.05 mg/L phosphate and 0.14 mg/L bromide. The lactate value included most other volatile fatty acids, such as formate, acetate, propionate, pyruvate, and butyrate (valerate has not been tested), as the analytical method does not resolve these compounds.

After withdrawing a 0.5 mL sample (as described in section 2.2.1), the sample was placed in a 1.5 mL micro-centrifuge tube. Samples were centrifuged for five minutes to settle out solids. The supernatant was removed, diluted 10-fold in deionized water and placed in a Dionex auto sampler vial with a cap that filters the sample during automated injection onto the IC.

2.2.4 Analysis of Chemical Oxygen Demand

The COD test measures the oxygen equivalent of the amount of organic matter oxidizable by potassium dichromate in a 50% sulfuric acid solution. When a sample is digested, the dichromate ion oxidizes COD material in the sample resulting in a change from the hexavalent (VI) to trivalent (III) valence state of the chromium. After the oxidation step is completed, the amount of chromic ion (Cr^{3+}) consumed is determined colorimetrically.

Analysis of COD was performed using HACH method 8000 test kit and commercially supplied, premeasured HACH reagents. A sample volume of 1 mL (sampled as described in section 2.2.1) was taken from the selected microcosms. The sample was diluted in deionized water and was digested at 150°C in a heating block for two hours



with a strong oxidizing agent (potassium dichromate and sulphuric acid). Sample concentrations were measured in a spectrophotometer at a wavelength of about 600 nanometers and compared to standard aqueous solutions of HRC^{TM} . A four-point calibration with HRC^{TM} was conducted at the start of the experiment but was not subsequently verified.

2.2.5 Analysis of *Dehalococcoides*

Genomic DNA was extracted from a 1 mL aqueous sample using the UltraClean Soil DNA Kit (Mo Bio Laboratories, Inc.). The concentration of *Dehalococcoides* was measured by the Gene-Trac assay, a real-time quantitative PCR technique that uses proprietary primers specific for variable regions of the *Dehalococcoides* 16S rRNA gene. These primers produce an amplicon of 512 base pairs in length and are similar to those described by Hendrickson et al.³ and protected under US patent US6894156B2 (Hendrickson and Ebersole). A six-point calibration is performed every six months using serial dilutions of a known concentration of plasmids containing cloned *Dehalococcoides* 16S rRNA genes. Two of these standards are included with every batch of samples to verify the calibration.

3. RESULTS AND DISCUSSION

The following sections present and discuss the results of the biotreatability study. Section 3.1 discusses the results for the sterile and intrinsic control microcosms. Section 3.2 presents and discusses the results for the corn syrup amended treatment microcosms. Section 3.3 discusses the results for the HRCTM amended treatment microcosms, and Section 3.4 discusses the results for the ethanol amended treatment microcosms.

Tables 3A and 3B provide chlorinated ethene, ethene, ethanol, and anion data from the control and treatment microcosms over the incubation period for the study. Ethane was not detected in any microcosm over its detection limit of 40 micrograms per liter (μ g/L). Table 3C provides COD data over the incubation period for the study. All chlorinated ethene and ethene concentrations are presented in units of mg/L and millimoles per microcosm bottle (mmol/bottle) to demonstrate mass balances on a molar basis. Table 4 provides dechlorination half-lives for TCE, *cis*-1,2-DCE, and VC calculated from data from the different microcosm treatments. Figures 1 through 5 present trends in the concentrations of chlorinated ethenes, ethene, and anions in the control and treatment microcosms over the incubation period for the study.



3.1 Sterile and Active Controls

As anticipated, the chlorinated ethene concentrations in the sterile control microcosms remained stable over the incubation period, showing no decline in TCE concentrations as well as no increase in *cis*-1,2-DCE, VC, ethene, or methane concentrations (Figure 1). Sulfate concentrations also remained stable. These results confirm that no significant mass loss of TCE in the various treatment microcosms resulted from abiotic degradation or experimental losses (e.g., sorption or loss through microcosm closures).

Chlorinated ethene, methane, and sulfate concentrations also remained stable in the anaerobic active control microcosms (Figure 2), although the third microcosm showed a small amount of TCE degradation to *cis*-1,2-DCE. These data suggest that the rate and extent of intrinsic biodegradation activity at the Site is limited, likely due to a lack of available nutrients (e.g., electron donors or cometabolites) and/or appropriate microorganisms to promote degradation.

3.2 Corn Syrup Amended Treatment Microcosms

In the first microcosm, the addition of corn syrup alone did not promote TCE dechlorination within 142 days (Figure 3). This microcosm was bioaugmented to a target concentration of 10^6 cells/L of KB-1TM culture on day 142, and within 6 days the TCE was completely converted to *cis*-1,2-DCE. VC production was slow between days 148 and 189, likely due to electron donor depletion as evidenced by the persistence of sulfate and lactate depletion despite relatively constant COD levels (Table 3C). On day 189, this microcosm was re-amended with corn syrup, and within 6 days *cis*-1,2-DCE dechlorination and sulphate reduction rates increased. Ethene production began on day 203, and VC and ethene concentrations were rising at the end of the study (Day 224). No significant methane production was observed. Nitrate was depleted by day 14 and sulfate reduction began between days 189 and 224. The calculated dechlorination half lives (the time to reduce the concentration by one half) for TCE, *cis*-1,2-DCE, and VC were 0.6, 27, and 9.7 days, respectively (Table 4). These half lives were determined after the microcosm was bioaugmented with KB-1TM.

In the second microcosm, the addition of corn syrup alone promoted TCE dechlorination to *cis*-1,2-DCE after a delay of 142-162 days (Figure 3). Stoichiometric conversion of TCE to *cis*-1,2-DCE was complete by day 189. This microcosm was reamended with corn syrup and bioaugmented to a target concentration of 10^8 cells/L of KB-1TM culture on day 189, which apparently stimulated the dechlorination of *cis*-1,2-DCE to VC, a small amount of methanogenesis, and the reduction of sulfate. VC concentrations were rising but ethene had not yet been detected at the end of the



incubation period (Day 224). Nitrate was depleted by day 14 and sulfate was depleted by day 224. The calculated dechlorination half lives for TCE and *cis*-1,2-DCE were 4.7 days (without KB-1TM) and 56 days (with KB-1TM), respectively (Table 4). Despite the 100-fold increase in initial KB-1TM concentration, the half life of *cis*-1,2-DCE in this microcosm was twice as long as in the first microcosm. Two possible phenomena may have contributed to this unexpected result. Firstly, microbial growth in the first microcosm during TCE conversion to *cis*-1,2-DCE may have enhanced the culture's ability to dechlorinate *cis*-1,2-DCE at somewhat higher rates. Secondly, corn syrup may have fermented too slowly for optimal KB-1TM growth in both microcosms. The comparatively low volatile fatty acid concentrations, as well as the long lag time prior to sulfate reduction, suggest that the rate of conversion of corn syrup to simpler electron donors and ultimately hydrogen was limiting.

In the third microcosm, the addition of corn syrup alone promoted partial dechlorination of TCE to *cis*-1,2-DCE commencing within 42 days (Figure 3). Stoichiometric conversion to *cis*-1,2-DCE was continuing at the end of the study (Day 189¹) without VC or ethene production. Methane levels rose throughout the incubation period. Nitrate was depleted by day 14 and sulfate was depleted by day 28. The calculated dechlorination half life for TCE was 108 days (Table 4).

These data suggest that microorganisms present at the Site are capable of partial dechlorination of TCE to *cis*-1,2-DCE, and that bioaugmentation with KB-1TM can promote dechlorination to ethene with corn syrup as an electron donor. However, the calculated dechlorination half lives were long and highly variable (Table 4).

The lack of dechlorination and sulfate reduction, as well as limited methanogenesis, in the first and second microcosms strongly suggests donor limitation despite concentrations greater than 60 mg/L of COD and 20 mg/L of lactate. It is therefore possible that the concentrations of donor, and/or the rate of corn syrup fermentation, were below the minimum thresholds for biomass growth. If corn syrup is to be explored further as a possible electron donor, higher initial concentrations should be tested. Also, hydrogen levels should be monitored (although such measurements can be difficult to obtain accurately at low concentrations) as this is believed to be the only donor used by *Dehalococcoides* species⁴. The ability to resolve acetate, *Dehalococcoides*' carbon source⁴, from lactate could also provide valuable insights in future experiments.

¹ This microcosm bottle was accidentally broken on day 189.



3.3 HRC[™] Amended Treatment Microcosms

In the first microcosm, the addition of HRC^{TM} alone promoted complete TCE dechlorination to *cis*-1,2-DCE within 14 days (Figure 4). Dechlorination did not proceed further until day 142 when this microcosm was bioaugmented to a target concentration of 10⁶ cells/L of KB-1TM culture. By day 175, ethene production had commenced, and by day 189, *cis*-1,2-DCE had been depleted to approximately 93 % VC and approximately 7 % ethene. This microcosm was re-amended with HRCTM on day 189 due to potential lactate depletion and decreasing COD concentrations. Stoichiometric conversion to ethene was complete by day 210 of the incubation period. Methane production began only after bioaugmentation, but rates accelerated after reamendment with HRCTM. Nitrate was reduced by day 14 and sulfate was depleted by day 126. The calculated dechlorination half lives for TCE, *cis*-1,2-DCE, and VC were 2.1 days (without KB-1TM), 9.8 days (with KB-1TM), and 3.4 days (with KB-1TM), respectively (Table 4).

A sample taken from HRC-1 on day 142 for Gene-Trac analysis showed that *Dehalococcoides* concentrations were less than the detection limit of 2.15×10^6 cells/L in the microcosm prior to bioaugmentation (Appendix B). This detection limit was higher than usual because only 1 mL of sample was analysed (instead of 1 L) to preserve liquid volume for future analyses. In SiREM's experience, it is unlikely that that the pre-bioaugmentation concentration of *Dehalococcoides* was near this detection limit because dechlorination past *cis*-1,2-DCE would be expected in the presence of sufficient electron donor. Given that dechlorination past *cis*-1,2-DCE did not occur in any microcosm prior to bioaugmentation, it is more likely that the indigenous level of *Dehalococcoides* in Site materials was orders of magnitude below the detection limit.

In the second microcosm, the addition of HRCTM alone promoted TCE dechlorination to *cis*-1,2-DCE after a delay of 70-84 days (Figure 4). Stoichiometric conversion of TCE was complete by day 162. This microcosm was re-amended with HRCTM and bioaugmented to a target concentration of 10^8 cells/L of KB-1TM culture on day 189. Within 7 days, VC, ethene, and methane production began. Stoichiometric conversion to ethene was complete by day 224. Nitrate was depleted by day 14 and sulfate was depleted by day 126. The calculated dechlorination half lives for TCE, *cis*-1,2-DCE, and VC were 17 days (without KB-1TM), 4.8 days (with KB-1TM), and 1.5 days (with KB-1TM), respectively (Table 4). The 100-fold higher KB-1TM inoculum concentration added to this microcosm decreased the half lives of *cis*-1,2-DCE and VC by greater than 50% compared to the first microcosm two weeks before the second because it was bioaugmented earlier in the study.



In the third microcosm, the addition of HRC^{TM} alone promoted TCE dechlorination after a delay of 56-70 days (Figure 4). Stoichiometric conversion to *cis*-1,2-DCE was complete by day 142. Despite re-amendment with HRC^{TM} on day 189, only a trace amount of VC and no ethene were detected by the end of the study (day 224). No methane production was observed during the incubation period. Nitrate was depleted by day 14 and sulfate was depleted by day 42. The calculated dechlorination half life for TCE was 8.8 days (Table 4).

These data suggest that microorganisms present at the Site are capable of partial dechlorination of TCE to *cis*-1,2-DCE with HRCTM as an electron donor. Differing lag times prior to TCE dechlorination did not appear to be caused by electron donor limitations early in the study because sulfate was reduced at consistent rates throughout the first four months. Bioaugmentation with KB-1TM promoted rapid, stoichiometric conversion of TCE to ethene with HRCTM as an electron donor. Increasing the inoculum concentration of KB-1TM can reduce dechlorination half lives, although this may not always offset the benefits of bioaugmenting earlier with a lower inoculum concentration.

3.4 Ethanol Amended Treatment Microcosms

In the first microcosm, the addition of ethanol alone did not promote TCE dechlorination within 142 days (Figure 5). Dechlorination proceeded only after day 142 when this microcosm was bioaugmented to a target concentration of 10⁶ cells/L of KB-1[™] culture. Within 6 days, stoichiometric conversion of TCE to *cis*-1,2-DCE was complete, with traces of VC and ethene. By day 175, stoichiometric conversion to ethene was complete. This microcosm was re-amended with 251 mg/L COD of ethanol six times throughout the study, resulting in high levels of COD and volatile fatty acids (measured as lactate, but likely acetate - see Section 2.2.3). Ethanol treatments were re-amended more frequently than other treatments not only because ethanol depletion is easy to determine from GC analyses, but also because this practice is more consistent with field-scale operations. Because ethanol is highly soluble and quickly degraded, it is usually added to groundwater semi-continuously, as opposed to "slow-release" donors such as HRCTM which are typically added once every few years. Methane production began between days 155 and 162, similar to the onset of ethene production, and reached relatively high levels (greater than those of the chlorinated ethenes) due to frequent re-amendment with electron donor. Nitrate was depleted by dav 14 and sulfate was depleted by day 126. The calculated dechlorination half lives for TCE, cis-1,2-DCE, and VC were 0.6 days, 6.9 days, and 1.4 days, respectively (Table 4). These half lives were determined after the microcosm was bioaugmented with KB-1[™].



In the second microcosm, the addition of ethanol alone promoted TCE dechlorination to *cis*-1,2-DCE after a delay of 70-105 days (Figure 5). Stoichiometric conversion of TCE to *cis*-1,2-DCE was complete by day 162. This microcosm was bioaugmented to a target concentration of 10^8 cells/L of KB-1TM culture on day 189. Within 7 days, VC, ethene, and methane production began. Stoichiometric conversion to ethene was complete by day 217. This microcosm was re-amended with ethanol seven times throughout the study, resulting in increasing levels of COD and volatile fatty acids. Nitrate was depleted by day 14 and sulfate was depleted by day 84. The calculated dechlorination half lives for TCE, *cis*-1,2-DCE, and VC were 5.7 days (without KB-1TM), 6.9 days (with KB-1TM), and 1.9 days (with KB-1TM), respectively (Table 4). The 100-fold higher KB-1TM inoculum concentration in this microcosm had no impact on the half lives of *cis*-1,2-DCE and VC compared to the first ethanol amended microcosm.

In the third microcosm, the addition of ethanol alone promoted TCE dechlorination after a delay of approximately 84 days (Figure 5). Stoichiometric conversion of TCE to *cis*-1,2-DCE was complete by day 105. Despite re-amendment with ethanol seven times throughout the study, neither VC nor ethene were detected by the end of the study (Day 224). Methane was not produced throughout the incubation period. Nitrate was depleted by day 14 and sulfate was depleted by day 84. The calculated dechlorination half life for TCE was 2.1 days (Table 4).

These data suggest that microorganisms present at the Site are capable of partial dechlorination of TCE to *cis*-1,2-DCE with ethanol as an electron donor. Bioaugmentation with KB-1TM can promote rapid, stoichiometric conversion to ethene with ethanol as an electron donor. Increasing the inoculum concentration of KB-1TM had no impact on dechlorination half lives.

4. CONCLUSIONS

Based on the results of the biotreatability study the following conclusions can be made:

- 1. The rate and extent of intrinsic degradation of TCE in Site groundwater is limited by the lack of available nutrients (e.g., electron donors) and the absence of suitable strains of bacteria capable of promoting complete reductive dechlorination of TCE to ethene at the Site.
- 2. Bioaugmentation was necessary in all treatments to achieve complete dechlorination of TCE to ethene in the time allotted.



- 3. Indigenous bacteria present at the Site are capable of partial dechlorination of TCE to *cis*-1,2-DCE with the addition of corn syrup, HRC[™], or ethanol as electron donors.
- Complete and rapid dechlorination of TCE through *cis*-1,2-DCE and VC to ethene can be achieved with the addition of HRC[™] or ethanol as the electron donors and bioaugmentation with KB-1[™].
- 5. Complete dechlorination of TCE to ethene appears possible with corn syrup and bioaugmentation with KB-1[™]; however, it occurs at slower and more variable rates than with HRC[™] or ethanol as electron donors. This may have been due to donor limitations which could not be determined conclusively with the analytical techniques applied herein.
- 6. Bioaugmentation with a lower target concentration of KB-1[™] at an earlier time in the study resulted in faster overall dechlorination to ethene than bioaugmentation with a higher target KB-1[™] concentration later in the study.
- 7. Increasing the target concentration of KB-1[™] had no consistent impact on dechlorination rates, possibly due to different inoculation times.
- 8. Methane production in the HRC[™] and ethanol treatments occurred during VC and/or ethene production, shortly after bioaugmentation with KB-1[™]. This was expected since KB-1[™] contains both dechlorinating and methanogenic populations². Methane levels greater than those of the chlorinated ethenes were reached only in the ethanol treatment due to a large excess of electron donor.

Based on the results of this study, it appears the use of HRC^{TM} or ethanol as electron donors and bioaugmentation with the KB-1TM culture is an effective remedial approach to reduce VOC concentrations in Site groundwater. Corn syrup may also be effective in conjunction with bioaugmentation with KB-1TM if slower dechlorination rates are acceptable at this Site, although further studies are recommended.

5. REFERENCES

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TABLES



FIGURES



APPENDIX A: Henry's Law Calculation



The following Henry's Law calculation was used to convert aqueous concentrations (Table 3A) to total mmoles of each analyte per microcosm bottle (Figures 1 to 5):

Total mmoles = $\frac{C_{liq} \times (V_{liq} + H \times V_{gas})}{Molecular Weight (mg/mmol)}$.

Where

$$\begin{split} &C_{liq} = liquid \text{ concentration (mg/L)} \\ &V_{liq} = liquid \text{ volume (0.18 L) per bottle} \\ &V_{gas} = \text{headspace volume (0.04 L) per bottle} \\ &H = \text{Henry's Law constant (dimensionless)} \end{split}$$

The Henry's Law constants used are summarized in the table below.

Analyte	Henry's Law Constant ^a (dimensionless)
Trichloroethene	0.48
cis-1,2-dichloroethene	0.31
Vinyl chloride	0.95
Ethene	8.76
Methane	27.2
Ethanol	0.00

^a Source: Montgomery, J.H. 2000. *Groundwater Chemicals Desk Reference, Third Edition.* CRC Press LLC, Boca Raton, FL.



APPENDIX B: SIREM Gene-Trac Report

Attachment 2

Certificate of Analysis: Quantitative Gene-Trac Dehalococcoides Assay



130 Research Lane, Suite 2 Guelph, Ontario N1G 5G3 Phone (519) 822-2265 Fax (519) 822-3151

Certificate of Analysis: Quantitative Gene-Trac Dehalococcoides Assay

Customer: S. Gregory/V.Madrid, LLNL Project: 3GIV Customer Reference: Not provided SiREM Reference: S-1462 Report Issued: 1-Dec-08 Data Files: QPCR-0412

Table 1: Test Results

Customer Sample ID	SiREM Sample ID	Sample Collection Date	Sample Matrix	Percent Dhc ^A	<i>Dehalococcoides</i> Enumeration ^B	
W-834-1825-GRBA	DHC-4531	11-Nov-08	Groundwater	18-44%	1 x 10 ¹⁰ /liter	

Notes:

Analyst:

^A Percent *Dehalococcoides* (Dhc) in microbial population. This value is calculated by dividing the number of Dhc 16S ribosomal ribonucleic acid (rRNA) gene copies by the total number of bacteria as estimated by the mass of DNA extracted from the sample. Range represents normal variation in Dhc enumeration.

^BBased on quantification of Dhc 16S rRNA gene copies. Dhc are generally reported to contain one 16S rRNA gene copy per cell; therefore, this number is often interpreted to represent the number of Dhc cells present in the sample.

J. Wilkinson

Jennifer Wilkinson Biotechnology Technologist

Jumena Druar

Ximena Druar, B.Sc. Molecular Biology Coordinator

Approved:



Table 2: Detailed Test Parameters, Gene-Trac Test Reference S-1462

Customer Sample ID	W-834-1825-GRBA
SiREM Sample ID	DHC-4531
Date Received	13-Nov-08
Sample Temperature	4.0 °C
Volume Used for DNA Extraction	25 mL
DNA Extraction Date	18-Nov-08
DNA Concentration in Sample (extractable)	100980 ng/L
PCR Amplifiable DNA	Detected
qPCR Date Analyzed	26-Nov-08
Laboratory Controls (see Table 3)	Passed
Comments	

Notes:

Refer to Table 3 for detailed results of controls.

ND = not detected

°C = degrees Celsius

PCR = polymerase chain reaction qPCR = quantitative PCR Dhc = *Dehalococcoides* ng/L = nanograms per liter mL = milliliters DNA = Deoxyribonucleic acid



Laboratory Control	Analysis Date	Control Description	Spiked Dhc 16S rRNA Gene Copies per Liter	Recovered Dhc 16S rRNA Gene Copies per Liter	Comments
Positive Control Low Concentration	26-Nov-08	qPCR with KB1 genomic DNA (CSLD-0054)	1.7 x 10 ⁶	1.1 x 10 ⁶	
Positive Control High Concentration	26-Nov-08	qPCR with KB1 genomic DNA (CSHD-0054)	1.7 x 10 ⁸	1.1 x 10 ⁸	
DNA Extraction Blank	26-Nov-08	DNA extraction sterile water (DB-0870)	0	ND	
Negative Control	26-Nov-08	Tris Reagent Blank	0	ND	

Notes:

Dhc = Dehalococcoides

DNA = Deoxyribonucleic acid

ND = not detected

qPCR = quantitative PCR

16S rRNA = 16S ribosomal ribonucleic acid

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Attachment 3

Summary of T2 Test Performance Data

Summary of T2 test performance data

•	
1) Overall trend	Pre-tracer test to present
2) Tracer test	Jan to Jun 2005
3) Biostimulation	Apr 2007 to Aug 2008
Post-bioaugmentation	Aug 2008 to present
	Pre-2005, if available / Most
	recent data (date posted,
5) Pre-test / Post-test data	otherwise 1st semester, 2011)

Well	Well Type	TVOC	TCE	Cis-1,2-DCE	Vinyl Chloride	Ethene	Ethane	Methane	NO3	Fe
Treatment Zone Wells							•		•	
W-834-1824	Injection	 Significant decrease, then slight rebound. Significant decrease due to dilution. Decrease, ranging from ND to 11.7 ug/L. Decrease to ND, then increase. TVOC = 23,100 / 169 µg/L. 	 Significant decrease, then slight rebound. Significant decrease due to dilution. Decrease, ranging from 7.2 to < 0.5 μg/L Decrease, ranging from 1.2 to < 0.5 μg/L, then increase. TCE = 23,000 / 100 μg/L. 	 Overall increase. Significant increase prior to biostimulation to 4,200 μg/L due to rodent. Significant decrease to < 0.5 μg/L. Increase to 54 μg/L. cis 1,2 DCE = 45 / 54 μg/L. 	 1) Overall increase. 2) None detected. 3) None detected. 4) Increase to 15 μg/L. 5) VC = <0.5 / 15 μg/L. 	 1) Overall increase. 2) None detected. 3) None detected. 4) Increase to 2.6 μg/L. 5) Ethene = No data / 2.6 μg/L. 	 Overall slight increase? None detected. None detected. Increase to 0.067 µg/L. Ethane = No data / 0.067 µg/L. 	 Overall significant increase. No data. No data Increase to 8,500 μg/L. Methane = No data / 8,500 μg/L. 	 1) Overall decrease. 2) Significant decrease due to dilution. 3) Remained low. 4) Remained low. 5) NO3 = 94 / < 1 mg/L. 	 1) Overall increase. 2) No significant change. 3) No significant change. 4) Significant increase. 5) Fe < 0.05 / 86 mg/L.
W-834-1825	Bioaugmentation	 Overall significant decrease. Some decrease due to dilution. No significant change. Significant decrease. TVOC = 16,000 / 24 μg/L. 	 Overall significant decrease. Some decrease due to dilution. No significant change. Significant decrease 69 μg/L. TCE = 16,000 / 8.3 μg/L 	 1) Overall significant increase, then decrease. 2) ND prior and during. 3) Significant increase to 1,200 μg/L. 4) Significant decrease to 5.3 μg/L. 5) cis 1.2 DCE < 30 / 5.3 μg/L. 	1) Increase, then decrease. 2) ND prior and during. 3) ND prior and during. 4) Increase to 71 μ g/L, then decrease. 5) VC = <0.5 / 10 μ g/L.	 1) Overall significant increase, then decrease. 2) No data. 3) Minor increase to 0.26 μg/L 4) Significant increase to 82 μg/L, then decrease. 5) Ethene = No data / 32 μg/L. 	 Slight increase, than decrease No data. Slight increase to 0.14 μg/L Slignt increase to 0.74 μg/L, then decrease. Ethane = No data / 0.052 μg/L. 	 1) Overall significant increase. 2) No data. 3) Increase to 2.4 μg/L. 4) Significant increase to 7,300 μg/L. 5) Methane = No data / 5,400 μg/L. 	 1) Overall significant decrease. 2) Some decrease due to dilution 3) Some decrease. 4) Significant decrease to ND. 5) NO3 = 83 / < 0.5 mg/L. 	 1) Overall slightly increase. 2) No significant change. 3) No significant change. 4) Significant increase to 1.4 mg/L. 5) Fe = < 0.05 / 1.4 mg/L.
W-834-T2	Performance Monitoring	 Significant decrease then rebound. Decrease due to dilution. Continue to decrease. Significant decrease to 33 ug/L, then significant rebound. TVOC = 30.059 / 3.906 ug/L 	 Significant decrease, then rebound. Decrease due to dilution. Continue to decrease. Significant decrease to 5 μg/L, then significant rebound. STCE = 30.000 / 1.100 μg/L. 	1) Overall increase. 2) Not detected. 3) Increase to 950 μ g/L. 4) Significant decrease to 10 μ g/L, then increase. 5) cis 1,2 DCE = <50 / 2,200 μ g/L.	 1) Overall increase. 2) Not detected. 3) Not detected. 4) Significant increase to 600 µg/L. 5) VC = <0.5 / 600 µg/L. 	 1) Overall increase. 2) No data. 3) Iincrease to 2.8 ug/L 4) Significant increase to 1,300 ug/L, then decrease. 5) Ethene = 0.22 / 410 μg/L. 	 1) Overall increase. 2) No data. 3) Increase to 0.88 μg/L. 4) Increase to 1.3 μg/L, then decrease. 5) Ethane = 0.15 / 0.84 μg/L. 	 1) Overall increase. 2) No data. 3) Significant increase to 2,300 µg/L. 4) Significant increase to 11,000 µg/L. 5) Methane = 0.15 / 11.000 µg/L. 	 1) Overall decrease. 2) No significant change. 3) No significant change. 4) Significant decrease to ND. 5) NO3 = 93 / < 1 mg/L. 	 1) Not detected. 2) Not detected. 3) Not detected. 4) Not detected. 5) Fe < 0.05 / < 0.2 mg/L.
W-834-1833	Performance Monitoring	 1) Overall decrease. 2) No significant change. 3) Some decrease. 4) Some decrease. 5) TVOC = 18,000 / 7,994 μg/L. 	 Overall slight decrease. No significant change. Some decrease. Some decrease. Some decrease. TCE = 18,000 / 7,900 μg/L. 	 Increase, then decrease. No significant change. Increase to 220 µg/L Increase to 1,400 µg/L, then decrease. cis 1,2 DCE < 30 / 78 µg/L. 	 1) Not detected. 2) Not detected. 3) Not detected. 4) Not detected. 5) VC < 0.5 /< 0.5 μg/L (Mar 2010). 	 1) Overall slight increase? 2) No data. 3) Increase to 0.15 ug/L 4) Increase to 0.73 ug/L 5) Ethene = No data / 0.22 µg/L 	 1) Overall slight increase? 2) No data. 3) Not detected. 4) Increase to 0.048 μg/L. 5) Ethane = No data / 0.025 μg/L. 	 Increase, then decrease. No data. No significant change. Increase to 50 ug/L, then decrease. Methane = No data / 0.83 µg/L. 	 1) Overall slight decrease. 2) No significant change. 3) No significant change. 4) Some decrease. 5) NO3= 78 / 48 mg/L. 	 1) Not detected. 2) Not detected. 3) Not detected. 4) Not detected. 5) Fe = No data / < 0.1 mg/L.
W-834-T2A	Performance Monitoring	 1) Overall slight decrease. 2) No significant change. 3) Slight decrease. 4) Slight decrease. 5) TVOC = 21,000 / 11,052 µg/L. 	 1) Overall slight decrease. 2) No significant change. 3) Slight decrease. 4) Slight decrease. 5) TCE = 21,000 / 11,000 µg/L. 	 Overall slight increase. No significant change. Slight increase. Increase to 120 μg/L. is 1,2 DCE = < 50 / 52 μg/L 	1) Not detected. 2) Not detected. 3) Not detected. 4) Not detected. 5) VC < 0.5 / <0.5 μg/L (Aug 2010).	 Slight increase? No data. Increase to 0.14 μg/L Increase to 0.57 μg/L Ethene = No data / 0.57 μg/L (Mar 2009). 	 Slight increase, then decrease No data. Increase to 0.029 µg/L Decrease to <0.025 µg/L Ethane = No data / <0.025 µg/L (Mar 2009). 	 ? 1) Overall increase. 2) No data. 3) Increase to 0.67 ug/L 4) Increase 370 ug/L 5) Methane = No data / 370 µg/L (Mar 2009). 	 1) Overall no change. 2) No significant change. 3) No significant change. 4) No significant change. 5) NO3 = 72 / 61 mg/L. 	1) Not detected. 2) Not detected. 3) Not detected. 4) Not detected. 5) Fe < 0.05 mg/L / No data?
W-834-T2D	Performance Monitoring	 1) Overall slight decrease. 2) No significant change. 3) Some decrease. 4) Some decrease. 5) TVOC = 12,041 / 7,400 μg/L. 	 1) Overall slight decrease. 2) No significant change. 3) Some decrease. 4) Some decrease. 5) TCE = 12,000 / 7,400 μg/L. 	1) Not detected. 2) Not detected. 3) Not detected. 4) Not detected. 5) cis 1,2 DCE <30 / < 0.5 μg/L	 1) Not detected. 2) Not detected. 3) Not detected. 4) Not detected. 5) VC < 0.5 / < 10 μg/L. 	 Slight increase? No data. Increase to 0.095 μg/L. No data. Ethene = No data / 0.095 μg/L (Mar 2007). 	 Slight increase? No data. Increase to 0.011 μg/L. No data. Ethane = No data / 0.011 μg/L (Mar 2007). 	 Slight increase? No data. Increase to 3 μg/L. No data. Ethene = No data / 3 μg/L (Mar 2007). 	 1) Overall no change. 2) No significant change. 3) No significant change. 4) No significant change. 5) NO3 = 89 / 110 mg/L. 	 1) Not detected. 2) No data. 3) Not detected. 4) Not detected. 5) Fe < 0.05 mg/L / No data?

						VFAs						
Well	Well Type	Mn	Sulfate	ORP	DO	Lactic Acid	Butyric Acid	Propionic Acid	Pyruvic Acid	Acetic Acid		
Treatment Zone Wells					· · · · · · · · · · · · · · · · · · ·	-			·			
W-834-1824	Injection	 1) Overall increase. 2) Significant increase from ND to 0.97 mg/L. 3) Moderate decrease to 0.05 mg/L. 4) Significant increase. 5) Mn = < 0.01 / 4.9 mg/L. 	 Overall decrease. Significant decrease from 82 mg/L to ND. Remained low to ND. Remained low to ND. SO4 = 78 / < 50 mg/L. 	 Overall decrease most likely due to rodent. Significant decrease from +110 to -89 mV one week after rodent. No data. No data. ORP = No data ? /-112 mV. (Jan 2006). 	1) No data. 2) No data. 3) No data. 4) No data. 5) No data.	 1) Overall increase. 2) No data. 3) No data. 4) Very significant increase. 5) Lactic Acid = No data / 180,000 mg/L. 	 Overall increase. No data. No data. Very significant increase. Butyric Acid = No data / 880 mg/L. 	 Overall increase. No data. No data. Very significant increase. Propionic Acid = No data / 6,800 mg/L. 	 Overall increase. No data. No data. Very significant increase. Pyruvic Acid = No data / 180 mg/L. 	 Overall increase. No data. No data. Very significant increase. Acetic Acid = 1.6 / 21,000 mg/L. 		
W-834-1825	Bioaugmentation	 Increase, then decrease. No significant change. No significant change. Significant increase to mg/L, then decrease. Mn = No data / 0.39 mg/L. 	 Overall decrease. No data. No data. Significant decrease to 20 mg/L. SO4 No data / < 20 mg/L. 	 Overall significant decrease. Decrease from 115 mV to 70 mV. Significant decrease to - 195 mV. Remained negative after bioaugmentation. ORP = + 200 / -367 mV. 	1) Overall decrease. 2) No data. 3) No data. 4) Decrease to 3 mg/L. 5) DO = 5.8 / 3 mg/L (Aug 2009).	 1) Overall increase. 2) No data. 3) Detected at 0.19 mg/L. 4) Significant increase after bioaugmentation to 140 mg/L, then decrease. 5) Lactic acid = 0.19 / 14 mg/L. 	 Increase then decrease. No data. Not detected. Significant increase to 2,500 mg/L, then decrease. Butyric acid = 0.05 mg/L. 	 Increase then decrease. No data. Not detected. Significant increase to 000 mg/L, then decrease. Propionic acid = 0.71 mg/L. 	 Increase then decrease. No data. Not detected. Significant increase to 64 mg/L then decrease. Pyruvic acid = 0.25 / 0.15 mg/L. 	 Increase then decrease. No data. Detected at 0.52 mg/L Significant increase 3 months after bioaugmentation to 4,900 mg/L. Acetic acid = 1.6 / 11 mg/L. 		
W-834-T2	Performance Monitoring	 1) Overall slight increase. 2) No significant change. 3) No significant change. 4) Increase to 0.84 mg/L. 5) Mn = < 0.01 / 0.62 mg/L. 	 Overall decrease. No significa change. Slight decrease. Significant decrease to ND. SO4 = 82 / 2 mg/L (Feb 2010). 	 Overall decrease. Significant decrease to 22 mV. 3) Significant decrease to 36.6 mV. 4) Continues to decrease. 5) ORP = -293 mV (Aug 2009). 	 1) Overall decrease. 2) No data. 3) Significant decrease to 0.06 mg/L. 4) Remained <1 mg/L. 5) DO = 7.9 / 0.53 mg/L (Aug 2009. 	 Overall slight increase, then decrease. No data. Not detected. Increase to 1.5 mg/L. Lactic acid = 0.89 mg/L. 	 Overall slight increase, then decrease. No data. Not detected. Increase to 0.16 mg/L. Butyric acid = < 0.5 / 0.5 mg/L. 	 Overall slight increase, then decrease. No data. Slight increase to 0.09 mg/L Increase to 3.8 mg/L, then decrease. Propionic acid = < 0.5 / 0.5 mg/L. 	 Overall slight increase, then decrease. No data. Not detected. Increase to 0.23 mg/L, then decrease. Pyruvic acid = < 0.15 / 1.5 mg/L. 	 Overall slight increase, then decrease. No data. Not detected. Increase to 0.76 mg/L, then decrease. Acetic acid = 1.5 / 0.7 mg/L. 		
W-834-1833	Performance Monitoring	 1) Overall slight increase, then decrease. 2) Not detected. 3) Not detected. 4) Increase to 0.048 mg/L. 5) Mn = No data / < 0.01 mg/L. 	 No significant change. No significant change. No significant change. No significant change. So4 = No data / 74 mg/L (Aug 2009). 	 1) Overall decrease. 2) Minor decrease to + 86 mV. 3) Moderate increase to +115 mV. 4) Significant decrease to -169 mV. 5) ORP = + 100 / -40 mV (Aug 2009). 	 Overall decrease. No data. Significant decrease to Impl. Remained low. DO = No data / 0.5 mg/L	 Overall increase. No data. Not detected. Slight increase to 3.2 mg/L. Lactic Acid = No data / 3.2 mg/L. 	 Overall slight increase, then decrease. No data. Not detected. Slight increase to 0.13 mg/L. Butyric = < 0.05 / 0.05 mg/L. 	1) Overall slight increase. 2) No data. 3) Not detected. 4) Slight increase to 0.64 mg/L 5) Propionic acid = < 0.5 / 0.64 mg/L.	 Overall slight increase, then decrease. No data. Not detected. Slight increase to 0.17 mg/L, then decrease. Pyruvic acid = No data / < 0.15 mg/L. 	 Overall slight increase. No data. Increase to 0.26 mg/L. Increase to 1.4 mg/L. Accetic acid = 1.3 / 0.2 mg/L. 		
W-834-T2A	Performance Monitoring	 1) Not detected. 2) Not detected. 3) Not detected. 4) Not detected. 5) Mn < 0.01 mg/L / No data? 	 No significant change. SO4 = 69 mg/L / No data? 	 Decrease, then increase. Decrease to 51 mV. No significant change. Significant decrease to -43 mV, then increase to 407 mV. ORP = +400 / +463 mV (Aug 2009). 	1) No data. 2) No data. 3) No data. 4) No data. 5) No data.	 Overall slight increase. No data. Not detected Increase to 0.12 mg/L Lactic acid = No data / 0.12 mg/L (Mar 2009). 	 Not detected. No data. Not detected. Not detected. Butryric acid No data / 0.5 mg/L (March 2009). 	1) Not detected. 2) No data. 3) Not detected. 4) Not detected. 5) Propionic acid = No data / < 0.05 mg/L.	 Overall slight indrease. No data. Not detected. Increases to 0.09 mg/L. Pyruvic acid = 0.09 mg/L. (Mar 2009). 	 Overall slight indrease. No data. Not detected. Increases to 1.3 mg/L. Acetic acid = 1.3 / 0.09 mg/L (Mar 2009). 		
W-834-T2D	Performance Monitoring	 1) Not detected. 2) No data. 3) Not detected. 4) Not detected. 5) Mn < 0.01 mg/L / No data? 	1) Overall no significant change. 2 No significant change. 3) No significant change. 4) No data. 5) SO4 = 70 / 78 mg/L (Dec 2007).	 Overall slight decrease. Decrease to +82 mV. No data. No data. ORP = No data / +68 mV (Aug 2006). 	1) No data. 2) No data. 3) No data. 4) No data. 5) No data.	 1) None detected. 2) No data. 3) None daetected. 4) No data. 5) Lactic acid = < 0.5 mg/L / No data. 	 None detected. No data. None daetected. No data. Butyric acid < 0.5 mg/L / No data. 	1) None detected. 2) No data. 3) None detected. 4) No data. 5) Propionic acid < 0.05 mg/L / No data.	 None detected. No data. None detected. No data. No data. Lactic acid < 0.15 mg/L / No data. 	 Slight increase No data. Increase to 1.1 mg/L. No data. Acetic acid = 1.1 mg/L / No data. 		

Well	Well Type	TVOC	TCE	Cis-1,2-DCE	Vinyl Chloride	Ethene	Ethane	Methane	<u>NO3</u>	Fe
Compliance Wells	•	•	•		•	•		•	•	•
W-834-2117	Tpsg Upgradient (Background)) 1) Overall decrease.	1) Overall decrease.	1) Not detected.	1) Not detected.	1) Slight increase.	1) Not detected.	1) Slight increase?	1) Overall slight decrease.	1) Not detected.
		2) Slight decrease.	2) Slight decrease.	2) Not detected.	2) Not detected.	2) No data.	2) No data.	2) No data.	2) Slight decrease.	2) Not detected.
		3) Slight decrease.	Slight decrease.	3) Not detected.	3) Not detected.	3) Increase to 0.13 ug/L	3) Not detected.	3) Increase to 1.9 µg/L.	Slight decrease.	3) Not detected.
		4) Slight decrease.	 Slight decrease. 	4) Not detected.	4) Not detected.	4) No data.	4) No data.	4) No data.	Slight decrease.	4) Not detected.
		5) TVOC = 16,169 / 7,810 µg/L.	5) TCE = 16,000 / 7,810 μg/L.	5) cis 1,2 DCE 81 / $< 0.5 \mu g/L$.	5) VC < 1 / < 0.5 μg/L	5) Ethene = No data / 0.13 μ g/L	5) Ethane = No data /	5) Methane = No data /	5) NO3 = 120 / 44 mg/L.	5) Fe < 0.1 / < 0.1 mg/L.
					(Feb 2010).	(Apr 2007).	< 0.10 µg/L (Apr 2007).	1.9 μg/L (Mar 2007).		
W-834-2118	Tpsg Downgradient					 Slight increase? 	1) Not detected.	 Slight increase? 		
		 Overall decrease. 	 Overall decrease. 	1) Not detected.	1) Not detected.	2) No data.	2) No data.	2) No data.	 No signficant change. 	1) Not detected.
		Slight decrease.	Slight decrease.	Not detected.	Not detected.	Increase to 0.58 µg/L.	Not detected.	Increase to 11 μg/L.	No signficant change.	2) No data.
		Slight decrease.	Slight decrease.	Not detected.	Not detected.	4) No data	4) No data.	4) No data	No signficant change.	Not detected.
		Slight decrease.	Slight decrease.	A) Not detected.	4) Not detected.	5) Ethene = No data / 0.58 µg/L	5) Ethene = No data /	5) Methane = 11 µg/L	4) No signficant change.	4) Not detected.
		5) TVOC = 230 / 173 μg/L.	5) TCE = 230 / 173 μg/L.	5) cis 1,2 < 0.5 / < 0.5 μg/L	5) VC < 0.5 / < 5 μg/L.	(Apr 2007)	< 0.025 µg/L (Apr 2007).	(Apr 2007).	5) NO3 = 110 / 120 mg/L	5) Fe < 0.1/ < 0.1 mg/L.
W-834-2119	Tps-Tnsc2				1) Not detected.	1) Slight increase?	1) Slight increase?	1) Slight increase?		
		1) Overall slight increase?	1) Overall slight increase?	1) Not detected.	Not detected.	2) No data.	2) No data.	2) No data.	 No signficant change. 	1) Not detected.
		Slight increase?	Slight increase?	Not detected.	Not detected.	Increase to 0.21 ug/L.	Increase to 0.097 ug/L.	Increase to 3 μg/L.	No signficant change.	2) No data.
		Slight increase?	Slight increase?	Not detected.	A) Not detected.	4) No data	4) No data.	4) No data.	No signficant change.	3) Not detected.
		4) No signidficant change.	No signidficant change.	4) Not detected.	5) VC < 0.5 / 0.5 μg/L	5) Ethene = No data / 0.21 µg/L	5) Ethane = No data $/0.097 \mu g/L$	5) Methane = No data / 3 µg/L	4) No signficant change.	4) Not detected.
		5) TVOC = 7,022 / 1,500 μg/L.	5) TCE = 7,000 / 1,500 μg/L.	5) cis 1,2 < 0.5 / 29 μg/L.	(Feb 2010).	(Apr 2007).	(Apr 2007).	(Apr 2007).	5) NO3 = 67 / 85 mg/L.	5) Fe < 0.1 / < 0.1 mg/L.
W-834-T1	UTnbs1	1) Not detected.	1) Not detected.	1) Not detected.	1) Not detected.	1) No data.	1) No data.	1) No data.	1) Not detected.	1) Not detected.
		2) Not detected.	2) Not detected.	2) Not detected.	2) Not detected.	2) No data.	2) No data.	2) No data.	2) Not detected.	2) Not detected.
		3) Not detected.	3) Not detected.	3) Not detected.	3) Not detected.	3) No data.	3) No data.	3) No data.	3) Not detected.	3) Not detected.
		4) Not detected.	4) Not detected.	4) Not detected.	4) Not detected.	4) No data.	4) No data.	4) No data.	4) Not detected.	4) Not detected.
		5) TVOC <0.5 / < 0.5 μg/L.	5) TCE <0.5 / < 0.5 µg/L.	5) cis 1,2 < 0.5 / < 0.5 μ g/L.	5) VC < 0.5 / < 0.5 μg/L.	5) No data.	5) No data.	5) No data.	5) NO3 <0.5 / <0.5 mg/L.	5) Fe < 0.05 /< 0.1 mg/L.
								VFAs		
Well	Well Type	Mn	Sulfate	ORP	DO	Lactic Acid	Butvric Acid	Propionic Acid	Pvruvic Acid	Acetic Acid
Compliance Wells										·
W-834-2117	Tosa Upgradient (Background)	1) Not detected.	1) Overall no significant	1) No data.	1) No data.	1) Slight increase?	1) Not detected.	1) Not detected.	1) Slight increase?	1) Slight increase?
·····		2) No data.	change.	2) No data.	2) No data.	2) No data.	2) No data.	2) No data.	2) No data.	2) No data.
		3) Not detected.	2) No data.	3) No data.	3) No data.	3) Slight increase.	3) Not detected.	3) Not detected.	3) Increase to 0.24 mg/L	3) Increase to 0.38 mg/L.
		4) Not detected.	3) No significant change.	4) No data.	4) No data.	4) No data.	4) No data.	4) No data.	4) No data.	4) No data.
		5) Mn < $0.03 / < 0.1 \text{ mg/L}$.	4) No significant change.	5) No data.	5) No data.	5) Lactic acid = $1.6 \text{ mg/L} / \text{No}$	5) Butyric acid < 0.5 mg/L / No	5) Propionic acid = $< 0.5 \text{ mg/L}$	(5) Pyruvic acid = 0.24 mg/L / No	5) Acetic acid = $0.38 \text{ mg/L} / \text{No}$
		, , ,	5) SO4 = 87 / 62 mg/L.	,		data.	data.	No data.	data.	data.
W-834-2118	Tosa Downgradient		, , , ,			1) Clight in groups 2	1) Not detected	1) Not detected	1) Not detected	
	i pog bonngi dalene	1) Not determined	1) No significant shares	1) N= d=t=	1) No. dot-	1) Slight Increase?	1) Not detected.	1) Not detected.	1) Not detected.	1) Net detected
		1) Not detected.	1) No significant change.	1) No data.	1) No data.		2) No data.	2) No data.	2) No data.	1) Not detected.
		2) No data.	2) No significant change.	2) No data.	2) No data.	3) Increase to 1.7 mg/L	3) Not detected.	3) Not detected	3) Not detected.	2) No data.
		3) Not detected.	3) No significant change.	3) No uala.	3) NO Udid.	(4) NO Udld. (5) Lestis Asid $= 1.7 \text{ mg/l}$ (Ne	4) NO Udid. E) Buturia acid $= < 0.5 mg/l / ($	4) NO Udld.	4) NO Udid.	(1) No. dete
		(4) Not detected.	4) NO significant change.	4) NO Udld.	4) NO Udid.	5) Lacue Aciu = 1.7 mg/L / No	S) Buturic acid = $< 0.5 \text{ mg/L}/$	S) Propionic aciu < 0.5 mg/L /	5) Pyruvic aciu < 0.5 mg/L / No	4) NO Udid.
		5) MIT < 0.03 / 0.097 Mg/L.	5 NO3 = 40 / 58 Mg/L.	5) NO UALA.	5) NO UALA.	uala.	No uala.	No data.	uala.	(5) ACELIC ACIU = < 0.5 / NO UALA.
W-834-2119	Ips-Insc2					1) Slight increase?	1) Not detected.	1) Not detected.	1) Slight increase?	1) Slight increase?
		1) Not detected.	1) No signficant change.	1) No data.	1) No data.	2) No data.	2) No data.	2) No data.	2) No data.	2) No data.
		2) No data.	No significant change.	2) No data.	2) No data.	3) Increase to 2.2 mg/L.	3) Not detected.	3) Not detected.	3) Increase to 0.24 mg/L.	3) Increase to 0.6 mg/L.
		3) Not detected.	No significant change.	3) No data.	3) No data.	4) No data.	4) No data.	4) No data.	4) No data.	4) No data.
		4) Not detected.	4) No significant change.	4) No data.	4) No data.	5) Lactic Acid = $2.2 \text{ mg/L} / \text{No}$	5) Butyric acid < 0.5 mg/L / No	5) Propionic acid < 0.5 mg/L /	5) Pyruvic Acid = $0.24 \text{ mg/L} / \text{No}$	5) Acetic Acid = $0.6 \text{ mg/L} / \text{No}$
		5) Mn < 0.03 / <0.1 mg/L.	5) SO4 = 130 / 52 mg/L.	5) No data.	5) No data.	data.	data.	No data.	data.	data.
W-834-T1	UTnbs1	1) Not detected.	1) No signficant change.	1) No data.	1) No data.	1) No data.	1) No data.	1) No data.	1) No data.	1) No data.
		2) No data.	2) No signficant change.	2) No data.	2) No data.	2) No data.	2) No data.	2) No data.	2) No data.	2) No data.
		3) Not detected.	3) No signficant change.	3) No data.	3) No data.	3) No data.	3) No data.	3) No data.	3) No data.	3) No data.
		4) Not detected.	4) No signficant change.	4) No data.	4) No data.	4) No data.	4) No data.	4) No data.	4) No data.	4) No data.
		/								

Attachment A

Building 834 Five-Year Review Inspection Checklist

Building 834 Five-Year Review Site Inspection Checklist Lawrence Livermore National Laboratory (LLNL) Site 300

I. SITE INFORMATION

Site Name: Building 834 Operable Unit (OU), LLNL Site 300

Date of inspection: March 30, 2010

Location and Region: Corral Hollow Road, San Joaquin/Alameda County, California

EPA Region: 9

EPA ID: CA 2890090002

Agency leading the Five-Year Review: U.S. Department of Energy (DOE) – Livermore Site Office (LSO)

Remedy Includes:

- Monitoring to evaluate the effectiveness of the remedial action in achieving cleanup standards.
- Risk and hazard management (including institutional and administrative controls) to prevent onsite workers exposure to volatile organic compounds (VOCs) volatilizing from subsurface soil and impacts to animals until risk and hazard is mitigated through active remediation.
- Extracting and treating soil vapor and ground water to mitigate risk and hazards posed by VOCs in the subsurface soil and reduce VOC, nitrate, and tetrabutyl orthosilicate/tetrakis (2-ethylbutyl) silane (TBOS/TKEBS) concentrations in ground water and VOCs in subsurface soil to cleanup standards.

II. INTERVIEWS

1. O&M Site Manager

Lawrence Livermore National Security (LLNS), LLC (M&O Contractor to DOE): Leslie Ferry, Site 300 Environmental Restoration (ER) Program Leader.

Remarks: As there is a full-time presence of the DOE-LSO Remedial Project Manager (RPM) and the LLNS Site 300 ER Program Leader, Site 300 ER Field Operations Manager, and the Building 834 treatment facility operator at the site, the

oversight, inspections, evaluations, and discussions of the Building 834 Operable Unit (OU) remedy are ongoing. Remedy performance, facility operations, and any related issues are managed in real-time in collaboration with the Field Operations Manager, the facility operator, and full-time staff from the Site 300 ER Field Operations, Hydrogeology, Engineering, Water Quality Sampling & Analysis Teams. As such, there was no single "interview" of DOE or LLNS O&M Managers or interview results that can be referenced. The information contained within this inspection checksheet is a compilation of this and other DOE-LSO RPM routine inspections, evaluations, and discussions with the LLNS Site 300 ER Program Leader and staff regarding the Building 834 remedy and treatment facility. In addition, DOE/LLNS presents and discusses any treatment facility operations and maintenance (O&M) or other remedy related issues with the regulatory agencies on an ongoing basis via monthly regulatory RPM project updates and meetings, and in the semi-annual and annual compliance monitoring reports.

2. O&M Staff

Lawrence Livermore National Security (LLNS), LLC (M&O Contractor to DOE):

- Steve Orloff, Site 300 ER Field Operations Manager.
- Todd Trammell, Operator Building 834 ground water and soil vapor extraction and treatment system.

Remarks: As there is a full-time presence of the DOE-LSO RPM, LLNS Site 300 ER Program Leader, Site 300 ER Field Operations Manager, and the Building 834 treatment facility operator at the site, the oversight, inspections, evaluations, and discussions of the Building 834 Operable Unit (OU) remedy are ongoing. Facility operations and any related issues are managed in real-time by the entities listed above in collaboration with full-time staff from the Site 300 ER Field Operations, Hydrogeology, Engineering, Water Quality Sampling & Analysis Teams. As such, there was no single "interview" of O&M staff or interview results that can be referenced. The information contained within this inspection checksheet is a compilation of this and other DOE-LSO RPM routine inspections, evaluations, and discussions regarding the Building 834 remedy and treatment facility.

3. Local regulatory authorities and response agencies (i.e., State and Tribal offices, emergency response office, police department, office of public health or environmental health, zoning office, recorder of deeds, or other city and county offices, etc.) Fill in all that apply.

Not applicable

III. ON-SITE DOCUMENTS & RECORDS VERIFIED

1. O&M Documents

O&M manual:	Readily available and up-to-date
As-built drawings:	Readily available and up-to-date
Maintenance logs:	Readily available and up-to-date

Remarks: As-built drawings for the Building 834 treatment facility are maintained in the LLNL Environmental Restoration Department files. The Building 834 treatment facility maintenance activities are recorded in a facility-specific logbook maintained by the facility operator. In addition, facility maintenance activities are discussed in monthly Project Updates submitted to the regulatory Remedial Project Managers (RPMs), at regular RPM meetings, and in the semi-annual and annual Site-Wide Compliance Monitoring Reports.

2. Site-Specific Health & Safety Plan

Site-Specific Health & Safety Plan: Contingency plan/emergency response plan: Readily available and up-to-date Readily available and up-to-date

Remarks: Site-specific health and safety information for Environmental Restoration activities is contained in the "Site Safety Plan for LLNL CERCLA Investigations at Site 300." Activity-specific hazards and controls are contained in the LLNL Environmental Restoration Integration Work Sheets. Activities conducted at LLNL Site 300 are also conducted in accordance with the LLNL Environment, Safety, and Health Plan.

The contingency plan, including contingency actions in the event of natural disasters or other emergencies, for the Building 834 remedial action is included in the "Compliance Monitoring Plan and Contingency Plan for the Environmental Restoration at LLNL Site 300."

Emergency responses are also contained in Volume II, Part 22 of the LLNL Environment, Safety, and Health Plan and the Self-Help Plans.

3. O&M and OSHA Training Records

Readily available and up-to-date

Remarks: Operation and maintenance activities associated with the Building 834 ground water and soil vapor extraction and treatment system are recorded and maintained in a facility-specific logbook maintained by the facility operator. In addition, O&M activities are discussed in monthly Project Updates submitted to the regulatory Remedial Project Managers (RPMs), at regular RPM meetings, and in the semi-annual and annual Site-Wide Compliance Monitoring Reports.

OSHA HAZWOPER training for LLNS ER Department staff are up-to-date. Training Records for LLNS ER Department staff are maintained electronically in the LLNL Laboratory Training Records and Information (LTRAIN) System.

4. Permits and Service Agreements

Air discharge permit: Effluent discharge permit: Waste Disposal: Other permits: Readily available and up-to-date Not applicable* Readily available and up-to-date Not applicable

Remarks:

Air discharge permit: The air permit to operate for the Building 834 soil vapor treatment system issued by the San Joaquin Valley Unified Air Pollution Control District is maintained at the Building 834 treatment facility, and in the files at Building 543.

*Effluent discharge – Effluent discharge limits are contained in the Substantive Requirements for Waste Discharge issued by the Regional Water Quality Control Board (RWQCB)-Central Valley Region and in the Site-Wide Record of Decision (ROD) for LLNL Site 300. The RWQCB Substantive Requirements and Site-Wide ROD are maintained in the administrative record at LLNL; the Site-Wide ROD is also available on-line at www-erd.llnl.gov/library/index.html

Waste Disposal: Spent treatment media is stored at a permitted onsite storage facility (EPA ID No CA2890090002) by the LLNL Radioactive and Hazardous Waste Department prior to shipment offsite to a permitted disposal facility.

Other permits: None

5. Gas Generation Records:	Not applicable
6. Settlement Monument Records:	Not applicable

7. Ground water Monitoring Records

Readily available and up-to-date

Remarks: Ground water monitoring records for the Building 834 Operable Unit are maintained in the LLNL ER Department's Taurus Environmental Information Management System (TEIMS) database. The ground water compliance monitoring results are presented in the semi-annual and annual Site-Wide Compliance Monitoring Reports that are sent to the U.S. EPA, the RWQCB, and the California Department of Toxic Substances Control (DTSC), and are available on-line at www-erd.llnl.gov/library/index.html

8. Leachate Extraction Records:

Not applicable

9. Discharge Compliance Records

Air: Water: Readily available and up-to-date Readily available and up-to-date

Remarks:

Air – Air discharge monitoring results for the Building 834 soil vapor treatment system are recorded in the Building 834 treatment facility logbook. The SJVUAPCD conducts annual inspections to ensure compliance with the air permit discharge requirements. The air permit compliance status is also reported in the monthly RPM Project Updates.

Water (effluent) – The Building 834 ground water treatment system effluent discharge compliance records are maintained in the LLNL ER Department's TEIMS data base, and are presented in the semi-annual and annual Site-Wide Compliance Monitoring Reports that are sent to the U.S. EPA, the RWQCB, and DTSC, and are available on-line at www-erd.llnl.gov/library/index.html

10. Daily Access/Security Logs:

Readily available and up-to-date

Remarks: The Building 834 treatment facility maintenance activities are recorded in a facility-specific logbook maintained by the facility operator. Site 300 is a restricted access facility and badging and clearance that must be presented to a security force guard is required to gain entry to the site.

IV. O&M COSTS

1. O&M Organization :

Contractor for Federal Facility: The Environmental Restoration Department of Lawrence Livermore National Security, LLC; the M&O contractor for the U.S. DOE at LLNL.

2. O&M Cost Records

Readily available and up-to-date Funding mechanism in place

Remarks: The actual annual costs for the Building 834 OU during the review period (2007-2011) are presented in Table 1 of the Five-Year Review. LLNS Environmental

Restoration Department provides monthly reports to the DOE-LSO RPM on Building 834 OU restoration planned and actual costs with explanations/justifications of any cost variances.

3. Unanticipated or Unusually High O&M Costs During the Review Period *Describe costs and reasons:* No unanticipated or unusually high O&M costs were incurred during the review period. As described in Table 1 of the Building 834 Five-Year Review, costs for the Building 834 OU were consistently under budget for the review period due to lower than expected operations, maintenance, and optimization costs.

V. ACCESS AND INSTITUTIONAL CONTROLS

A. Fencing

1. Fencing :

In good condition Gate secured Yes Yes

Remarks: LLNL Site 300 is a restricted access facility that is surrounded by fencing to prevent unauthorized access. In addition, the Building 834 treatment facility is located in a Q-clearance area that has additional fencing and can only be accessed by authorized personnel.

B. Other Access Restrictions

1. Signs and other security measures

Remarks: LLNL Site 300 is a restricted access facility that is surrounded by fencing and has a full-time security force to prevent unauthorized access to the site.

C. Institutional Controls (ICs)

1.	Implementation and enforcement	
	Site conditions imply ICs not properly implemented	No
	Site conditions imply ICs not being fully enforced	No

Frequency: Physical ICs are inspected annually. ICs are reviewed annually for adequacy and protectiveness. Responsible party/agency: U.S DOE Contact: Name: Claire Holtzapple Title[.] DOE-LSO Site 300 Environmental Restoration RPM Date: March 30, 2010 Phone No.: 925/422-0670 Reporting is up-to-date Yes Reports are verified by the lead agency: Yes Specific requirements in deed or decision document have been met: Yes Violations have been reported: No Other problems or suggestions: None

Remarks: Refer to Section 4.4. (Institutional Controls) of the Building 834 Five-Year Review for further details on institutional controls in the Building 834 OU.

2. Adequacy

ICs are adequate:

Type of monitoring:

Remarks: Refer to Section 4.4. (Institutional Controls) of the Building 834 Five-Year Review for further details on institutional controls in the Building 834 OU.

D. General

1. Vandalism/trespassing:

Remarks: LLNL Site 300 is a restricted access facility that is surrounded by fencing and has a full-time security force to prevent unauthorized access to the site.

2. Land use changes on site:

Remarks: There have been no changes in land, building, or ground water use in the Building 834 OU since the Interim Site-Wide Record of Decision and none are anticipated. The Building 834 Complex is still used for thermal cycling experiments and is accessible only to DOE/LLNL workers. Building 834D, where an unacceptable risk for VOC inhalation was identified, is still used only for storage and building occupancy restrictions remain in place. There are no onsite water supply

No vandalism evident

Yes

None

wells in use or planned near the OU. Refer to Section 3.2. (Land and Resource Use) of the Building 834 Five-Year Review for further details on institutional controls in the Building 834 OU.

3. Land use changes off site:

Remarks: Current offsite land use near the OU includes agriculture, private residences, and an ecological preserve. The nearest major population center (Tracy, California) is 8.5 miles to the northeast. While there is offsite development proposed adjacent to and north of Site 300 (the Tracy Hills Development), this development does not border the Building 834 OU. There is no known planned modification or proposed development of the offsite land adjacent to the OU. There are no private offsite water-supply wells in use or planned near the OU. Refer to Section 3.2. (Land and Resource Use) of the Building 834 OU.

VI. GENERAL SITE CONDITIONS

A. Roads:

1. Roads:

Remarks: The Building 834 treatment facility and wells are accessed by roads maintained by the LLNL Site 300 management.

B. Other Site Conditions

Remarks: The Building 834 treatment facility and wells are located in the Building 834 Complex Area that is maintained in good condition by the LLNL Site 300 management.

VII. LANDFILL COVERS:

VIII. VERTICAL BARRIER WALLS

IX. GROUND WATER/SURFACE WATER REMEDIES

Applicable

Adequate

Applicable

Not applicable

Not applicable

Not applicable

1.	Pumps, Wellhead Plumbing, and Electrical	
	Good condition:	Yes
	All required wells properly operating:	Yes

Remarks: All 13 ground water and soil vapor extraction wells are inspected weekly and are in good condition and operating properly. Photographs of a dual-phase extraction wellhead are included in Attachment A.

2. Extraction System Pipelines, Valves, Valve Boxes, and Other Appurtenances Good condition: Yes

Remarks: All extraction system pipelines and valves are inspected weekly and are in good condition. A photograph of the pipelines that convey extracted ground water and soil vapor from the wells to the treatment facilities is included in Attachment A.

3.	Spare Parts and Equipment	
	Readily available:	Yes
	Good condition:	Yes

Remarks: Spare parts for routine equipment maintenance are readily available and in good condition.

B.	Surface Water Collection Structures, Pumps, and Pipelines:	Not applicable
C.	Treatment System:	Applicable
1.	Treatment Train (check components that apply)	
	Metals removal:	N/A
	Air Stripping:	N/A
	Oil/Water separation:	X*
	Bioremediation:	N/A
	Carbon adsorbers:	Х
	Filters: Cuno particulate filters	Х
	Additive (e.g., chelation agent, flocculent):	N/A
	Good condition:	Х
	Sampling ports properly marked and functional:	Х
	Sampling/maintenance log displayed and up-to-date:	Х

Equipment properly identified: Quantity of ground water treated annually: Quantity of surface water treated annually: Quantity of soil vapor treated annually:

* Any floating silicone oil (TBOS) is removed from water stream using floating hydrocarbon adsorption devices.

** Quantities based on 2010 annual totals.

Remarks: Refer to Section 4.3 (System Operations/Operations and Maintenance of the Building 834 Five-Year Review for further details about the Building 834 ground water and soil vapor extraction and treatment system operations and maintenance. Photographs of the ground water and soil vapor treatment systems are included in Attachment A.

2. Electrical Enclosures and Panels (properly rated and functional) Good condition:

Remarks: The electrical control panel and enclosure are in good condition, properly rated, and functional.

3. Tanks, Vaults, Storage Vessels:

4. Discharge Structure and Appurtenances Good condition:

Remarks: The effluent from the Building 834 ground water treatment system is discharged via misting towers. The misting towers are in good condition and operating properly. A photograph of treatment facility effluent discharge structure is included in Attachment A.

5. Treatment Buildings:

6.	Monitoring Wells	
	Properly secured/locked:	Yes
	Functioning:	Yes
	Routinely sampled:	Yes
	Good condition:	Yes
	All required wells located:	Yes
	Needs maintenance:	None

Yes

Not applicable

Not applicable

Yes

Х

57,000 gallons**

Not applicable

20,000 scfm**

Remarks: The current Building 834 wellfield consists of 13 ground water and soil vapor extraction wells and 52 ground water monitor wells. In 2010, 27 ground water monitor wells had either insufficient water or were dry due to a low water table and therefore could not be sampled. (Water levels are measured in all wells quarterly.)

D. Monitoring Data

1. Monitoring Data	
Is routinely submitted on time:	Yes
Is of acceptable quality:	Yes

2. Monitoring data suggests:

Ground water plume is effectively contained:	Yes
Contaminant concentrations are declining:	Yes

Remarks: Refer to Section 7.5.2 (Ground Water Remediation Progress) of the Building 834 Five-Year Review for further details on the progress of the remedial action at the Building 834 OU in ground water and soil vapor cleanup.

E. Monitored Natural Attenuation:

Not applicable

X. OTHER REMEDIES

If there are remedies applied at the site which are not covered above, attach an inspection sheet describing the physical nature and condition of any facility associated with the remedy:

The wells from which soil vapor is extracted at Building 834 are dual-phase (ground water and soil vapor) extraction wells and the extracted soil vapor is treated using granular activated carbon. Therefore, the inspection of the soil vapor system is included in the checklist for the ground water extraction and treatment system in Section IX above.

XI. OVERALL OBSERVATIONS

A. Implementation of the Remedy

Begin with a brief statement of what the remedy is to accomplish (i.e., to contain contaminant plume, minimize infiltration and gas emission, etc.). Describe issues and observations relating to whether the remedy is effective and functioning as designed.

The remedy selected for the Building 834 OU is intended to contain contaminant sources, prevent further plume migration, remove contaminant mass from the subsurface, reduce contaminant concentrations in ground water to cleanup standards, and mitigate VOC inhalation risk to onsite workers. Refer to Section 4.1 (Remedy Section) for further details on the remedial action objectives of the Building 834 OU remedy.

The remedy at the Building 834 OU is effective, functioning as designed, and is protective of human health and the environment for the site's industrial land use. Refer to Section 8 (Technical Assessment) and Section 11 (Protectiveness Statement) of the Building 834 Five-Year Review for further details regarding the remedy effectiveness, functionality, and protectiveness.

No deficiencies in the remedy for the Building 834 OU were identified during this evaluation. Refer to Section 9 (Deficiencies) and Section 10 (Recommendations and Follow-up Actions) of the Building 834 Five-Year Review for further details regarding deficiency conclusions and recommendations for follow-up actions developed as part of the review process.

B. Adequacy of O&M

Describe issues and observations related to the implementation and scope of O&M procedures. In particular, discuss their relationship to the current and long-term protectiveness of the remedy.

There were no issues or observations related to the implementation and scope of operation and maintenance procedures for the Building 834 extraction and treatment facility.

C. Early Indicators of Potential Remedy Problems

Describe issues and observations such as unexpected changes in the cost or scope of O&M or a high frequency of unscheduled repairs, that suggest that the protectiveness of the remedy may be compromised in the future.

There were no issues or observations that suggest that the protectiveness of the remedy at the Building 834 OU may be compromised in the future. DOE's long-term plans include periodic assessments and upgrades to the Building 834 extraction and treatment system to ensure the effectiveness and protectiveness of the remedy.

D. Opportunities for Optimization

Describe possible opportunities for optimization in monitoring tasks or the operation of the remedy.

DOE identified the following opportunities to improve remedy performance:
- Monitor concentrations in Tps-Tnsc₂ HSU monitoring wells W-834-A1 and -2119. If concentrations remain stable or increase, consider installing extraction wells in the vicinity of these wells.
- Monitor concentrations in wells W-834-B4 and W-834-C5. If concentrations remain stable or increase, consider the installation of extraction wells in the vicinity of these two wells.

In addition, DOE will continue to evaluate alternate remedial technologies that could improve the long-term performance of the Building 834 remedy or shorten the cleanup time.

Refer to Section 10 (Recommendations and Follow-up Actions) in the Building 834 Five-Year Review for further details on DOE recommendations for remedy optimization.

Building 834 Operable Unit Five-Year Review Inspection Checklist

Ground water and soil vapor extraction and treatment system photographs



Dual-phase extraction wellhead

Separate pipelines convey soil vapor and ground water from the extraction wells to the treatment systems. Thirteen dual-phase wells extract contaminated soil vapor and ground water from the vadose zone and the Tpsg hydrostratigraphic unit.



Dual-phase extraction wellhead and soil vapor and ground water pipelines.

Building 834 Soil Vapor and Ground Water Extraction System



Misting towers

Treated ground water is then discharged via misting towers. Three 1,000 lb aqueous-phase granular activated carbon (GAC) are connected in-series to remove volatile organic compounds from extracted ground water to meet effluent discharge limits.



Building 834 Ground Water Treatment System



Eight 2,000 lb vapor-phase granular activated carbon (GAC) units are connected in-series to remove volatile organic compounds from extracted soil vapor. Soil vapor is treated to meet San Joaquin Valley Unified Air Pollution Control District permit limits and is then discharged to the atmosphere via a stack.



Building 834 Soil Vapor Treatment System



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