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Bioremediation Unit: *In Situ* Bioremediation of the Upper Aquifer

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Champion International Superfund Site, Libby, Montana Field Performance Evaluation Bioremediation Unit:

In Situ Bioremediation of the Upper Aquifer

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NOTICE

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Foreword

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet these mandates, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory is the Agency's center for investigation of technological and management approaches for reducing risks from threats to human health and the environment. The focus of the Laboratory's research program is on methods for the prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites and ground water; and prevention and control of indoor air pollution. The goal of this research effort is to catalyze development and implementation of innovative, cost-effective environmental technologies; develop scientific and engineering information needed by EPA to support regulatory and policy decisions; and provide technical support and information transfer to ensure effective implementation of environmental regulations and strategies.

The performance evaluation of in-situ bioremediation at the Champion International Superfund Site in Libby, Montana, was made possible by the Bioremediation Field Initiative established in 1990. Two objectives of the Initiative were to (1) more fully document the performance of full-scale bioremediation field applications in terms of treatment effectiveness, operational reliability, and cost; and (2) to disseminate this information to the public and private sectors. This project represents a significant cooperative effort between industry (Champion International), academia (Utah State University), and the Environmental Protection Agency. Results from this study provide valuable insight to the biodegradation of soil contaminants associated with wood preserving wastes and to the operation of land treatment systems.

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EXECUTIVE SUMMARY

The Office of Solid Waste and Emergency Response (OSWER) and the Office of Research and Development (ORD) of the U.S. Environmental Protection Agency (U.S. EPA) jointly established the Bioremediation Field Initiative (BFI) in 1990 as part of a strategy to develop bioremediation as an effective alternative remediation technology. The Initiative was designed to address the need for additional field experience concerning the implementation of bioremediation techniques, including the collection and dissemination of performance data from field experiences.

Specifically, the BFI has three primary objectives: (1) to document more fully the performance of full-scale bioremediation field applications in terms of treatment effectiveness and operational reliability; (2) to provide technical assistance to U.S. EPA and State remediation managers responsible for overseeing or considering use of bioremediation as a remedial alternative for hazardous waste sites; and (3) to develop biotreatability data bases, available through the U.S. EPA's Alternative Treatment Technology Information Center (ATTIC). This report focuses on Objective 1 by providing an evaluation of a full-scale field application of bioremediation at a specific site, the Champion International Superfund Site in Libby, Montana.

The Champion International Superfund Site, a former wood preserving facility in Libby, Montana (referred to as the Libby Site), was nominated by the Robert S. Kerr Environmental Research Laboratory (RSKERL), Ada, Oklahoma, as a candidate site for bioremediation performance evaluation. The potentially responsible party (PRP), Champion International, agreed to cooperate with the RSKERL and the Utah Water Research Laboratory (UWRL) of Utah State University (USU) in conducting the proposed bioremediation performance evaluation studies for biological treatment processes in operation at the Libby Site.

The Libby Site uses three distinct biological processes in the site remediation scenario: (1) surface soil biological treatment in a prepared-bed, lined land treatment unit (LTU); (2) aqueous phase treatment of extracted ground water in an above-grade, fixed-film bioreactor; and (3) *in situ* bioremediation of the Upper Aquifer. Results of the evaluation of *in situ* bioremediation of the Upper Aquifer are presented in this report.

Objectives of the evaluation of the *in situ* bioremediation in the Upper Aquifer in this BFIsponsored study were to: (1) describe and summarize previous and current remediation activities; (2) conduct a field evaluation to assess the performance of remediation activities with regard to removal of contaminants associated with the subsurface solid particles and oily materials; and (3) perform a laboratory evaluation to assess the microbial metabolic potential of subsurface aquifer materials to accomplish bioremediation of target chemicals under various management conditions.

With regard to the objectives of the evaluation of *in situ* bioremediation in the Upper Aquifer, conclusions included:

(1) With regard to objective 1: *describe and summarize previous and current remediation activities*, site characterization and remediation activities undertaken by the PRP indicated that concentrations of target chemicals in water in monitoring wells decreased in response to the addition of oxygen and nutrients that were added for the purpose of enhancing microbial activity. This evidence for *in situ* bioremediation was based upon field-scale pilot studies and demonstration studies conducted by the PRP.

As a result of site characterization activities, long-term sources of ground-water contamination were attributed to the presence of contaminants in aquifer nonaqueous phases that included sediments and nonaqueous phase liquids (NAPLs). Contamination occurred during the downward movement of

creosote, a dense nonaqueous phase liquid (DNAPL), through the Upper Aquifer sediments. NAPLs and sediments provide a continuous source of contaminants to the water phase through diffusion, desorption, and solubilization processes, and therefore represent a challenge for bioremediation of the Upper Aquifer.

The heterogeneous nature of the subsurface and preferential pathways for water through more permeable layers were indicated as a result of a field pilot-scale study undertaken by the PRP where one site responded to injection of hydrogen peroxide into the ground water by demonstrating reduced contaminant concentration at a downgradient monitoring well, while one site did not respond to treatment, as determined in a different downgradient monitoring well.

(2) With regard to objective 2 : *conduct a field evaluation to assess the performance of remediation activities with regard to removal of contaminants associated with the subsurface solid particles and oily materials*, field performance evaluation activities executed as part of this BFI study demonstrated that, with respect to the ground-water phase, total polycyclic aromatic hydrocarbon (TPAH) compounds and pentachlorophenol (PCP) were present at lower, nondetectable, concentrations in wells under the influence of the treatment injection system consisting of nutrients and hydrogen peroxide, while TPAH and PCP were present at higher concentrations in wells outside of the influence of the injection system. Therefore, treatment appears to have occurred in the water phase under the influence of the treatment injection system.

An evaluation of the water phase in monitoring wells located in contaminated and uncontaminated areas demonstrated the presence of reduced inorganic compounds, including ferrous iron and manganous manganese in both sets of wells. Concentrations of reduced chemicals were inversely related to dissolved oxygen concentrations. These chemicals may exert a demand on the oxygen supplied by the hydrogen peroxide. Although oxygen concentrations in several wells downgradient from the injection system exceeded 20 mg/L, the presence of reduced inorganic species that could be oxidized by the injected hydrogen peroxide has the potential to reduce the mass of injected hydrogen peroxide that is available for use by microorganisms.

With respect to the NAPL phase, both TPAH and PCP were found in the highest concentrations in the light nonaqueous phase liquids (LNAPLs), greater than 10,000 and 1,000 mg/L, respectively, than in any other phase at the Libby Site. These results indicated that there is contamination of the Upper Aquifer remaining in the form of a pure phase that represents significant potential contamination by transfer of contaminants from the NAPL phase to the water phase.

There was an observed difference between low levels of contaminants in monitoring well water and high levels in aquifer NAPL/sediment samples. TPAH and total petroleum hydrocarbons (TPH) were present within the NAPL/sediment associated phases of the aquifer under the influence of the treatment injection system at concentrations of 5 to 687 mg/Kg and 70 to 2,525 mg/Kg, respectively. PCP, the most water soluble contaminant, was present in the lowest concentrations (0.1 to 7.9 mg/Kg). The occurrance of the three contaminants together, PAH, PCP, and TPH was highly correlated. The heterogeneous distribution of TPAH, PCP, and TPH contaminants was consistent among all three boreholes evaluated from the water table to the deepest sampling point. NAPL/sediment phases are often expected to be more difficult to bioremediate *in situ* than the aqueous phase due to limitations of mass transport of oxygen and nutrients from the water phase to the nonaqueous phases that contain the target chemicals.

Because this project was initiated five years after pilot injection wells were installed, initial adsorbed contaminant concentrations before treatment were not available to compare with contaminant concentrations at the time of sampling. However, the detection of high concentrations of polycyclic aromatic

hydrocarbons (PAHs) and TPH associated with NAPL/sediment phases below the water table in the area of influence of the treatment (injection) wells after approximately three years (full-scale injection system) and five years (pilot injection wells) of treatment may indicate a lack of rapid response of parts of the site to the stimulation of *in situ* bioremediation. The delay in response is related to the nature of the source (NAPL and sediment) and the subsurface heterogeneity that provides areas of high conductivity and areas of low conductivity for water carrying nutrients and oxygen.

Information obtained through the field sampling conducted as part of this BFI study and through previous site characterization activities by the PRP demonstrates the vertical heterogeneous stratigraphy of the subsurface as well as the heterogeneous distribution of contaminants. This heterogeneous nature of the subsurface results in preferential pathways through permeable layers that may be responsible for carrying large volumes of injected water containing nutrients and oxygen. However, the permeable layers may not coincide with the layers containing the highest degree of contamination. In addition, even where subsurface areas are hydrodynamically connected and therefore received nutrients and oxygen from the injection system, the presence of immiscible NAPL in these areas results in the presence of NAPL-associated contaminants (TPAH, PCP, and TPH) that are less susceptible to injection system influence than contaminants in the water phase.

An evaluation of the gas phase in selected areas near an injection well used to introduce hydrogen peroxide and nutrients into the subsurface indicated that hydrogen peroxide was degassing and passing into the overlaying unsaturated zone. The concentrations of oxygen gas in the vadose zone pore space at 5 and 7 feet below ground surface (bgs) were 48 and 54 percent, respectively. This degassing represents an abiotic loss pathway for oxygen in the subsurface. Therefore, some of the hydrogen peroxide that is injected may not be available for microbial stimulation due to escape of peroxide into the vadose zone and the atmosphere, thus reducing the oxygen available for microbial utilization. Although oxygen concentrations in several wells downgradient from the injection system exceeded 20 mg/L, the degassing of hydrogen peroxide into the overlaying unsaturated zone acts to reduce the mass of injected hydrogen peroxide that is available for use by aquifer microorganisms.

An evaluation of *in situ* bioremediation activity in the water phase, by measuring oxygen utilization based upon differences in oxygen concentrations in injected and recovered water using a push (injection)/pull (recovery) test, was conducted. However, high flow rates (greater than 50 feet per day) prevented injected water from being naturally contained long enough for microbial activity to decrease the oxygen concentration of the injected water and for the water to be recovered for measurement. Therefore, the use of push/pull tests at this site for measuring subsurface microbial activity was not successful, due to site characteristics related to average high hydraulic conductivities and average high ground-water flow velocities.

(3) With regard to objective 3: *perform a laboratory evaluation to assess the microbial metabolic potential of subsurface aquifer materials to accomplish bioremediation of target chemicals under various conditions*, an evaluation of the microbial metabolic potential of aquifer samples indicated that aquifer materials contain indigenous microorganisms that have the ability to mineralize PAH compounds that can serve as a metabolic source of cell carbon, as indicated by the mineralization of the PAH compound, phenanthrene. There was no significant mineralization observed in poisoned aquifer samples. PCP mineralization, however, was insignificant (less than two percent) with results similar for non-poisoned and poisoned samples.

Chemical mass balance experiments for phenanthrene and PCP assisted in the evaluation of field results. Results demonstrated that up to 30 percent of phenanthrene was mineralized and up to 70 percent became incorporated into the aquifer matrix and was non-solvent extractable, while less than

six percent was volatilized. With regard to PCP, mineralization was less than two percent in all evaluations and incorporation into the aquifer matrix of up to 40 percent (non-solvent extractable) was lower than that observed for phenanthrene. Volatilization of PCP was less than two percent. Therefore significant mineralization and reaction with the solid phase aquifer matrix into non-solvent extractable residue was observed with phenanthrene, while little mineralization and some reaction with solid phase aquifer matrix into non-solvent extractable residue was observed with PCP.

Temperature, oxygen, and nutrient addition were evaluated, as potential management variables, with regard to effects on treatment of phenanthrene and PCP. In non-poisoned samples, temperature and oxygen influenced rate and extent of mineralization of phenanthrene. Addition of nutrients did not have a significant effect on rate or extent of mineralization of phenanthrene or PCP. An acclimation period was consistently indicated by the presence of a lag phase in the occurrence of mineralization. Mineralization of PAH compounds in the aquifer samples appears to be primarily related to biological processes and is influenced by temperature and oxygen levels.

Results of the laboratory evaluation provided information concerning major treatment pathways for phenanthrene and PCP within the aquifer material taken from the site. Major pathways for phenanthrene were biological mineralization and incorporation into aquifer material such that phenanthrene became non-extractable. The major pathway for PCP was incorporation into the aquifer material such that PCP became non-extractable. Biological processes were less evident with PCP transformation in aquifer samples and were more evident with phenanthrene transformation.

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Chapter 1
Introduction

1.0 Bioremediation Field Initiative

The Office of Solid Waste and Emergency Response (OSWER) and the Office of Research and Development (ORD) of the U.S. Environmental Protection Agency (U.S. EPA) jointly established the *Bioremediation Field Initiative* (BFI) in 1990 as part of a strategy to develop bioremediation as an effective alternative remediation technology. The BFI was designed to address the need for additional field experience concerning the implementation of bioremediation techniques, including the collection and dissemination of performance data from field experiences.

Specifically, the BFI has three primary objectives: (1) to document more fully the performance of full-scale bioremediation field applications in terms of treatment effectiveness and operational reliability; (2) to provide technical assistance to U.S. EPA and State remediation managers responsible for overseeing or considering use of bioremediation as a remedial alternative for hazardous waste sites; and (3) to develop biotreatability data bases that will be available through the U.S. EPA's Alternative Treatment Technology Information Center (ATTIC). This report focuses on Objective 1 by providing an evaluation of a full-scale field application of bioremediation at a specific site, the Champion International Superfund Site in Libby, Montana.

The first step in the implementation of Objective 1 of the BFI involved the identification of sites where bioremediation was currently being planned, demonstrated, or implemented as an alternative remediation technology. The Champion International Superfund Site, a former wood preserving facility in Libby, Montana (referred to as the Libby Site), was nominated by the Robert S. Kerr Environmental Research Center (RSKERC), Ada, Oklahoma, as a candidate site for bioremediation performance evaluation. The Libby Site was subsequently selected for study during implementation of the initial set of bioremediation field performance evaluations. The potentially responsible party (PRP), Champion International, agreed to cooperate with the RSKERC in conducting the proposed bioremediation performance evaluation studies for biological treatment processes in operation at the Libby Site.

The Libby Site uses three distinct biological processes in the site remediation scenario: (1) surface soil biological treatment in a prepared-bed, lined land treatment unit; (2) oil-water separation of extracted ground water, followed by aqueous phase treatment in an above-grade, fixed-film bioreactor; and (3) *in situ* bioremediation of the Upper Aquifer. Results of the evaluation of *in situ* bioremediation of the Upper Aquifer are presented in this report.

1.1 Project Objectives

Objectives of the evaluation of the *in situ* bioremediation of the Upper Aquifer in this BFIsponsored study were to: (1) describe and summarize previous and current remediation activities; (2) conduct a field evaluation to assess the performance of remediation activities with regard to removal of contaminants associated with the subsurface solid particles and oily materials; and (3) perform a radiolabeled chemical mass balance laboratory evaluation to assess the microbial metabolic potential of subsurface aquifer materials to accomplish bioremediation of target chemicals under different management conditions and to evaluate major fate mechanisms of target chemicals.

Chapter 2
Conclusions

2.0 Conclusions

With regard to the objectives of the evaluation of *in situ* bioremediation of the Upper Aquifer identified in Section 1.1, conclusions include:

(1) With regard to objective 1, described in Chapter 4: *describe and summarize previous and current remediation activities*, site characterization and remediation activities undertaken by the PRP indicated that some *in situ* bioremediation could be accomplished at the site. Evidence for *in situ* bioremediation was based upon field-scale pilot studies and demonstration studies conducted by the PRP. The conclusion that bioremediation was occurring was based upon information generated that indicated that concentrations of target chemicals in water from monitoring wells decreased in response to the addition of oxygen and nutrients that were added for the purpose of enhancing microbial activity.

As a result of site characterization activities, long-term sources of ground-water contamination were attributed to the presence of contaminants in aquifer nonaqueous phases, including nonaqueous phase liquids (NAPLs) and sediments. Contamination occurred during the downward movement of creosote, a dense nonaqueous phase liquid (DNAPL), through the Upper Aquifer sediments. NAPLs and sediments provide a continuous source of contaminants to the water phase through diffusion, desorption, and solubilization processes, and therefore represent a challenge for bioremediation of the Upper Aquifer.

The heterogeneous nature of the subsurface and preferential pathways for water flow through more permeable layers was indicated as a result of a field pilot-scale study undertaken by the PRP. One pilot-scale site responded to injection of hydrogen peroxide into the ground water by demonstrating reduced contaminant concentration at a downgradient monitoring well, while another site did not respond to treatment (Piotrowski, 1991), as determined in a different downgradient monitoring well. Results observed during a 1990 evaluation by the PRP showed several additional wells with persistent high oxygen and non-detectable dissolved contaminant concentrations (Piotrowski, 1991).

(2) With regard to objective 2, described in Chapter 5: *conduct a field evaluation to assess the performance of remediation activities with regard to removal of contaminants associated with the subsurface solid particles and oily materials*, field performance evaluation activities executed as part of this BFI study demonstrated that, with respect to the water phase, total polycyclic aromatic hydrocarbon (TPAH) compounds and pentachlorophenol (PCP) were present at lower concentrations in wells under the influence of the treatment injection system that included nutrients and hydrogen peroxide, while TPAH and PCP were present at higher concentrations in wells outside of the influence of the injection system. Therefore, treatment appears to have occurred in the water phase under the influence of the treatment injection system.

An evaluation of the water phase in monitoring wells located in contaminated and uncontaminated areas demonstrated the presence of reduced inorganic compounds, including ferrous iron and manganous manganese in both sets of wells. Concentrations of reduced chemicals were inversely related to dissolved oxygen concentrations. These chemicals may exert a demand on the oxygen supplied by the hydrogen peroxide and reduce the oxygen available for microbial utilization.

With respect to the NAPL phase, both TPAH and PCP were found in the highest concentrations in the LNAPL, greater than 10,000 and 1,000 mg/L, respectively, than in any other phase at the Libby Site. These results indicated that there is contamination of the Upper Aquifer remaining in the form of a NAPL phase that represents significant potential contamination by transfer of contaminants from the NAPL phase to the water phase.

There was an observed difference between low levels of contaminants in monitoring well water and high levels in aquifer NAPL/sediment samples. TPAH and total petroleum hydrocarbons (TPH) were present within the NAPL/sediment associated phases of the aquifer under the influence of the treatment injection system at concentrations of 5 to 687 mg/Kg and 70 to 2,525 mg/Kg, respectively. Pentachlorophenol (PCP), the most water soluble contaminant, was present in the lowest concentrations (0.1 to 7.9 mg/Kg). The heterogeneous distribution of TPAH, PCP, and TPH contaminants in the aquifer solid phase was consistent among all three borcholes evaluated from the water table to the deepest sampling point. NAPL/sediment phases are often expected to be more difficult to bioremediate *in situ* than the aqueous phase due to limitations of mass transport of oxygen and nutrients from the water phase to the nonaqueous phases that contain the target chemicals.

The detection of such high concentrations of TPAH and TPH associated with NAPL/sediment phases below the water table in the area of influence of the treatment (injection) wells after approximately five years of treatment indicates a lack of rapid response of the site to the stimulation of *in situ* bioremediation. The delay in response is related to the nature of the source (NAPL and sediment) and the subsurface heterogeneity that provides areas of high conductivity and areas of low conductivity for water carrying nutrients and oxygen.

Information obtained through the field sampling conducted as part of this BFI study and through previous site characterization activities by the PRP demonstrates the vertical heterogeneous stratigraphy of the subsurface as well as the heterogeneous distribution of contaminants. This heterogeneous nature of the subsurface results in preferential pathways through permeable layers that may be responsible for carrying large volumes of injected water containing nutrients and oxygen. However, the permeable layers may not coincide with the layers containing the highest degree of contamination. In addition, even where subsurface areas are hydrodynamically connected, and therefore received nutrients and oxygen from the injection system, the presence of immiscible NAPL in these areas results in the presence of NAPL associated contaminants (TPAH, PCP, and TPH) that are less susceptible to injection system influence than contaminants in the water phase.

An evaluation of the gas phase in selected areas near an injection well used to introduce hydrogen peroxide and nutrients into the subsurface indicated that hydrogen peroxide was degassing and passing into the overlaying unsaturated zone. The concentrations of oxygen in the soil gas in the vadose zone pore space at 5 and 7 feet below ground surface (bgs) were 48 and 54 percent, respectively. This degassing represents a pathway for abiotic loss of oxygen in the subsurface, thus reducing oxygen available for microbial utilization in the saturated zone.

An evaluation of *in situ* bioremediation activity in the water phase was conducted by measuring oxygen utilization as determined by differences in oxygen concentrations in injected and recovered water using a push (injection)/pull (recovery) test. However, high flow rates (greater than 50 feet per day) prevented injected water from being naturally contained long enough for microbial activity to decrease the oxygen concentration of the injected water and for the water to be recovered for measurement. Therefore, push/pull tests at this site were not successful for measuring subsurface microbial activity, due to site characteristics related to average high hydraulic conductivities and average high subsurface ground-water flow velocities.

(3) With regard to objective 3, described in Chapter 6: *perform a lradiollabeled chemical mass balance aboratory evaluation to assess the microbial metabolic potential of subsurface aquifer materials to accomplish bioremediation of target chemicals under various conditions and to evaluate majro fate mechanisms of target chemicals*, an evaluation of the microbial metabolic potential of aquifer samples indicated that aquifer materials contain indigenous microorganisms that have the ability to mineralize PAH compounds that can serve as a metabolic source of cell carbon, as indicated by the mineralization of the PAH compound, phenanthrene. There was no significant mineralization observed in poisoned aquifer samples. PCP mineralization, however, was insignificant (less than two percent) with results similar for nonpoisoned and poisoned samples.

Chemical mass balance experiments for phenanthrene and PCP assisted in the evaluation of field results. Results demonstrated that up to 30 percent of phenanthrene was mineralized and up to 70 percent became incorporated into the aquifer matrix and was non-solvent extractable, while less than six percent was volatilized. With regard to PCP, mineralization was less than two percent in all evaluations and incorporation into the aquifer matrix of up to 40 percent (non-solvent extractable) was lower than that observed for phenanthrene. Volatilization of PCP was less than two percent. Therefore significant mineralization and reaction with the solid phase aquifer matrix into non-solvent extractable residue was observed with phenanthrene, while little mineralization and some reaction with solid phase aquifer matrix into non-solvent extractable residue was observed with PCP.

Temperature, oxygen, and nutrient addition were evaluated with regard to their influence on the treatment of phenanthrene and PCP. In non-poisoned samples, temperature and oxygen influenced rate and extent of mineralization for phenanthrene. Addition of nutrients did not have a significant effect on rate or extent of mineralization of phenanthrene or PCP. An acclimation period was consistently indicated by the presence of a lag phase in the occurrence of mineralization. Therefore, mineralization of PAH compounds in the aquifer samples appears to be primarily related to biological processes.

Results of the radiolabeled chemical mass balance laboratory evaluation were used to demonstrate major treatment pathways for phenanthrene and PCP within the aquifer material taken from the site. The major treatment pathway for phenanthrene was biological degradation and incorporation into aquifer material. The major pathway for PCP was incorporation into the aquifer material. Biological processes were more evident with phenanthrene transformation than with PCP transformation.

Chapter 3
Recommendations

3.0 Recommendations

Based upon the information generated in the execution of the objectives of this evaluation of field-scale *in situ* bioremediation of ground water at the Libby Site, several recommendations are presented.

(1) Because the free product NAPL present in the subsurface may represent a long-term source of contamination to ground water, source removal technologies and techniques should be evaluated. Large sources as well as dispersed sources of NAPL within the aquifer should be identified. Areas with the largest masses of source material should be removed in order to enhance the efficiency and effectiveness of *in situ* bioremediation. Therefore, the use of a treatment train, which would include more emphasis on free product removal methods, in addition to the existing treatment technologies that include above-ground treatment of the water phase and *in situ* treatment of PAH compounds sorbed to the solid phase as well as treatment of residual saturation of PAH compounds in the soil pores, may be appropriate.

(2) Because hydrogen peroxide reacts with reduced iron to create highly oxidizing agents, (e.g., Fenton's reagent) the combination of chemical and biological treatment may be possible by optimizing the addition of ferrous iron and hydrogen peroxide to the subsurface. The chemical oxidation may transform residual NAPL to make it more bioavailable through oxidation processes that render the components more water soluble. Preliminary studies should be conducted to evaluate effectivenss and to identify the processes occurring in the reactions involving ferrous iron and hydrogen peroxide in the subsurface environment present of the Upper Aquifer.

(3) An evaluation of mixing effectiveness for hydrogen peroxide and nutrients within the subsurface should be conducted for the area under treatment, since field-scale sampling results indicate a heterogeneous stratigraphy with large differences in chemical contaminant concentrations with depth, and pilot-scale studies performed by the PRP indicated differential responses to the addition of hydrogen peroxide. Mixing effectiveness will be influenced by properties of the injected fluid (water) and properties of the aquifer, including stratigraphy and heterogeneity. Identification of areas where mixing is inadequate and where desorption and/or dissolution of contaminants result in threats to offsite contamination would indicate that management techniques should be developed to enhance mixing in those specific areas. Potential measures to enhance mixing include tighter well spacings and multiple vertically-oriented injection intervals.

(4) Based upon results obtained for solid and NAPL phases at the Libby Site, the Upper Aquifer solid phase and NAPL phase should be monitored to determine the effectiveness of treatment of PAHs and PCP at the site. Although determination of attainment of cleanup standards requires groundwater monitoring, solid phase and NAPL monitoring would help elucidate impacts of bioremediation on long-term groundwater quality. Characteristics of the water phase cannot be used to indicate the extent of a NAPL phase at this site.

(5) Reactions of reduced manganese, identified at the site, and hydrogen peroxide should be evaluated for their effect on target contaminants. Abiotic treatment may occur whereby reduced manganese, oxidized by hydrogen peroxide, reacts with PAH transformation products and PCP.

Chapter 4
Site Characteristics and Remediation Activities

4.0 BFI Study Objective 1: Previous and Current Remediation Activities

As part of the field performance evaluation of *in situ* bioremediation of the Upper Aquifer at the Libby Site, information concerning remediation activities was summarized in order to understand the purpose and design of the remedial system. However, Champion International operates the *in situ* bioremediation system in a dynamic capacity. To improve or optimize the system, modifications to system operations are implemented as required. Therefore, the activities and plans summarized here were current at the time of the study. Several of the operational procedures used at the time of the study have been changed. For example, hydrogen peroxide injection has been changed to injection of compressed oxygen gas.

4.1 Site Description, History and Extent of Contamination

The Libby Site is an active lumber mill located southeast of the town of Libby in northwest Montana (Figures 4.1 and 4.2) (Piotrowski, 1991). The site is located in an alluvial valley adjacent to the Kootenai River. Surface soils vary from clays to gravels. Due to alluvial processes and past glaciation, the stratigraphy beneath the site is complex, consisting of interbedded layers of highly coarse deposits with lenses and layers of lower permeability. The intermingled deposits include clays, silts, sands, gravels, cobbles, and boulders (Figure 4.3). The lateral extent of the deposits are usually limited. The deposits can typically be correlated from borehole to borehole in the subsurface over very short distances (Woodward-Clyde Consultants, 1990).

Two ground-water bearing units underlie the site (Piotrowski, 1991). The shallowest unit (referred to as the Upper Aquifer) extends approximately 12 to 70 feet bgs. The sediments are generally coarse-grained, composed of laterally discontinuous, interbedded sequences of gravel and sand, clayey gravels, and sand, silt and clay, and have few confining layers. The depth of the water table surface varies seasonally. Regional ground-water flow is primarily to the northwest, although the complex stratigraphy of the aquifer results in flow paths of variable directions on a micro-scale. The complex geology of the aquifer also results in broad ranges of aquifer characteristics such as transmissivity and conductivity. Transmissivities have been estimated as high as about 2,000,000 gallons per day per square foot (gpd/ft^2), based on pumping tests. Additional information on the Upper Aquifer is provided in Section 4.5 (see Figure 4.17).

Beneath the Upper Aquifer is a discontinuous, semi-permeable, fine-grained layer composed of clays, silts, fine sands, etc. that restricts, but does not preclude, vertical migration of ground-water (middle aquitard) (Piotrowski, 1991). The layer is approximately 30 feet thick and ranges from about 70 to 100 feet bgs. The second water-bearing unit (referred to as the Lower Aquifer) lies below the fine-grained layer and extends from 100 to approximately 180 feet bgs. Regional ground-water flow in this aquifer unit is to the north. This aquifer appears to be a more consolidated water-bearing unit than the Upper Aquifer.

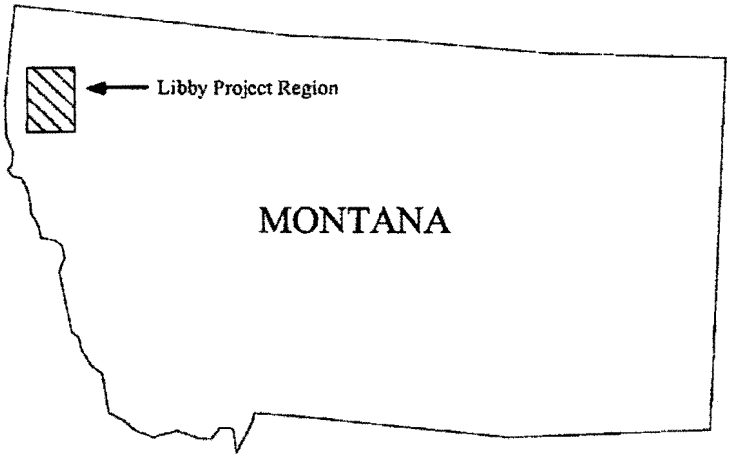


Figure 4.1. Location of Libby Project.

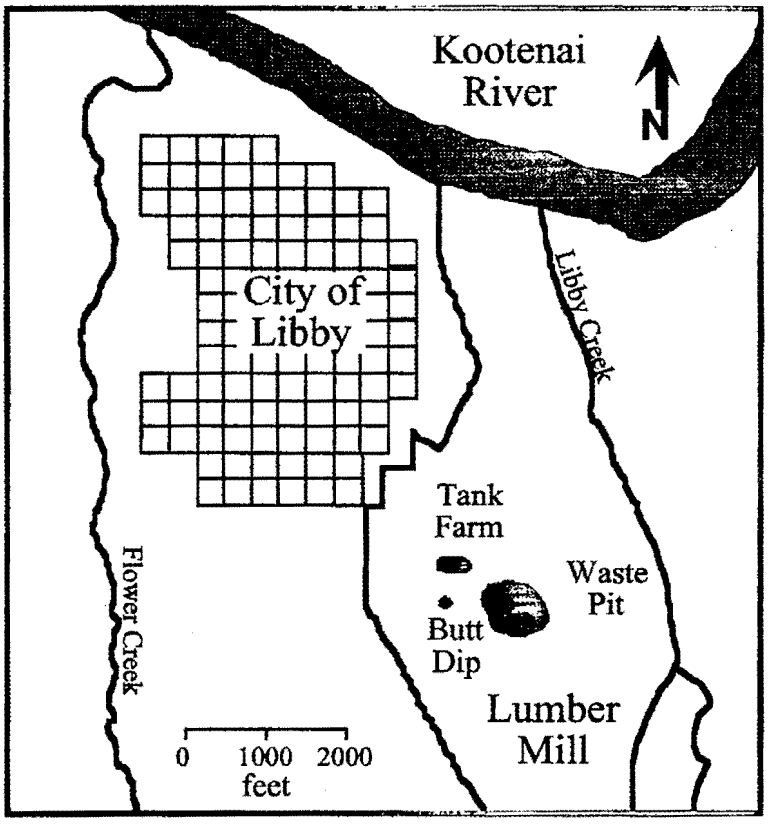


Figure 4.2. Libby Site

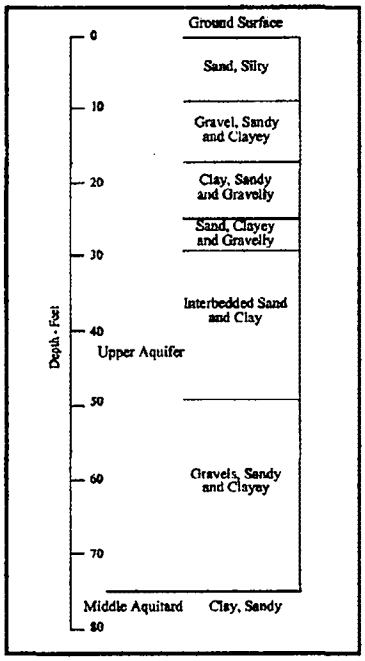


Figure 4.3. An Example of the Stratigraphy of the Upper Aquifer (Woodward-Clyde Consultants, 1990)

Wood preservative wastes (including creosote, PCP at 5 percent in a diesel fuel-like carrier, and waste sludges) were released into the soil environment at the site. Creosote is a complex mixture of over two hundred organic compounds derived from coal tar (McGinnis et al., 1991). Creosote consists primarily of neutral fractions containing single- to multiple-ring compounds. Tar acids, such as phenol and cresols, and tar bases, such as quinolines, pyridines, and acridines, constitute a small percentage of the total weight of creosote. Chemical and physical properties of specific creosote products are influenced by the characteristics of the tar from which it originates, the type of equipment used in the distillation process, and the particular process used for preserving wood.

Primary contaminants of concern in creosote are PAH compounds, which are found in the neutral fraction. PAH compounds consist of two or more fused benzene rings, with each ring sharing two carbon atoms. Sixteen PAH compounds have been designated as priority pollutants by the U.S. EPA due to their toxic, mutagenic, carcinogenic, teratogenic, and/or fetotoxic properties (40 Code of Federal Regulations (CFR) Part 423, Appendix A) and have also been listed as hazardous constituents by the U.S EPA (40 CFR Part 261, Appendix XIII and IX). Properties of these priority pollutant compounds are presented in Table 4.1. The major PAH compounds present in creosote include two-, three-, and four-ring compounds and their methyl derivatives (Sims et al., 1986). Creosote also contains smaller amounts of five- and six-ring PAH compounds.

Two- and three-ring PAH compounds can be utilized by soil microorganisms as sole carbon sources and are usually easily degraded (Sims and Overcash, 1983; Sims et al., 1986). PAH compounds with a greater number of rings are not known to be utilized as sole carbon sources but can be cometabolized with other organic compounds (Keck et al., 1989). Cometabolism involves concurrent metabolism of a carbon source capable of sustaining growth with a compound that the microorganism is unable to use as a sole source of energy.

Table 4.1 Properties of 16 Priority Pollutant PAH Compounds (Sims et al., 1986).

		Molecular Weight	Aqueous Solubility µg/L	Melting Point °C	Boiling Point °C	Vapor Pressure @ 20°C torr	Low K_{ow}	Length of Molecule A°	K_{oc}
1. Two Rings Naphthalene		128	31,700	80	218	4.92×10^{-2}	3.37	8.0	1,300
2. Three Rings Acenaphthylene		152	3,470	92	265	2.9×10^{-2}	4.07		
Acenaphthene		154	3,930	96	279	2.0×10^{-2}	4.33		
Fluorene		166	1,980	116	293	1.3×10^{-2}	4.18		
Anthracene		178	73	216	340	1.96×10^{-4}	4.45	10.5	2,600
Phenanthrene		178	1,290	101	340	6.80×10^{-4}	4.46	9.5	23,000
3. Four Rings Fluoranthene		202	260	111	—	6.0×10^{-6}	5.33	9.4	
Pyrene		202	135	149	360	6.85×10^{-7}	5.32	9.5	62,700 84,000

Table 4.1 (Continued)

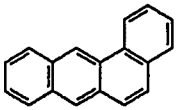
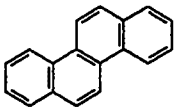
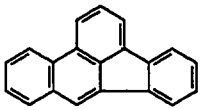
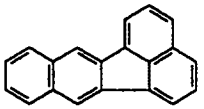
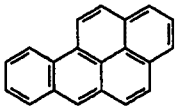
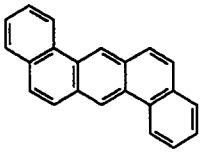
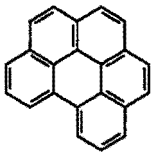
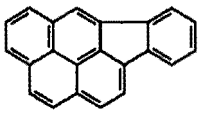
	Molecular Weight	Aqueous Solubility µg/L	Melting Point °C	Boiling Point °C	Vapor Pressure @ 20°C torr	Low K_{ow}	Length of Molecule A°	K_{oc}
Benz(a)anthracene 	228	14	158	400	5.0×10^{-9}	5.61	11.8	
Chrysene 	228	2	255	—	6.3×10^{-7}	5.61	11.8	
4. Five Ring  Benzo(b)fluoranthene	252	1.2	167	—	5.0×10^{-7}	6.57		
Benzo(k)fluoranthene 	252	0.55	217	480	5.0×10^{-7}	6.84		
Benzo(a)pyrene 	252	3.8	179	496	5.0×10^{-7}	6.04		4,510,651
Dibenz(a,h)anthracene 	278	2.49	262	—	1.0×10^{-10}	5.97	13.5	2,029,000

Table 4.1 (Continued)

	Molecular Weight	Aqueous Solubility µg/L	Melting Point °C	Boiling Point °C	Vapor Pressure @ 20°C torr	Low K_{ow}	Length of Molecule A°	K_{oc}
5. <u>Six Rings</u> Benzo(g,h,i)perylene 	276	0.26	222	—	1.0×10^{-10}	7.23		
Indeno(1,2,3-Cd)pyrene 	276	62	163	—	1.0×10^{-10}	7.66		

PAH compounds are nonionic, nonpolar compounds that do not ionize significantly in aqueous systems. Sorption of nonionic compounds is primarily a function of solubility. PAH compounds participate in hydrophobic sorption in a soil system, where the nonpolar PAH compounds partition out of the polar water phase onto hydrophobic surfaces of the soil matrix. Hydrophobic sites include fats,

Table 4.2. Physical Properties of PCP (McGinnis et al., 1991)

Property			Value	
Empirical formula			C_6Cl_5OH	
Molecular weight			255.36	
Melting point			190° C	
Boiling point			293° C	
Density			1.85 g/cm^3	
pK_A (25°C)			4.70 -4.80	
Partition coefficient (K_p), 25° C				
Octanol-water			1760	
Hexane-water			1.03×10^5	
Vapor pressure, torr (mm Hg)				
0° C			1.7×10^{-5}	
20° C			1.7×10^{-4}	
50° C			3.1×10^{-3}	
100° C			0.14	
200° C			25.6	
300° C			758.4	
Solubility in water (g/L)				
0° C			0.005	
20° C			0.014	
30° C			0.020	
50° C			0.035	
70° C			0.085	
Solubility in water (25C)*	pH	(mg/L) (Std Dev)		
	4.2		13.2	2.2
	5.0		21.6	1.5
	6.3		147	25
	7.7		1460	8
	9.0		8130	98
Solubility in organic solvents (g/100 g solvent)				
in methanol, 20° C			57	
in diethylether, 20° C			53	
in ethanol, 20° C			47	
in acetone, 20° C			21	
in xylene, 20° C			14	
in benzene, 20° C			11	
in carbon tetrachloride, 20° C			2	

* Data from A. Ramaprasad (1994)

waxes, and resins of the soil organic matter. The organic matter content of the soil or aquifer system is, therefore, more important in determining the extent of sorption of PAH compounds than substrate pH, cation exchange capacity, texture, or clay mineralogy (Means et al., 1979). Most PAH compounds tend to be nonvolatile, with acenaphthalene and naphthalene being the most volatile.

Technical-grade PCP (4% - 8%) dissolved in a diesel fuel-like carrier was also used as a wood preservative at the site. Physical properties of PCP are presented in Table 4.2. Technicalgrade PCP usually contains 85 to 90 percent PCP, while the remaining materials are 2,3,4,6tetrachlorophenol (4 to 8 percent), "higher chlorophenols" (2 to 6 percent), and chlorinated dioxins and furans (0.1 percent) (McGinnis et al., 1991). Tetrachlorophenol is added to PCP to increase the rate of solubilization, while the other compounds are formed as contaminant by-products during manufacture. PCP is manufactured from phenol using a catalytic chlorination process. PCP, a highly chlorinated, exceptionally toxic compound, has been listed as a 40 Code of Federal Regulations (CFR) Part 261, Appendix IX hazardous constituent by the U.S EPA; wastes containing PCP are classified as hazardous.

PCP is stable and considered to be chemically inert. Though the chlorinated ring structure of PCP increases its stability, the polar hydroxyl group facilitates biological degradation (Renberg, 1974; McGinnis et al., 1991). The transport of PCP is related to the pH of the environment, since the protonated (phenolic) form is practically insoluble in water, while monovalent alkali metal salts of PCP are soluble in water. The pK_a of PCP at 25° C is 4.7 to 4.8; therefore, sorption of PCP significantly increases with decreased pH. Greatest sorption occurs at a soil pH between 4.6 and 5.1. Little sorption occurs above a soil pH of 6.8, which is the near the pH of the Upper Aquifer at the Libby site, therefore PCP would be expected to be present in the water phase.

The wastes were released in three primary areas of the site: (1) an unlined waste pit that received waste sludges and other organic residues from wood-treating operations and wood preservative liquids that did not meet user specifications; (2) a former tank farm area that had been contaminated during chemical transfer operations; and (3) an unlined butt dip area, where wood preservatives were released directly to an unlined excavation and were used to treat the ends of telephone poles (Piotrowski, 1991). The quantities of wood preservatives released in each area were not recorded.

The released contaminants migrated downward through the soils from the source areas into the Upper Aquifer. LNAPLs spread out over the surface of the water table in the Upper Aquifer, were dispersed by ground-water flow, and are still present in some areas of the site (Piotrowski, 1991). DNAPLs moved down through the Upper Aquifer, passed through the more permeable regions of the fine-grained intervening layer, and entered the Lower Aquifer, where they may have accumulated in pools and/or began to migrate horizontally. During the downward movement of the DNAPLs, sediments in the Upper Aquifer, the fine-grained intervening layer, and the Lower Aquifer became contaminated by both sorption of organic compounds and residual saturation of the DNAPL (residual saturation describes the saturation level at which the DNAPLs become discontinuous and are immobilized by capillary forces within soil pores; the DNAPLs under low moisture conditions in the unsaturated zone may exist as a wetting fluid around the contact points of adjacent grains; under higher moisture conditions in the unsaturated zone and in the saturated zone, the DNAPLs may exist as isolated droplets in the open pores (Huling and Weaver, 1991). These sorbed and residual contaminants are serving as long-term sources of ground water contamination. A conceptual schematic of possible flow scenarios of the DNAPLs at the Libby Site, as illustrated in Figure 4.4, demonstrates the complexity of contamination at the site.

Ground-water flow in the Upper Aquifer distributed the wood-treating fluids downgradient from the points of release, and by 1986, the plume of contaminated ground water in the Upper Aquifer was about two kilometers long and encompassed 94 hectares (Piotrowski, 1991; Piotrowski and Doyle,

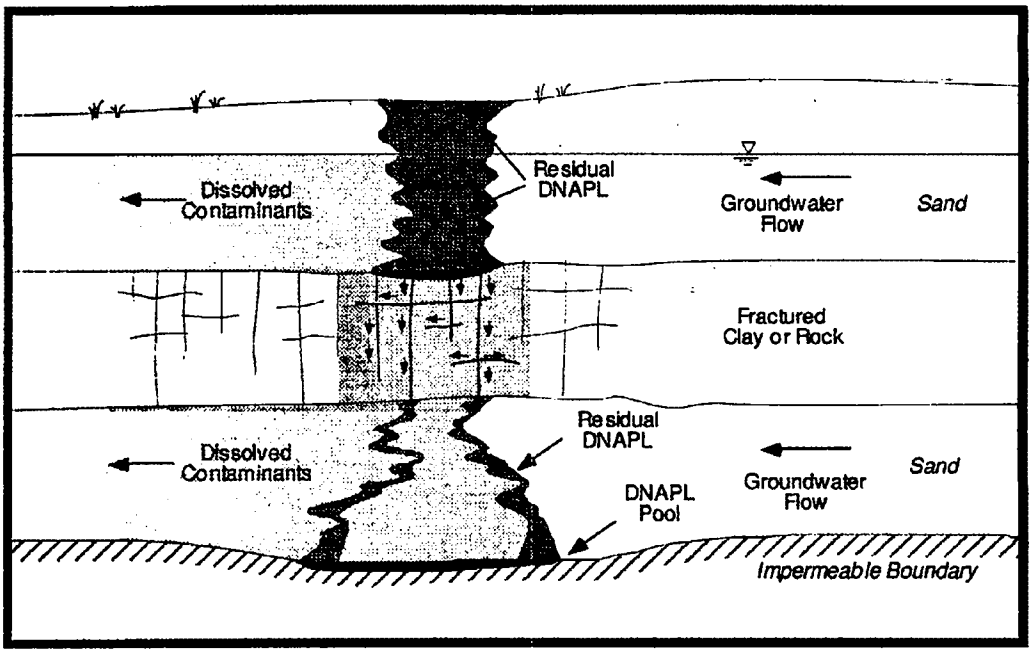


Figure 4.4. DNAPL Transport in the Subsurface (Huling and Weaver, 1991)

1990; Woodward-Clyde Consultants, 1986b). Contaminant concentrations in the Upper Aquifer groundwater plume range from percent levels in the waste pit area to partsper-billion (ppb) levels at the downgradient edge of the plume. The Upper Aquifer also contains mobile NAPL as well as residually-trapped NAPL.

Off-site, private drinking and irrigation wells became contaminated by the plume. Complaints by the residents of Libby with wells affected by the contamination led to an investigation by the U.S. EPA and placement of the site in 1983 on the National Priority List (NPL) for cleanup (Piotrowski, 1991). Remedial investigations were initiated and conducted through 1986 (Woodward-Clyde Consultants, 1986a,b). In 1985, the feasibility study (FS) process was initiated to evaluate remedial options for treatment of the site. During the FS process, on-site, feasibility studies were conducted that indicated that biological treatment could result in appreciable reductions in contaminants in the Upper Aquifer. These studies demonstrated that as ground water passed through the contaminated zone of the aquifer, the concentrations of dissolved oxygen and other electron acceptors (i.e., nitrate, nitrite, and sulfate) were reduced (Piotrowski and Doyle, 1990; Woodward-Clyde Consultants, 1986a, b). These observations suggested than the presence of contaminants in the Upper Aquifer was stimulating *in situ* biological activity. These results also suggested that lack of oxygen may have been limiting the microbial degradation of the wood preserving contaminants, since the major contaminants present were known to degrade more rapidly under oxic conditions than under anoxic conditions.

In 1986, a "Buy Water" plan was implemented in which Libby residents with contaminated wells were reimbursed for using municipally-supplied water in place of using contaminated water from their private wells. Also, there was a prohibition placed on new well installation within Libby City Limits. This plan was initially implemented by the owner of the lumber mill and the City of Libby in the spring

of 1986 and was later mandated by the U.S. EPA in the fall of 1986 (U.S. EPA, 1986a). The "Buy Water" plan resulted in the elimination of human exposure to the contaminated ground water. However, due to the potential risks associated with the contaminant plume and the potential for contamination of additional private off-site wells, target remedial (cleanup) levels and remedial plans for the Upper Aquifer were developed.

In 1988, following a pilot-scale study conducted in 1987-1988 (see Sec. 4.4), the U.S. EPA promulgated the *Record of Decision* (ROD) for the site that stipulated that *in situ* enhanced biological restoration would be used for treatment of the Upper Aquifer. The remedial action plan (RAP) for treatment of the site was prepared (Woodward-Clyde Consultants, 1989) and approved by the U.S. Department of Justice and the U.S. EPA in October 1989 by consent decree (Civil Action No. CV 89-127-M-CCL).

The extent of contamination in the Lower Aquifer is not as well understood as in the Upper Aquifer (U.S. EPA, 1990). There are no residential or irrigation wells in the Lower Aquifer downgradient from the site. A study has been initiated to assess the potential for bioremediation of the Lower Aquifer. A combined approach of bioremediation and oil recovery techniques will also be studied.

4.2 Target Remediation Levels

The final target remediation levels in the Upper Aquifer, as specified in the ROD (U.S. EPA, 1988), were defined as:

(1) 40 ng/L (part per trillion, or ppt) of total carcinogenic PAH compounds;
(2) 400 ng/L (ppt) of total PAH compounds;
(3) 1.05 mg/L of PCP;
(4) 5 mg/L of benzene;
(5) 50 mg/L of arsenic; and
(6) a human health threat of no greater than 10^{-5} for ground-water concentrations of other organic and/or inorganic compounds.

Existing U.S. EPA analytical methodology has limits of detection for total carcinogenic PAH compounds in ground water of greater than 1 part per billion (ppb). Therefore, the determination as to whether target remediation levels are being achieved is beyond the capability of existing accepted analytical methods. In addition, although background PAH levels in ground water at the site are generally below detection limits, whether these concentrations are also below remediation levels has not been established (Woodward-Clyde Consultants, 1990).

4.3 *Full-Scale System*

The objectives of the *in situ* bioremediation program are to achieve, to the fullest extent possible, removal of PCP and PAH compounds from the ground water in the Upper Aquifer. A combination of treatment technologies is being used to achieve this goal, including: (1) *in situ* bioremediation of the aquifer; and (2) extraction of contaminated ground water and treatment in an above-ground, fixed film bioreactor. An evaluation of the first technology is presented in this report; a second report is available that includes evaluation of the bioreactor system (Stevens et al., 1994). The objective of the bioreactor system is to recover and treat highly contaminated ground water associated with the waste pit source area so that subsequent *in situ* bioremediation of this area of the Upper Aquifer will result in more

efficient removal of residual contamination. The bioreactor system consists of three components: ground water extraction wells, ground-water bioreactor unit with equalization tank, and infiltration trench for reinjection of treated ground water (Woodward-Clyde Consultants, 1990).

Design of the full-scale *in situ* bioremediation system proposed for the site will be implemented and installed in a sequence of phases (Woodward-Clyde Consultants, 1990; Piotrowski, 1991). The initial phases of study included pilot-scale and demonstration studies. After the demonstration study, Phase I of the remedial activity was initiated. Design and implementation of Phase II will be initiated after information from Phase I concerning the performance of the injection wells and their effects on the aquifer is evaluated.

The variable nature of contamination at the site complicates the ability to remediate the site. Since aqueous phase contamination has been transported along tortuous pathways within the complex stratigraphy of the site, delivery of oxygen and nutrients to the contaminants is difficult to achieve. DNAPL contaminants are also likely to have sorbed to and/or formed areas of residual contamination in fine-grained strata; such areas are difficult to treat rapidly *in situ* because of the slow diffusion of nutrients and oxygen into areas of residual saturation. Because of these factors, the final design will be implemented in phases so that the ability of the system to degrade contamination in this heterogenous aquifer can be properly assessed and modified as necessary. A phased implementation should also allow for better design of the final system since additional data collected during the initial remedial actions can be used in the final design. Specific data that are being collected during the initial phases include: (1) interactions between adjacent injection wells; (2) long-term effectiveness of the *in situ* program; and (3) efficiency of the system to remediate low levels of PAH compounds.

The full-scale, *in situ* system was originally conceived to consist of three separate injection systems. The locations of the injection systems (illustrated in Figure 4.5) include: (1) the waste pit source area, which is at the head of the contaminant plume; this injection system (referred to as the source area or upgradient injection system) will be installed to treat the most heavily contaminated region of the Upper Aquifer; (2) in the vicinity of the existing pilot-scale system in an intermediate location (in the tank farm source area) in the contaminant plume (referred to as the intermediate injection system; this system was the primary focus of this BFI study, since it has been operated the longest and more data were available at the beginning of the study); and (3) along the downgradient boundary of the lumber mill site to treat off-site plume areas (referred to as the boundary injection system). The upgradient and intermediate systems are designed to remediate their respective source areas. The boundary injection system is located approximately 1,000 to 2,000 feet downgradient of the intermediate system and 1,000 to 2,000 feet upgradient from the boundary of the contaminated plume. At the time of this investigation, however, not enough information was available to elaborate on the Phase II remedial design with additional detail.

The effectiveness of the *in situ* bioremediation program will be assessed by periodic monitoring of the ground water through a network of monitoring wells (Woodward-Clyde, 1990). Each well will be monitored monthly for dissolved oxygen, water level, and temperature, and quarterly for PCP and PAH compounds during operation of the injection systems. The injection and extraction rates for each well will be measured weekly.

Each injection system consists or will consist of injection sites connected by subsurface piping for year-round use of surface water amendment facilities, which are currently used to add hydrogen peroxide and nutrients to the injection water. The addition of an oxygen source (*i.e.*,hydrogen peroxide) and nutrients is expected to stimulate biodegradation of PCP and PAH compounds in the ground water as well as those sorbed and trapped in the aquifer sediments. Each injection well has been or will be

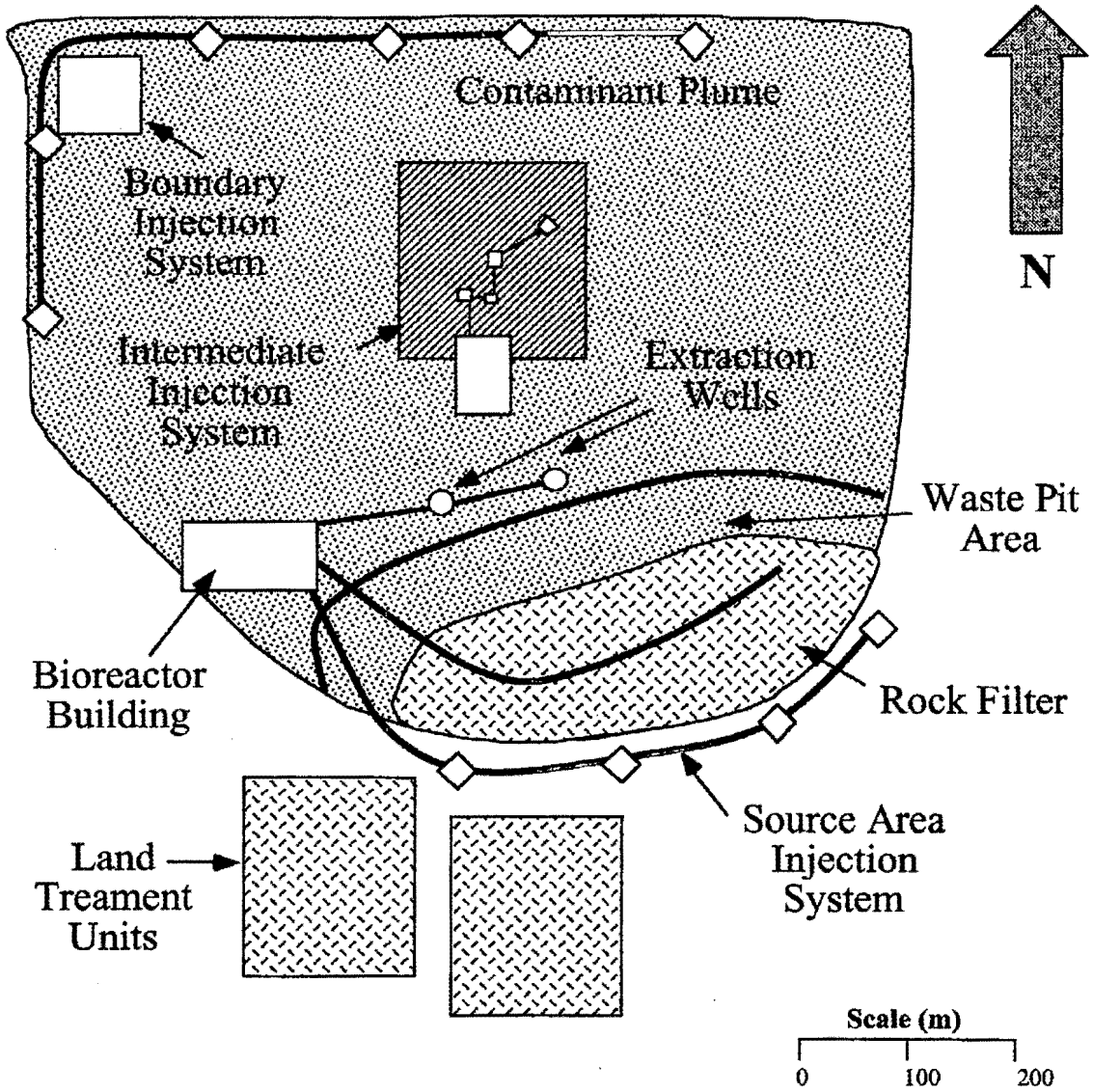


Figure 4.5. Source Area, Intermediate, and Boundary Injection Systems (Piotrowski, 1991).

completed and screened to a depth that fully penetrates the Upper Aquifer (Woodward-Clyde Consultants, 1990). The well screen is a 4-inch stainless steel (to withstand the corrosive effects of hydrogen peroxide) screen with 0.03 inch slots. Selection of the slot size was based on gradational analyses of the formation material. Above the well screen, 4inch steel casing is used to the ground surface. The sand pack for the wells is either a natural pack or an approximate 8 to 12 grade sand pack.

Each new injection well is tested before use (Woodward-Clyde Consultants, 1990). In addition, a bromide tracer test is performed in each new injection well. The test consists of injecting bromide in the injection well and monitoring the appearance of bromide in downgradient monitoring wells for approximately five days. These tests provide information concerning aquifer properties such as aquifer flow patterns and hydraulic properties that can be used in the design of Phase II injection systems.

The source of the injection water is the fire protection system for the facility, which includes the fire pond and water mains throughout the site. Injection water is filtered through a sand filter to remove particulate matter (solids greater than 0.45 mm in diameter) that could clog injection well screens. After filtering, hydrogen peroxide and nutrients are added to the water from storage tanks. The intermediate injection system operates at nearly 100 gallons per minute (gpm) and the boundary injection system operates at 245 gpm total. This injection rate is divided into the different injection wells within each system. Operational monitoring requirements include monthly measurements of water depth in injection wells (to check for clogging), periodic backwashing of sand filters, periodic recharging of the hydrogen peroxide and nutrient tanks, and routine visual inspections. If clogging of the injection wells does occur, high concentrations of hydrogen peroxide or low concentrations of acids will be added to remove accumulations of microorganisms or chemical precipitates that may have formed around the injection well screens.

The source area injection system will consist of injection sites located around the head of the contaminant plume (Figure 4.6) (Piotrowski, 1991). Hydrogen peroxide and nutrients will be added to the aquifer region that underlies the former waste pit area to stimulate biodegradation. When this area of the aquifer is remediated, the major source of ground-water contamination at the site will have been removed. No injection wells will be installed in this area during Phase I so that the ground-water flow in the area can be further investigated (Woodward-Clyde Consultants, 1990). This area has a complex flow pattern due to: (1) mounding from the fire pond, which can cause seasonal variations in the ground-water flow pattern; and (2) operation of the ground-water infiltration trench and extraction wells, which are a part of the bioreactor system for treatment of ground water. Monitoring of ground-water levels will be conducted during Phase I in order to characterize hydraulic head distribution and ground-water flow patterns in the area as affected by the infiltration trench and extraction wells. These data are required to define well placement, spacing, and flow rates so that oxygen and nutrients can be effectively delivered to this area of the Upper Aquifer during Phase II.

The injection sites of the intermediate and boundary injection systems will be located along transects that run perpendicular to the direction of regional ground-water flow (i.e., across the contaminant plume) (Piotrowski, 1991). In Phase I, the intermediate system will consist of all the wells used in the pilot-scale and demonstration studies (referred to as Well Nos. 3004, 3007, 9500, and 9501) (Figure 4.7). This system is designed to provide oxygen and nutrients to the middle part of the contaminated ground-water plume and to the tank farm area. In the intermediate injection system, hydrogen peroxide is used as the oxygen source. Approximately 50 gpm of hydrogen peroxide will be injected in the full-scale injection well and 10 to 40 gpm in the existing pilot-scale/demonstration study wells (Woodward-Clyde Consultants, 1990).

The monitoring wells to assess the performance of the intermediate injection system will consist of the wells used for the demonstration program as well as two new wells (Well Nos. 3038 and 3039). The location of the new wells was selected to provide data for determining the lateral and downgradient effects near the northeast end of the intermediate injection system.

The boundary injection system, designed to enhance degradation in the off-site portion of the contaminated ground-water plume, is located along the property boundary (Figure 4.8). Two injection wells are being installed during Phase I so that the effects of the *in situ* injection system in this area can

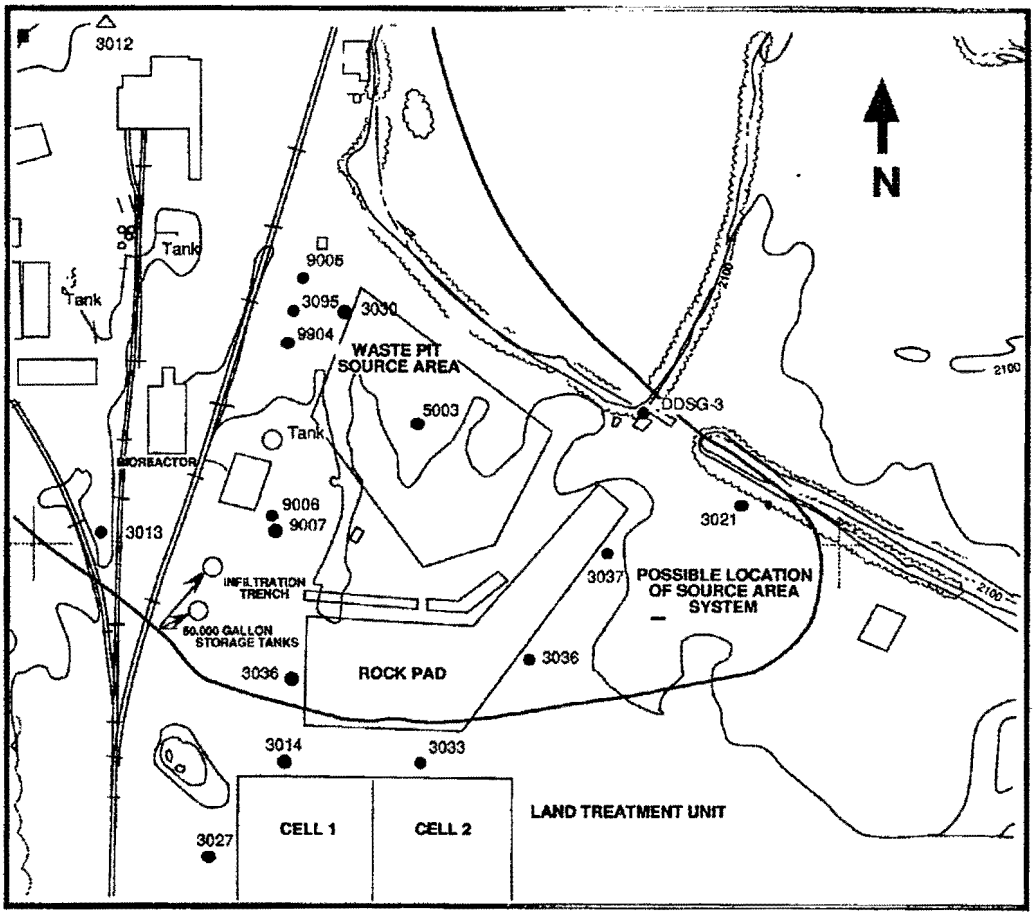


Figure 4.6. Source Area Injection System (Woodward-Clyde Consultants, 1990).

be better defined (Woodward-Clyde, 1990). Data collected during Phase I will be used to design the remaining part of the boundary injection system in Phase II. The use of an oxygen generator to provide oxygen (95 percent pure) will be investigated to determine if sufficient oxygen can be provided for microbial activity while reducing operational costs. The levels of contaminants in this region of the plume are relatively low compared to upgradient regions of the plume, and less oxygen may be required for remediation. Oxygen injection rates using the generator will be set to deliver oxygen concentrations of approximately 40 mg/L (WoodwardClyde Consultants, 1990). The injection wells will be operated at rates ranging from 50 to 100 gpm. These higher injection rates, as compared to the rates used in the intermediate injection system, were selected due to higher transmissivity estimated to exist in this area. The higher injection rates are required to affect the same area affected during the demonstration study.

The monitoring network for the boundary injection system during Phase I consists of onsite and offsite monitoring wells and privately owned offsite wells (Woodward-Clyde Consultants, 1990). Prior to initiating the injection program in this system, these monitoring wells will be sampled for PAH compounds, PCP, dissolved oxygen, and nutrient concentrations to establish baseline conditions.

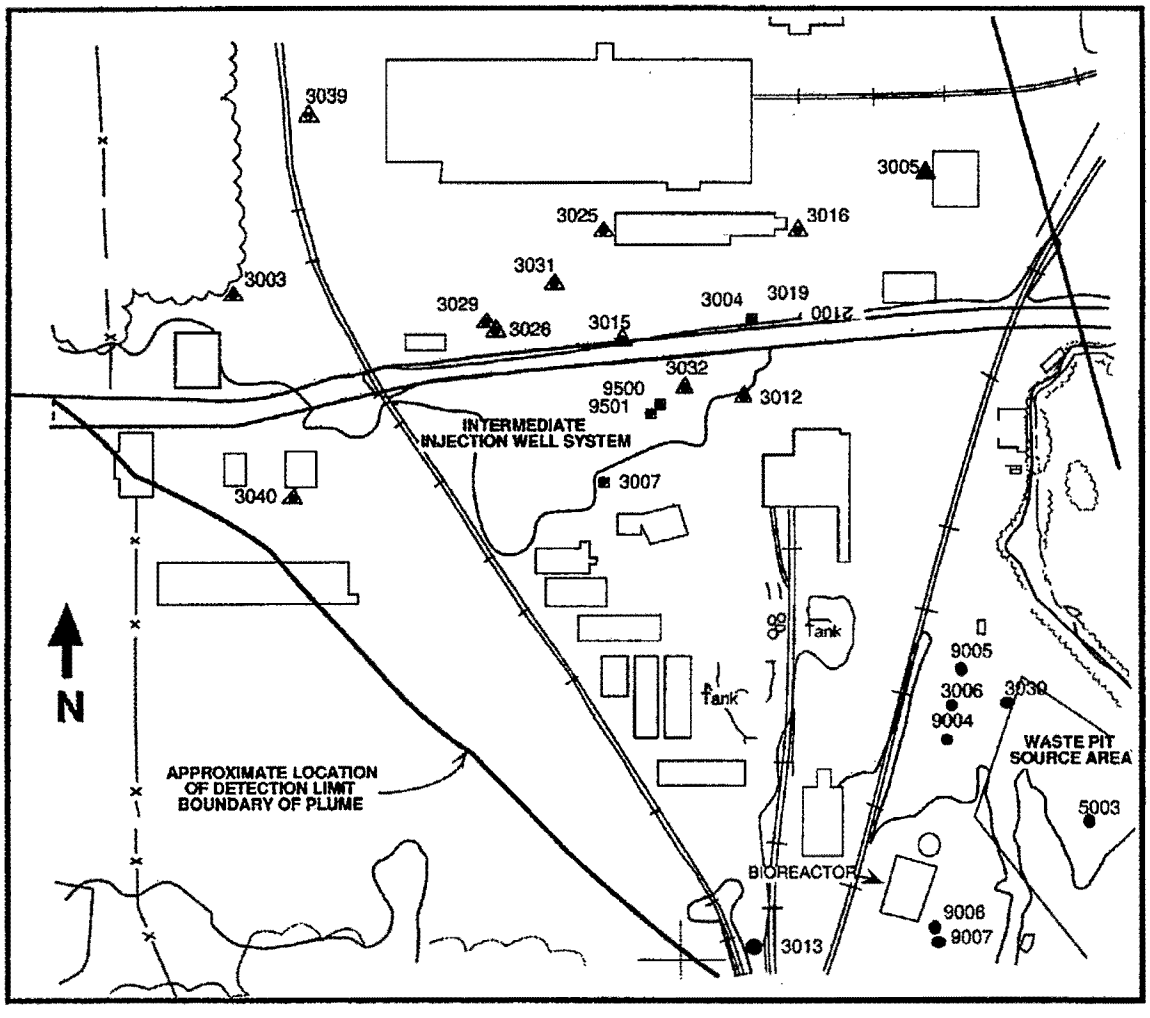


Figure 4.7. Intermediate Injection System (Woodward-Clyde Consultants, 1990).

Ideally, as injection of nutrients and an oxygen source continue in the injection areas and as contaminants are degraded, oxygen consumption rates in the immediate vicinity of the injection wells should decline, and zones of elevated dissolved oxygen (D.O.) (i.e., oxic zones) should form and extend further downgradient. The formation and expansion of the oxic zones produced at each injection site should eventually create elongated oxic zones in the Upper Aquifer that are perpendicular to the direction of regional ground-water flow (i.e., across the contaminant plume). These extended oxic zones should be biologically active zones that will result in the degradation of PCP and PAH compounds passing into the zones from upgradient aquifer regions (Piotrowski, 1991).

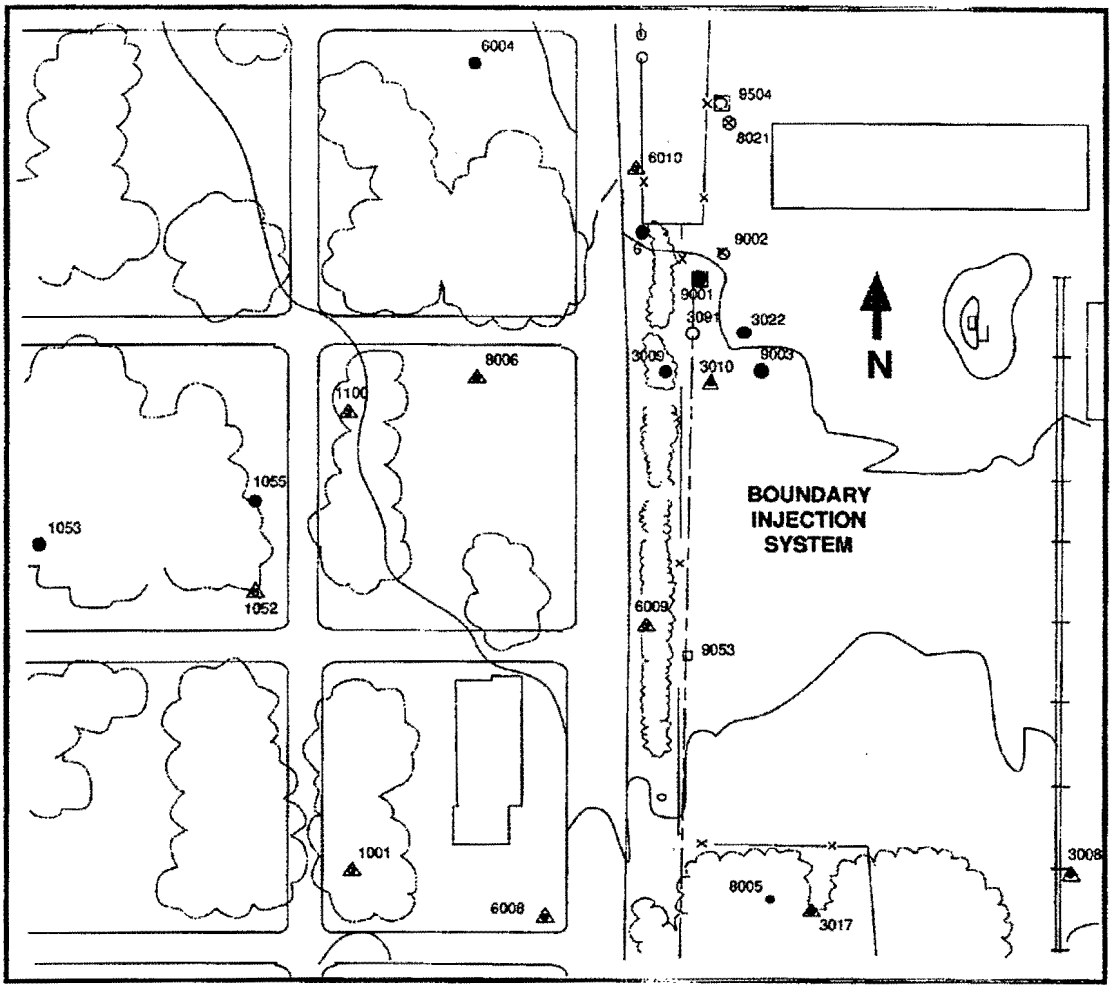


Figure 4.8. Boundary Injection System (Woodward-Clyde Consultants, 1990).

4.4 Pilot-Scale Study of the Intermediate Injection System

A pilot-scale *in situ* bioremediation system was designed and installed in July 1987 at the site of the intermediate injection system (Piotrowski, 1991). The study, using smaller injection wells and lower injection rates than those planned for full-scale operation, was conducted for over one year. A preliminary feasibility assessment had indicated that dissolved oxygen was a primary limiting factor for aerobic contaminant biodegradation within the aquifer. The pilot-scale study involved operation of an injection system to supply dissolved oxygen to the contaminated plume, located approximately 750 feet downgradient from the waste pit area.

Hydrogen peroxide (H_2O_2) was selected to serve as the oxygen source. Hydrogen peroxide decomposes to dissolved oxygen in the environment at a ratio of two peroxide molecules to one oxygen molecule. Some oxygen can be lost via Fenton's reaction and other oxidative processes that can be facilitated by the presence of H_2O_2. Hydrogen peroxide was injected into the aquifer at 100 mg/L, therefore, calculation indicates an oxygen concentration of approximately 50 mg/L in the groundwater ideally.

The pilot design utilized two injection sites (Well Nos. 3004 and 3007) located within the contaminant plume approximately 600 feet downgradient of the waste pit area (Figure 4.9). The two well sites were approximately 250 feet apart perpendicular to the direction of ground-water flow. Each site consisted of paired wells constructed so that water was injected at depths approximately 15 and 30 feet bgs in each well. The injection sites were connected by subsurface piping to an injection system that delivered filtered fire pond water containing hydrogen peroxide at a total flow rate of 40 gpm. Injection was conducted under atmospheric pressure and gravity.

Two 4-inch diameter monitoring wells (Well Nos. 3025 and 3026) were installed approximately 200 feet downgradient from the two injection sites. Each well had an extended vertical screen (15 or 20 feet in length) that was located at such depths as to sample the aquifer region under the influence of the injection system (i.e., the treatment zone). A monitoring well (Well No. 3012) located upgradient of the injection system was sampled to provide information on water quality characteristics of the ground water entering the treatment zone.

An initial bromide tracer study was conducted to evaluate ground-water flow conditions during operation of the injection system and to verify that the downgradient monitoring wells were hydraulically connected to the injection system (Piotrowski, 1991). Results of the tracer study indicated that the injection system produced a ground-water flow rate greater than 100 feet per day in the Upper Aquifer immediately downgradient from the injection system. In addition, the injected water was reaching the monitoring wells 200 feet downgradient in a period of less than two days.

Injection of the hydrogen peroxide began in July 1987. The three monitoring wells were purged and sampled bi-weekly for D.O. concentrations. Nutrient concentrations and total microbial densities were also measured periodically. For the first four months of the study, D.O. concentrations in the upgradient monitoring well and in the two downgradient monitoring wells remained below 1 mg/L (Piotrowski, 1991). Approximately 150 days after the initiation of the injection program, the D.O. concentrations in one of the primary downgradient monitoring wells initially increased to approximately 12 mg/L and continued to increase and remain between 15 and 20 mg/L for over one year. These results suggested that injection of the hydrogen peroxide solution created a zone of elevated D.O. (an oxic zone) within the contaminant plume that extended at least 200 feet downgradient from one of the injection sites (Figure 4.10). At oxygen breakthrough, however, there still may exist flow paths between injection and extraction wells that are not receiving proportional groundwater and oxygen.

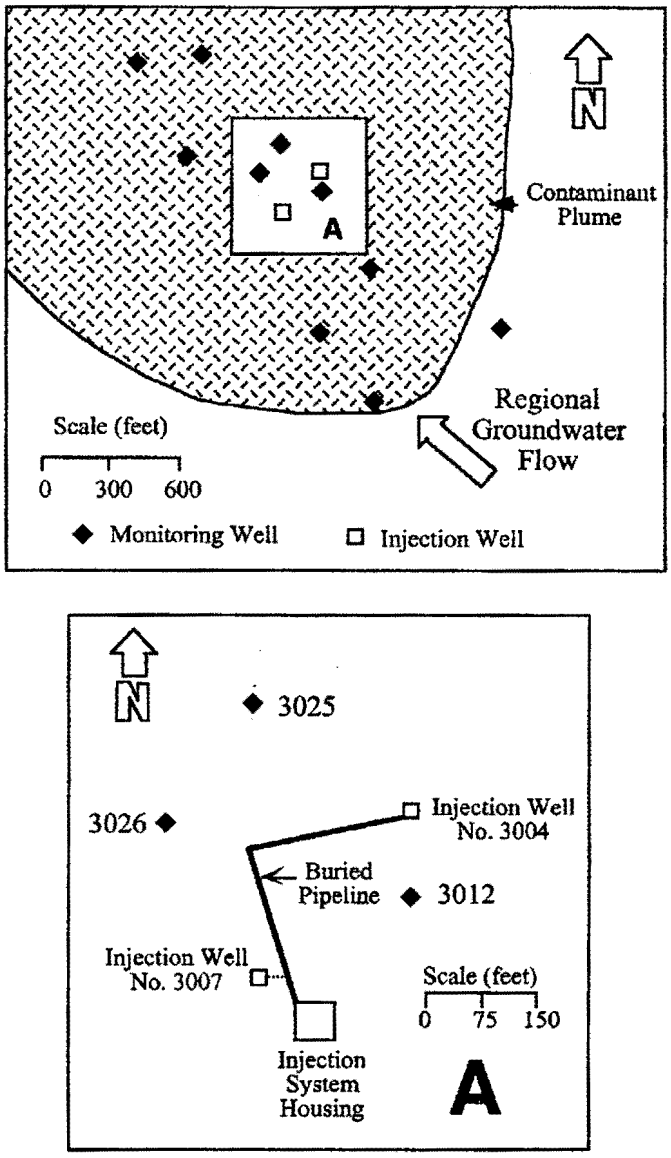


Figure 4.9. Pilot-Scale Injection System in the Intermediate Injection Area (Piotrowski, 1991).

Ground-water samples collected from within this zone indicated lower concentrations of total hydrocarbon contaminants compared to the untreated region of the contaminant plume. During the first four months of the study, PAH and PCP concentrations were similar to levels observed in the upgradient control well (greater than 1000 mg/L total contaminant concentration (Piotrowski, 1989). However, once the D.O. concentration in the monitoring well increased, dissolved contaminant concentrations decreased to less than 20 mg/L. Contaminant concentrations continued to decrease so that 454 days after hydrogen peroxide injection, PAH compounds were not detectable in a sample collected from the monitoring well with increased D.O. levels, while the PCP concentration was 1 mg/L. How-

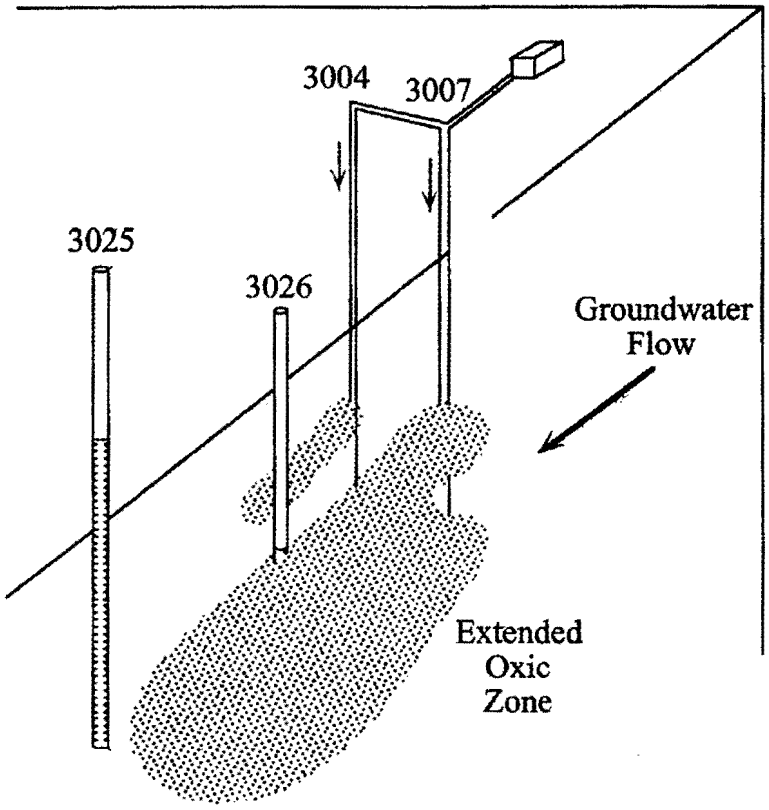


Figure 4.10. Development of an Oxic Zone in the Intermediate Area during the Pilot-Scale study (Piotrowski, 1991).

ever, only one of the two monitoring wells exhibited oxygen breakthrough and produced ground-water samples containing reduced contaminant concentrations, indicating that the subsurface influence of the injection system varied across the treatment zone in the Upper Aquifer. Preferential pathways through permeable layers may be responsible for carrying relatively large volumes of injected water, but the permeable layers may not coincide with the layers with the highest degree of contamination.

4.5 Demonstration Study

A demonstration program for remediation of the Upper Aquifer using full-scale injection wells (in contrast to the smaller wells used in the pilot-scale study) was designed, constructed, and operated from January to June, 1990. Because the stratigraphy of the site is complex and the hydraulic characteristics of the Upper Aquifer vary considerably over short distances, the demonstration program was conducted to gain additional information on full-scale system performance for enhancing biodegradation and to evaluate the operational performance of the injection system before implementation of full-scale operations in Phase I (Piotrowski, 1991). Data obtained from the demonstration program were

used to: (1) further evaluate the effectiveness of the injection of an oxygen source into the Upper Aquifer; (2) investigate the potential for the addition of a nutrient injection program to further enhance subsurface microbial activities; (3) acquire more information on the zone of influence of the full-scale injection wells to use in final design; and (4) gain more knowledge about the operational components of the system (WoodwardClyde Consultants, 1990).

For the demonstration study, one full-scale injection system was installed at a location in the intermediate injection system area midway between the two injection sites used in the pilot-scale study (Piotrowski, 1991). The location was selected to be near the center of the contaminated ground-water plume, in proximity to several downgradient monitoring wells, and close to the injection building, where the hydrogen peroxide and nutrients are mixed with the injection water. The site consisted of two adjacent injection wells (Well Nos. 9500 and 9501) (Figures 4.7 and 4.11), each 4 inches in diameter with a 20 foot wire-wrap screen section. Well No. 9500 was installed with a screen interval of 45 to 65 feet bgs in an interval where the sediments have moderate permeability (Figure 4.12). Well No. 9501 was screened at a shallower depth, with its screen interval at depths ranging from 18 to 38 feet bgs in sediments that have higher permeabilities than those in Well No. 9500 (Figure 4.13). These depths were selected to distribute the injected water across the thickness of the Upper Aquifer so that oxygen and nutrients could be applied evenly over the Upper Aquifer zone. The two existing pilot-scale injection wells (Well Nos. 3004 and 3007) were not used during the demonstration study since the purpose

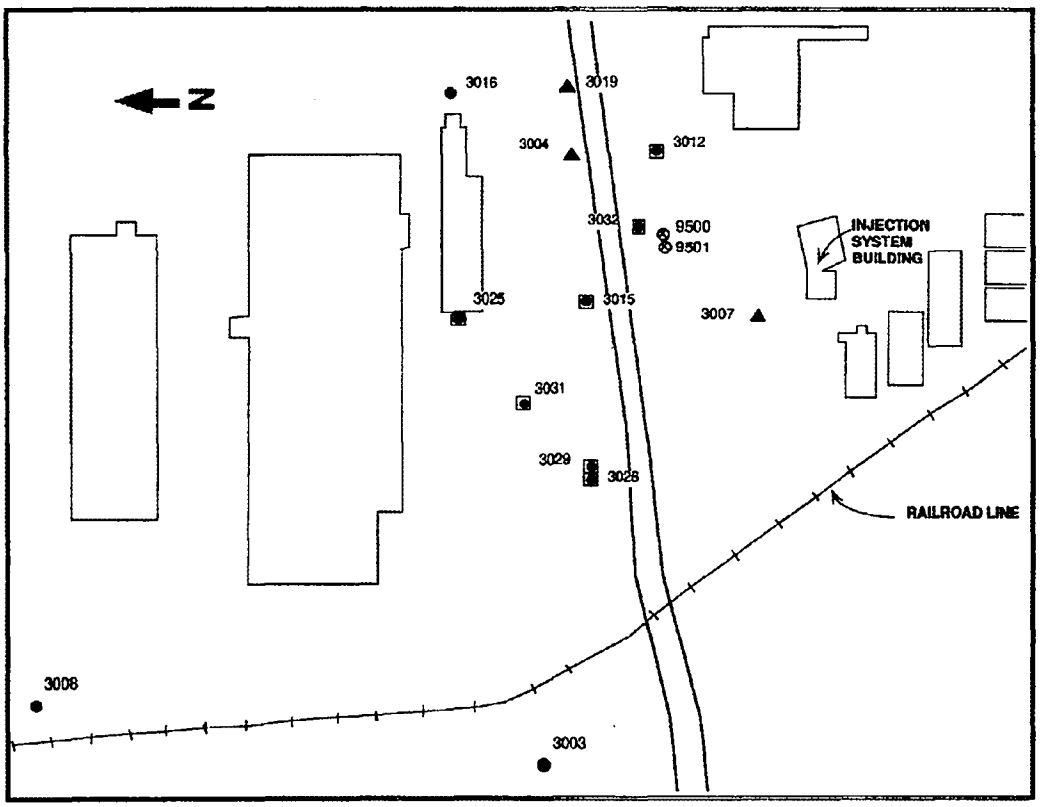


Figure 4.11. Location of Injection Wells and Monitoring Wells in the Immediate Area during the Demostration Program (Woodward-Clyde Consultants, 1990).

PROJECT NAME CHAMPION-LIBBY HOLE NO. 9500

BORING LOCATION	CHAMPION-LIBBY, MONTANA	ELEVATION AND DATUM	
DRILLING AGENCY	B & B DRILLING — DRILLER DAVE ILIFF	DATE STARTED 9/29/89 DATE FINISHED 10/5/89	
DRILLING EQUIPMENT		COMPLETION DEPTH 67'	SAMPLER
DRILLING METHOD	AIR ROTARY W/CASING ADVANCE — DRILL BIT	NO. OF SAMPLES — DIST.	UNDIST.
SIZE AND SHAPE OF CASING	4" DIA. STEEL	WATER ELEV. — FIRST	COMPL. 24 HRS.
TYPE OF PERFORATION	4" STAINLESS 0.03" — FROM 45 TO 65	LOGGED BY BILL TURNER	CHECKED BY KAREN PHILLIPS
SIZE AND TYPE OF PACK	SAND PACK — FROM 42 TO 67		
TYPE OF SEAL	BENTONITE SLURRY — FROM 15 TO 40		

DEPTH (FEET)	DESCRIPTION	DISCHARGE	HEAD-SPACE	REMARKS (Drill Rate, Fluid loss, Odor, etc.)
	Brown, Silty, Gravelly, Fine to Medium Sand, Occasional Cobbles			
5				
	Gravel, Brown, Green and Gray, Coarse Sand, Occasional Cobbles, Subangular to Subrounded	L		
10			0	10'-13.5' Rocky and Very Slow Drilling
15		L-M	.5	
	Boulder			
20		M	.5	
25	Silty Sandy Gravel with Cobbles, Brown-Green and Gray	M-H	.5	
30		M	5ppm	Inc. Contamination in Discharge; Further Inc. in Cont. in Discharge, Drilling Faster
35	Gravel, Brown, Green and Gray Coarse Sand, Occasional Cobbles, Subangular		10ppm	
40	Tight Formation		20ppm	Low Cont. in Disharge
45		M-H	8ppm	Inc. Drilling Rate
50	Inc. Silty Sand		13ppm	Fast Drill Rate
55		L-H	2ppm	Slight Sheen in Discharge
60	Gravel, Brown, Highly Sandy, Fine to Coarse With Occasional Cobbles	H	8ppm	Mod. Drilling Cont. Inc. in Discharge
	Rocky Zone			NOTE: Mostly low contamination noted during drilling
65	Decreasing Sand			
70	T.D. 67'			

GRAPHIC LOG: Lithology; Piezometer Installation (Natural Pack; Sand Pack); Water Content. SAMPLES: Type No.; Recov. ft.

Figure 4.12. Drilling Log for Injection Well No. 9500 (Woodward-Clyde Consultants, 1990).

of the study was to determine the zone of influence for a single injection well. During Phase I of the remediation program, the cumulative effects of multiple injection wells are being investigated (WoodwardClyde Consultants, 1990).

Four monitoring wells were installed in locations to expand the existing downgradient network of monitoring wells. The monitoring wells used in the demonstration study had screened intervals that allowed an evaluation of the effects of the full-scale injection site on hydrogeological aspects downgradient from the injection wells and at different depths in the Upper Aquifer (Table 4.3). Examples of the drilling logs for three of the monitoring wells are presented in Figures 4.14 and 4.15. In addition, one well (Well No. 3032) was installed approximately 25 feet from the injection wells to provide an evaluation of the extent of ground-water mounding induced by injection (Figure 4.16) (Woodward-Clyde Consultants, 1990).

A geologic cross-section of the Upper Aquifer through Well Nos. 9500, 3015, 3031, and 3017 in the demonstration area is shown in Figure 4.17 (Woodward-Clyde Consultants, 1990). This cross-section illustrates the lenticular nature of the sediments and the lack of correlation of individual layers among well locations. The most continuous layers are the three sand and gravel units.

After installation of the injection wells, a bromide tracer test was conducted to determine the hydraulic interconnections between the injection wells and the monitoring wells (Woodward-Clyde Consultants, 1990; Piotrowski, 1991). A bromide tracer solution (2.8 percent sodium bromide) was introduced into the injection wells, and the downgradient wells were monitored for bromide over four days. Results of the tracer test indicated that the downgradient monitoring wells were hydraulically connected to the full-scale injection well (Woodward-Clyde Consultants, 1990), with some wells more connected than others in the near-field region. The tracer arrived at wells closest to the injection wells at relatively high concentrations in two to three days, followed by its detection at lower concentrations further downgradient in three to four days. The area affected by the bromide injection was approximately 500 feet wide lateral and 1,000 feet downgradient. However, there was relatively poor hydraulic connection observed between Injection Well Nos. 9500/9501 and Monitoring Well Nos. 3026/3029.

Table 4.3. *Screened Intervals of Monitoring Wells (Woodward-Clyde Consultants, 1990)*

Monitoring Well No.	Screen Interval (feet bgs)
3003.1	21.5 - 23.5
3003.2	31-34
3008.1	27 - 30
3008.2	70 - 73
3012.1	77 - 83
3015.1	68 - 71
3016.1	66 - 69
3017.1	31 - 34
3017.2	49 - 52
3017.3	75 - 78
3025.1	14 - 34
3026.1	18 - 33
3029.1	51 - 71
3031.1	16 - 31
3031.2	37 - 52
3032	10.5 - 20.5

PROJECT NAME CHAMPION-LIBBY HOLE NO. 9501

BORING LOCATION	CHAMPION-LIBBY, MONTANA	ELEVATION AND DATUM	
DRILLING AGENCY	B & B DRILLING — DRILLER DAVE ILIFF	DATE STARTED / DATE FINISHED	
DRILLING EQUIPMENT		COMPLETION DEPTH 38'	SAMPLER
DRILLING METHOD	AIR ROTARY W/CASING ADVANCE — DRILL BIT	NO. OF SAMPLES — DIST.	UNDIST.
SIZE AND SHAPE OF CASING	4" DIA. STEEL	WATER ELEV. — FIRST 12'	COMPL. 12.5' 24 HRS.
TYPE OF PERFORATION	WIRE WRAPPED — FROM 18 TO 38	LOGGED BY: BILL TURNER	CHECKED BY: KAREN PHILLIPS
SIZE AND TYPE OF PACK	NATURAL PACK — FROM 15 TO 38		
TYPE OF SEAL	BENTONITE PELLETS — FROM 9 TO 15		

DEPTH (FEET)	DESCRIPTION	GRAPHIC LOG: Lithology	GRAPHIC LOG: Piezometer Installation	Water Content	DISCHARGE	SAMPLES: Type No.	SAMPLES: Recov. ft.	SAMPLES: HEAD-SPACE	REMARKS (Drill Rate, Fluid loss, Odor, etc.)
	Brown, Silty, Gravelly, Pine to Medium Sand, Occasional Cobbles				L				
5	Gravel, Brown, Green and Gray Coarse Sand, Occasional Cobbles, Subangular to Subrounded								
10									
15					L-M				Slight Sheen On Samples
20									
25	Silty, Sandy Gravel with Cobbles Brown-Green and Gray		Natural Pack		M				
30								1ppm	
35	Gravel, Brown, Green and Gray Coarse Sand, Occasional Cobbles, Subangular								
40	T.D. 38'								
45									
50									
55									
60									
65									
70									

Figure 4.13. Drilling Log for Injection Well No. 9501 (Woodward-Clyde Consultants, 1990).

PROJECT NAME CHAMPION-LIBBY HOLE NO. 3029

BORING LOCATION	CHAMPION-LIBBY, MONTANA	ELEVATION AND DATUM	
DRILLING AGENCY	B & B DRILLING	DRILLER DAVE ILIFF	DATE STATED 9/28/89 DATE FINISHED 10/3/89
DRILLING EQUIPMENT		COMPLETION DEPTH 71'	SAMPLER
DRILLING METHOD	AIR ROTARY W/CASING ADVANCE	DRILL BIT 8 1/4"	NO. OF SAMPLES DIST. 0 UNDIST.
SIZE AND SHAPE OF CASING	4" DIA. STEEL	WATER ELEV. FIRST 12'	COMPL. 24 HRS.
TYPE OF PERFORATION	4" STAINLESS .03" FROM 71 TO 51	LOGGED BY BILL TURNER	CHECKED BY KAREN PHILLIPS
SIZE AND TYPE OF PACK	NATURAL PACK FROM 71.5 TO 48.5		
TYPE OF SEAL	BENTONITE SLURRY AND CEMENT FROM 48.5 TO Surf		

DEPTH (FEET)	DESCRIPTION	GRAPHIC LOG: Lithology	GRAPHIC LOG: Piezometer Installation	Water Content	DISCHARGE	SAMPLES: Type No.	SAMPLES: Recov. ft.	SAMPLES: HEAD SPACE	REMARKS (Drill Rate, Fluid loss, Odor, etc.)
	Gravel, Sandy with Cobbles, Very Angular, Tan and Brown		Cement; Cement						
5									0 ppm HNU
10									Drilling Slower
15								25ppm	
					L				Rocky Drilling; Making Little WTR
	Gravel, Coarse to Fine, Green, Brown and Black, Subangular								
20			Bentonite Slurry + Cement; Bentonite Slurry + Cement					25ppm	Faster Drilling
25								5ppm	
	Gravel, Sandy Brown, Black and Green Subrounded, Slight Amount of Silty Clay								Increased Discharge in Well 3026
30								11ppm	Little Returns
35	Gravel, Loose, Coarse Grained, Sandy, Clayey, Brown with Sheen				H			25ppm	33'-38' Very Fast Drilling
40					L			13.5ppm	Very Slow Drilling 42'-44'
	Gravel, with Boulders and Cobbles, Subangular to Subrounded with Sheen								
45	Gravel, Medium to Coarse Sand, Occasional Cobbles, Subangular with Sheen							20ppm	Note: Lost a lot of cement slurry in hole added 440 gal. to raise annuius seal from 48' to 7' bgs.
50								10ppm	High Contamination in Discharge
55	Inc. Sands		Natural Pack		H			20ppm	
									Fast Drilling
60								9ppm	Slow Drilling
65								21ppm	Mod. Discharge
70	Inc. Sands							22ppm	
	T.D. 72'								

Figure 4.14. Drilling Log for Monitoring Well No. 3029 (Woodward-Clyde Consultants, 1990).

3031-1
PROJECT NAME CHAMPION-LIBBY HOLE NO. 3031-2

BORING LOCATION	CHAMPION-LIBBY, MONTANA	ELEVATION AND DATUM	
DRILLING AGENCY	B & B DRILLING	DRILLER DAVE ILIFF	DATE STARTED / DATE FINISHED
DRILLING EQUIPMENT		COMPLETION DEPTH 52'	SAMPLER
DRILLING METHOD	AIR ROTARY W/CASING ADVANCE	DRILL BIT 6 1/4"	NO. OF SAMPLES DIST. / UNDIST.
SIZE AND SHAPE OF CASING	2" DIA. STEEL	WATER ELEV. FIRST 12'	COMPL. 24 HRS.
TYPE OF PERFORATION	2" STAINLESS .03"	FROM 16 TO 31; FROM 37 TO 51	LOGGED BY BILL TURNER
SIZE AND TYPE OF PACK	NATURAL PACK	FROM 14 TO 52; FROM 37 TO 52	CHECKED BY KAREN PHILLIPS
TYPE OF SEAL	BENTONITE PELLETS	FROM 10 TO 14; FROM 31 TO 37	

DEPTH (FEET)	DESCRIPTION	GRAPHIC LOG: Lithology	GRAPHIC LOG: Piezometer Installation	Water Content	DISCHARGE	SAMPLES: Type No.	SAMPLES: Recov. ft.	SAMPLES: HEAD-SPACE	REMARKS (Drill Rate, Fluidloss, Odor, etc.)
5	Sand, Fine to Coarse, Brown, Gravelly, Slightly Clayey, Occasional Cobbles		Grout; 3031-1					0	Rocky Drilling
10	Gravel, Brown, Green and Gray, Sandy, Coarse, Subangular to Subrounded				L			0	Initial HNU Reading 2 ppm
15	Inc. Sandy Cement							5ppm	
20	Gravel, Brown, Tan and Green, Highly Sandy, Coarse, Subrounded		Sand		L			5ppm	Low Contamination
25					L-M			2ppm	Inc. Contamination at 26'
30					M			12ppm	
35	Silt, Brown, Clayey C., Occasional Gravel				L			6ppm	
40	Gravel, Brown, Green and Gray, Slightly Sandy with Cobbles, Subrounded		Natural Pack		L-M			1ppm	Highly Contaminated Oil on Pit Sheen to T.D.
45	Sand, Coarse, Gray and Brown, Gravelly, Semi-Rounded (Sheen on Sample)				M-H			22ppm	
50	Gravel, Green and Gray, Sandy, Coarse, Occasional Cobbles, Semi-Rounded, Good Sheen							13ppm	
55	T.D. 52'		3031-2						
60									
65									
70									

Figure 4.15 Drilling Log for Monitoring Well No. 3031.1 and 3031.2 (Woodward-Clyde Consultants, 1990).

PROJECT NAME CHAMPION-LIBBY HOLE NO. 3032

BORING LOCATION	CHAMPION-LIBBY, MONTANA	ELEVATION AND DATUM	
DRILLING AGENCY	B & B DRILLING	DRILLER DAVE ILIFF	DATE STARTED 10/2/89 DATE FINISHED 10/3/89
DRILLING EQUIPMENT		COMPLETION DEPTH 20.5'	SAMPLER
DRILLING METHOD	AIR ROTARY W/CASING ADVANCE	DRILL BIT 8 1/4"	NO. OF SAMPLES DIST. NONE UNDIST.
SIZE AND SHAPE OF CASING	2" DIA. STAINLESS STEEL	WATER ELEV. FIRST 15'	COMPL. 20.5' 24 HRS.
TYPE OF PERFORATION	.02" SLOTTED FROM 20.5 TO 10.5	LOGGED BY BILL TURNER	CHECKED BY KAREN PHILLIPS
SIZE AND TYPE OF PACK	#16 MONT. + NATURAL PACK FROM 20.5 TO 8		
TYPE OF SEAL	BENTONITE PELLETS FROM 8 TO 6		

DEPTH (FEET)	DESCRIPTION	GRAPHIC LOG: Lithology	GRAPHIC LOG: Piezometer Installation	Water Content	DISCHARGE	SAMPLES: Type No.	SAMPLES: Recov. ft.	SAMPLES: HEAD SPACE	REMARKS (Drill Rate, Fluid loss, Odor, etc.)
	Brown, Silty, Gravelly, Fine to Medium Sand, Occasional Cobbles		Cement / Cement						
5	Gravel, Brown, Green and Gray, Coarse Sand, Occasional Cobbles, Subangular to Subrounded				L-M				Rocky, Slow Drilling
10									
					M			5ppm	
15	Boulders Encountered								
					L-M				
20									
	T.D. 20.5'								
25									
30									
35									
40									
45									
50									
55									
60									
65									
70									

Figure 4.16. Drilling Log for Monitoring Well No. 3032 (Woodward-Clyde Consultants, 1990).

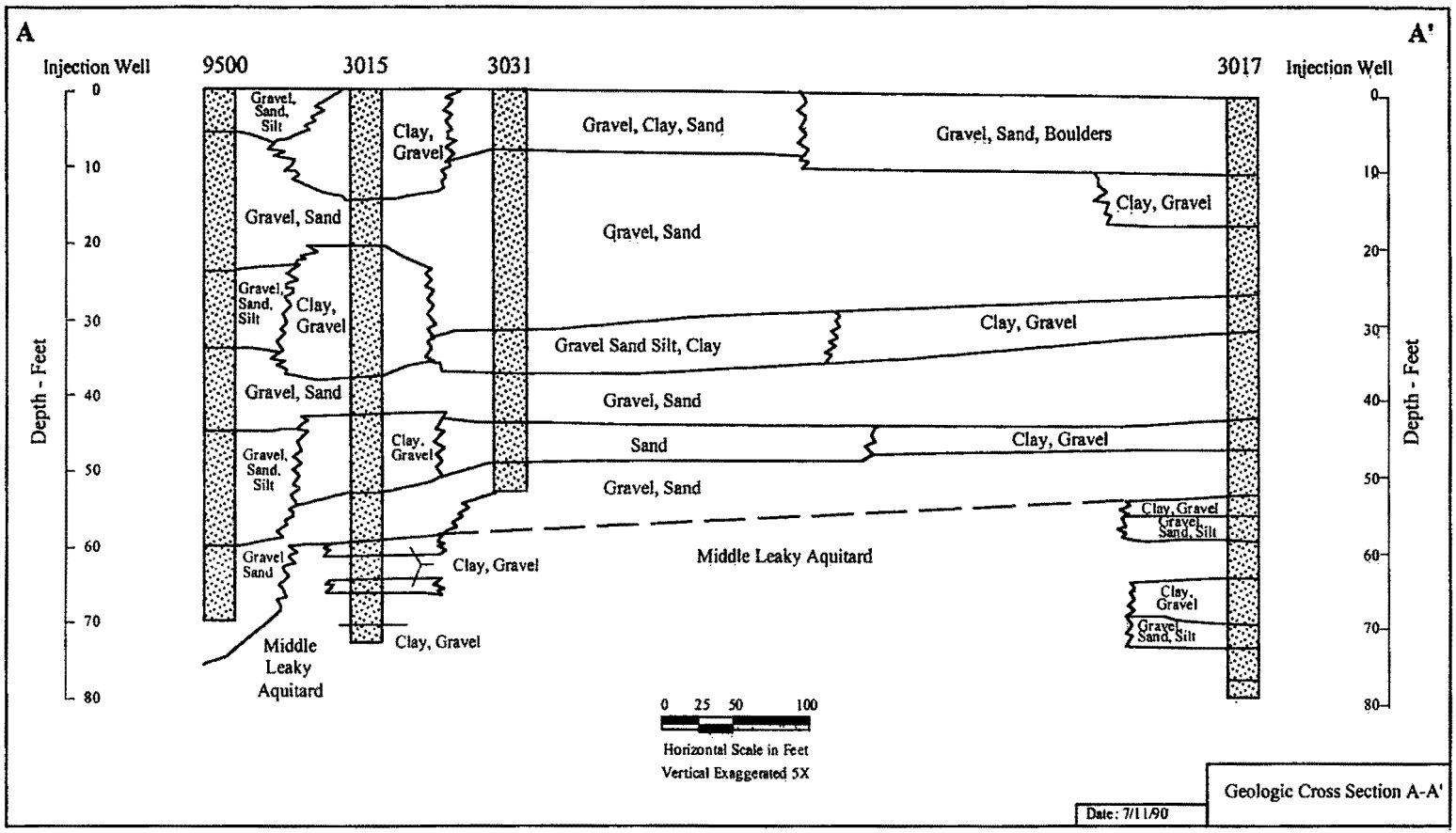


Figure 4.17. Geologic Section of the Upper Aquifer through Injection Well No. 9500 and Monitoring Wells No. 3015, 3031, and 3017 (Woodward-Clyde, 1990).

No bromide was detected in Well No. 3029 and lower-than-expected concentrations were measured in the adjacent monitoring well (Well No.3026). These results were probably due to heterogenous and lenticular deposits of finegrained sediments in those areas.

There were only slightly higher concentrations of bromide detected in shallow monitoring wells compared to the deeper zones. There did not seem to be differences in ground-water flow with depth, but rather a fairly uniform vertical flow occurred in the Upper Aquifer (WoodwardClyde Consultants, 1990).

Ground-water flow rates, estimated from the bromide tracer test, ranged from 175 feet per day at Well No. 3003 to 300 feet per day at Well No. 3017 (Woodward-Clyde Consultants, 1990; Piotrowski, 1991). These ground-water flow rates are similar to those estimated in the pilot-scale study.

The approach used in the demonstration program to accomplish *in situ* bioremediation involved the addition of hydrogen peroxide as a source of D.O. and inorganic nutrients to stimulate growth of contaminant-specific populations (Piotrowski, 1991). The hydrogen peroxide injection rates were designed to maintain a concentration of approximately 100 mg/L of hydrogen peroxide. Inorganic nutrients in the form of potassium tripolyphosphate and ammonium chloride were continuously added to achieve concentrations in the injection water of 27 mg/L and 22 mg/L, respectively.

To conduct the full-scale demonstration program in the intermediate injection system area, the injection water delivery and conditioning system had to be upgraded in order to introduce larger amounts of both hydrogen peroxide and nutrients into the ground water. The source of injection water was from the fire pond, which is part of the fire protection system for the lumber mill. Injection water was filtered to remove particulate matter that could clog injection well screens.

The anticipated maximum capacity of the upgraded injection system was greater than 70 gpm. To accommodate this increase in flow, the following measures were taken:

(1) the existing sand filter system was upgraded by operating an additional sand filter in parallel with the original filter to remove particulate matter from the fire pond water;
(2) the existing piping network was continuously monitored to assess corrosion by hydrogen peroxide;
(3) flow meters were installed in-line for flow rate determinations in each well; and
(4) hydrogen peroxide storage, pumping capacities, and nutrient addition capabilities were expanded.

The flow through the full-scale injection site was started in January 1990 and discontinued in June 1990 (Piotrowski, 1991). The deeper well (Well No. 9500, which was screened lower in the Upper Aquifer) had a maximum flow rate of approximately 20 gpm; injection rates during the study were about 13 gpm. The rate of injection was limited by the geological formation, which consisted of sediments of lower permeability. Mounding in this well reached near the top of the casing during injection. The shallower well (Well No. 9501) had a maximum rate in excess of 50 gpm; during the study, the injection rate was about 45 gpm. This rate was considered to be an appropriate flow rate to provide sufficient oxygen to enhance downgradient biodegradation. Less mounding was noticed in the shallower well, indicating the presence of more permeable sediments in the upper part of the aquifer. The total injected flow that could be delivered to the Upper Aquifer was therefore at least 70 gpm; during the demonstration study, the total flow rate was about 58 gpm. Water was injected at atmospheric pressure. No significant operational problems were encountered during the period of the demonstration study. No evidence of clogging of the well screens was observed.

Operational procedures included the periodic recharging of the hydrogen peroxide and nutrient tanks. The peroxide tank was recharged with 50 percent hydrogen peroxide approximately every two months, based on continuous operation. The nutrient addition tank was recharged approximately every two weeks, based on continuous operation. Other operational procedures included periodic backwashing of the sand filters and routine visual inspections of the system.

The response of the contaminated plume to hydrogen peroxide and nutrient injection was evaluated by monitoring dissolved concentrations of PCP and selected PAH compounds, total bacterial counts, and Microtox™ toxicity in samples collected in March and May from eight monitoring wells located in the vicinity and downgradient from the injection wells (WoodwardClyde Consultants, 1990; Piotrowski, 1991). Operational guidelines for the demonstration system also required monthly measurements of D.O., water depth, and temperature in 15 monitoring wells. Ground-water mounding was evaluated by monitoring the water levels in the injection wells and in the adjacent Monitoring Well No. 3032. After injection was completed, water levels in the wells were monitored for 24 hours to determine recovery curves for the wells. Based on these data, a distance mounding plot was developed to estimate the lateral distance affected by mounding.

D.O. concentrations in wells located in regions potentially under the influence of the injection site were compared to oxygen concentrations in wells located upgradient from the site (Woodward-Clyde Consultants, 1990; Piotrowski, 1991). A well that exhibited a D.O. concentration greater than normal concentrations (less than 1 mg/L) within the contaminant plume or greater than concentrations within pristine ground water (approximately 5 mg/L) was considered to be under the biogeochemical influence of the injection site. Increases in D.O. concentrations were often variable between adjacent wells and over time within the same well, likely due to variability in sampling and analyses and variability in the migration of the D.O. downgradient. However, in general, monitoring wells that showed increased bromide concentrations during the bromide tracer test also showed increase in D.O. concentrations. The area of increased D.O. levels due to hydrogen peroxide addition, as determined by D.O. monitoring, was estimated to be about 400 feet wide, as measured perpendicular to the general ground-water flow direction, and approximately 1000 feet downgradient from the injection well.

Increased D.O. concentrations downgradient of the injection wells also seemed to be distributed vertically within the Upper Aquifer, with monitoring wells screened in both shallow and deep horizons showing increased D.O. levels (Woodward-Clyde Consultants, 1990). Similar to the results obtained in the bromide tracer experiment, Well Nos. 3026 and 3029 showed only slight increases in D.O. concentrations, indicating poor hydraulic connections between these wells and the injection wells.

To determine if degradation was occurring in the aquifer, results of sampling for PAH compounds and PCP were compared between the March and May sampling dates (Table 4.4) (Woodward-Clyde Consultants, 1990). Carcinogenic PAH compounds were detected in only a few monitoring wells, so no overall relationship for degradation of those compounds could be established. For concentrations of PCP and for total noncarcinogenic PAH compounds, five of the eight wells monitored showed decreasing concentrations, while three wells showed increasing concentrations. The decrease in total noncarcinogenic PAH compounds and PCP were 10 percent and 18 percent, respectively, between March and May, 1990. The results may indicate that enhanced biodegradation was occurring (Woodward-Clyde Consultants, 1990).

Comparison of the D.O. measurements and the results of the chemical analyses indicated a reasonable but variable and mixed relationship between these factors (Woodward-Clyde Consultants, 1990). For example, wells that showed a decrease in organic contaminants also showed a trend of increasing D.O. with time. Another well showed a slight increase in PCP and PAH concentrations and a decrease

in D.O. content. Another well showed a substantial increase in total PAH compounds and a slight decrease in PCP, but little fluctuation in the D.O. concentrations was observed. Based on these results, the parameter D.O. cannot be used with a high degree of confidence to indicate changes in PAH and PCP concentrations.

Operation of the full-scale injection site during the six-month demonstration period produced a mounding of the water table of the Upper Aquifer in the vicinity of the injection site that averaged approximately three feet in height (Piotrowski, 1991). In addition, some mounding effects may have occurred at distances over 100 feet on either side (i.e., perpendicular to groundwater flow) of the injection site. Water table mounding at the site may also have been influenced by infiltration from the nearby fire pond.

Based on results from the assessment of mounding during the demonstration program of the full-scale system, it was determined that spacings between adjacent injection sites of the intermediate injection system should be at least 200 feet (Piotrowski, 1991). Additional final design details for the *in situ* bioremediation program are being based on the aquifer properties determined from the bromide injection tests and the monitoring data from the demonstration program, as well as additional information being generated as the full-scale system continues to be implemented in phases.

4.6 Cost Estimates for the In Situ Bioremediation Program for the Upper Aquifer

Table 4.4. *PCP, Total Noncarcinogenic PAH, and Total Carcinogenic PAH in Monitoring Wells During the Demonstration Program (Woodward-Clyde Consultants, 1990).*

	March 1990			May 1990		
Well Number	PCP	Total Non-Carcinogenic PAH	Total Carcinogenic PAH	PCP	Total Non-Carcinogenic PAH	Total Carcinogenic PAH
	(μg/L)			(μg/L)		
3012.1	566	1199	——	371	764.5	——
3015.1	267	426	——	989	600	——
3025.1	1020	2458	304	528	1657	——
3026	1321	1147	——	803	4070	——
3029.1	2440	8686	——	2708	7108	——
3031.1	760	3840	——	454	2374	——
3031.2	1060	5006	——	760	2116	10
3032.1	173	288	——	205	123.5	57
Totals	7607	23050	——	6818[1]	18813[2]	——

1 This represents a 10% decrease from March
2 This represents an 18% decrease from March

In 1990, preliminary cost estimates were prepared for the entire *in situ* bioremediation program for the Upper Aquifer (Woodward-Clyde Consultants, 1990). A summary of the cost estimates is presented in Table 4.5. The low capital costs for the intermediate injection system reflect the presence of equipment already installed as part of the pilot-scale and demonstration programs that have been completed. Detailed cost estimates for each injection area and for operations and maintenance activities are presented in Appendix A.

Table 4.5. *Cost Estimates for the Upper Aquifer* In Situ *Bioremediation Program (WoodwardClyde Consultants, 1990).*

Injection Area	Capital Costs	Annual Operations and Maintenance Costs
Intermediate Injection System (Upgrade)	$ 41,900	$ 46,700
Boundary Injection System	$183,500	$ 42,100
Source Area Injection System	$ 57,600	$ 38,400
Total:	$283,000	$127,200

Chapter 5
Field Performance Evaluation of *In Situ* Bioremediation of the Upper Aquifer

5.0 BFI Study Objective 2: Field Evaluation to Assess Performance of In Situ Bioremediation of the Upper Aquifer

Previous ground-water studies conducted at the Libby, Montana, wood treating site have focused on biodegradation of soluble organic compounds. This approach to evaluating *in situ* bioremediation may have resulted in over-estimating the rate and extent of biodegradation of organic contaminants at the site. The PAH compounds of concern at the site have limited solubility in the water phase but have a preference, due to high octanol-water partition coefficient values (K_{ow}), for nonaqueous phase liquids (NAPLs) that may be located within the pore space of aquifer solids as a water-immiscible oily phase. Also, the PAH compounds of concern have a preference to be associated with the solid phase of an aquifer matrix due to high solid-water partition coefficient values (K_d). The hydrophobicity, or "water-hating" characteristics, of PAHs as a class of compounds has been addressed in detail by Grady and Lim (1980), Sawhney and Brown (1989), and Sims and Overcash (1983). PCP, however, has increasing water solubility with increasing environmental pH values above 4.75 and, therefore, has less preference than PAH compounds to be associated with oil and solid phases at the Libby Site, which has a pH of 6.9. Therefore, an evaluation of the aquifer solid phase and associated NAPL was performed to evaluate whether PAH compounds as well as PCP have been removed from aquifer solids in subsurface areas where nutrients and oxygen were injected.

Bioremediation of subsurface environments involves the interaction of four main components: (1) microbiology, (2) terminal electron acceptor, (3) nutrients, and (4) the target chemical, which may be a substrate or a co-substrate (McFarland and Sims, 1991). These components must be present and must interact for biodegradation to occur. The rate and extent of interaction will be determined primarily by the subsurface stratigraphy. In addition, there are four phases in the subsurface in which one or more of these components may be present: (1) solid (aquifer materials, soil), (2) gaseous (oxygen, hydrocarbon vapors), (3) aqueous liquids, and (4) nonaqueous phase liquids (NAPLs) (Sims, 1990). Because of the tendency of PAH compounds to be associated with the solid phase and especially the NAPL phase in the subsurface, PAH compounds have limited interaction with microorganisms, oxygen (terminal electron acceptor), and nutrients due to the water-immiscible nature of the NAPL as well as the heterogeneous nature of the subsurface at the Libby Site. Therefore, the bioavailability of the PAH compounds within the aquifer may be limited, and analysis of ground-water samples only may not provide a clear indication of whether bioremediation is occurring in other phases in the aquifer.

Therefore, the second objective of this BFI study was to conduct a field evaluation to assess the performance of remediation activities with regard to the removal of contaminants associated with subsurface solid particles and oily (NAPL) materials. The field evaluation was conducted in three phases: (I) assessment of potential for *in situ* biodegradation in the Upper Aquifer; (II) assessment of the performance of remediation activities with regard to removal of contaminants associated with the subsurface solid particles and oily materials in the Upper Aquifer; and (III) investigation of the role of preferential flow pathways in the intermediate injection area of the Upper Aquifer.

5.1 Phase I - Assessment of Potential for In Situ Biodegradation in the Upper Aquifer

Preliminary studies were performed to determine if an *in situ* assessment of biodegradation in the water phase could be performed at the Libby Site. These studies consisted of: (1) singlewell injection (push/pull) tests to measure subsurface microbial activity in the Upper Aquifer; and (2) ground-water analyses to evaluate the oxidative-reductive status of the Upper Aquifer.

5.1.1 Performance of Push/Pull (Single-Well Injection) Tests to Measure Subsurface Microbial Activity

An evaluation of *in situ* bioremediation activity in the water phase was conducted by measuring oxygen utilization based upon differences in oxygen concentrations in injected and recovered water using a push (injection)/pull (recovery) test (i.e., single-well injection test). As part of push/pull testing, a conservative tracer is injected to determine the dilution or concentration of various compounds that indicate the presence of biological transformation activities by comparing the concentrations of the compounds with the concentrations of the conservative tracer. For example, if biological activity or abiotic oxygen demand is present, concentrations of added oxygen or nitrate, which are electron acceptors, should decrease below those concentrations predicted by dilution.

5.1.1.1 Experimental Approach and Methods for the Performance of Push/Pull Tests

The first set of push/pull tests was conducted September 16 - 21, 1991. Two wells were selected for use in the testing. Well No. 3014.1 was located outside the contaminant plume, while Well No. 3017.1 was located within the contaminated plume.

Bromide was used as a conservative tracer to monitor the dilution of the injection plume with native ground water. Two hundred gallons of fire pond water used for injection into Well No. 3014.1 was spiked with 40 g of sodium bromide (NaBr) and 400 mL of a 25 percent solution of hydrogen peroxide. For Well No. 3017.1, the injection water was only spiked with 40 g of NaBr. After injection of the spiked water, water samples were pumped from the wells immediately after injection and six more times over the next 23 hours. The water samples were analyzed for bromide (Br^-) and dissolved oxygen (D.O.).

Additional push/pull tests were conducted October 14 - 20, 1991. The tests were performed on five wells: Well Nos. 3014.1 and 3034 (located outside the contaminated plume) and Well Nos. 3003.2, 3010.1, and 3017.2 (located within the contaminated plume). Each well was injected with 500 gallons of fire pond water spiked with 500 g of NaBr for a Br^- concentration of approximately 205 mg/L. The wells were sampled immediately after injection and an additional two to four times in the next 24 to 36 hours.

5.1.1.2 *Results of Push/Pull Tests*

In the first push/pull injection tests, in Well No. 3014.1, as illustrated in Figure 5.1, bromide concentration in the injection plume gradually was reduced to 16.5 percent of its initial value (33.3 mg/L) during the duration of the test. These results were not expected, based on the estimated ground-water velocities of 50 to 300 feet per day. D.O. concentrations increased during the first two hours of the test, due to degradation of hydrogen peroxide to oxygen. The D.O. appeared to disappear from the plume at a faster rate than bromide was diluted. In Well No. 3017.1 (Figure 5.2), the bromide concentration decreased at approximately twice the rate as it decreased in Well No. 3014.1. D.O. appeared to behave as a conservative tracer; i.e., it appeared to be diluted in the plume at a similar rate as bromide.

The results of the first push/pull injection tests showed that tracer plumes formed by injecting 200 gallons of spiked water could only be monitored for 12 to 24 hours. Since biodegradation is expected to be a slower process, this procedure using 200 gallons did not provide sufficient time to evaluate biodegradation *in situ*. Therefore, the push/pull tests were repeated using 500 gallons of spiked injection water in the second test.

In the second test, the bromide concentrations also decreased rapidly (Figures 5.3 to 5.7), indicating that high flow rates (probably greater than 50 feet per day) prevented the injected water from being contained long enough for microbial activity to decrease measurably the oxygen concentration of the injected water and for the water to be recovered for measurement. The D.O. was being lost from the plume by dilution, though the reactions that were consuming oxygen (i.e., microbial activity or chemical reactions) are not known.

During sampling of the ground water to determine bromide concentrations, a test was conducted to determine how many times a well had to be bailed before a constant bromide concentration was achieved in the bailed

samples. As shown in Figure 5.8, a constant value for bromide was not achieved even after 25 bailings (in this well, one water column in the well was equivalent to eight bailings). The injected plume was probably moving away from the well screen at a rate too great to obtain constant bromide concentrations.

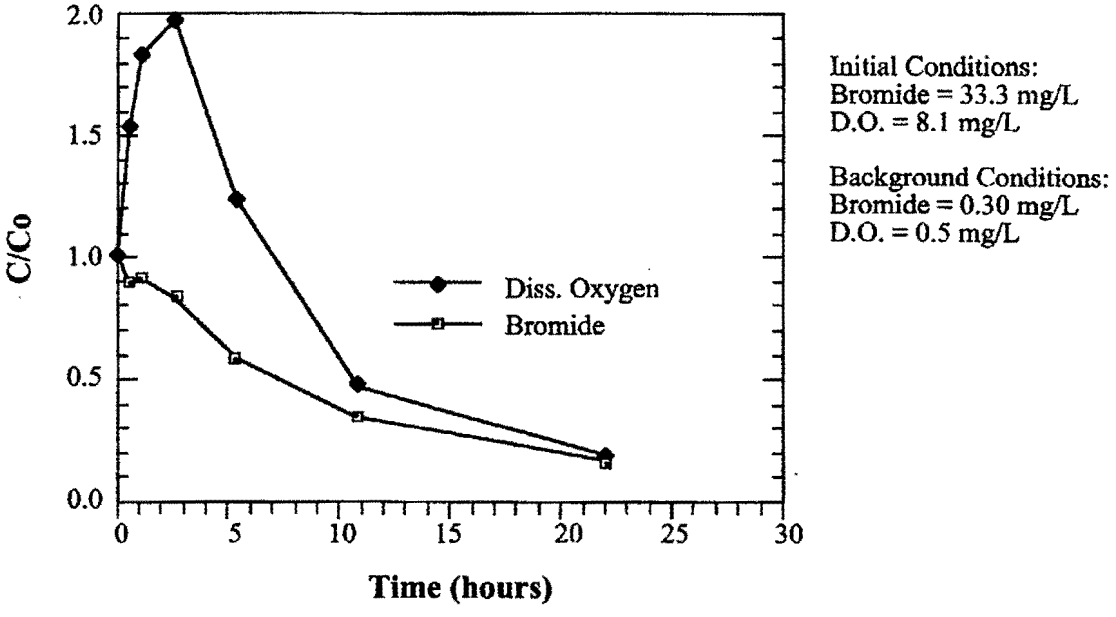


Figure 5.2. Bromide Tracer Push/Pull Test for Well No. 3104.1: September, 1991.

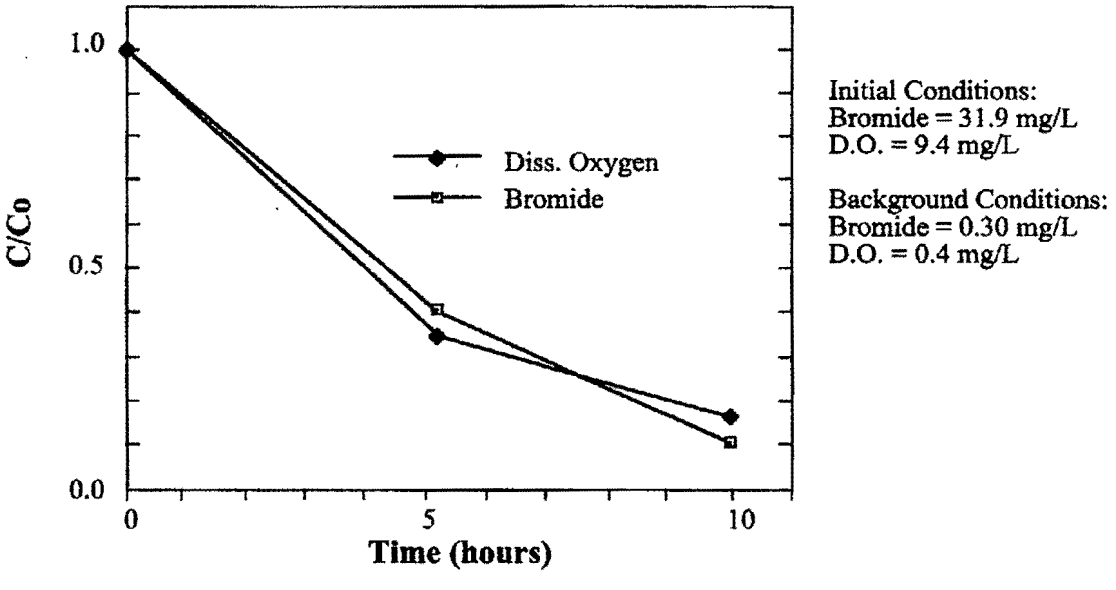


Figure 5.2. Bromide Tracer Push/Pull Test for Well No. 3107.1: September, 1991.

Therefore, the use of push/pull tests at this site for measuring subsurface microbial activity was not successful, due to site characteristics related to high hydraulic conductivities and high subsurface ground-water flow velocities.

5.1.2 Ground-Water Analyses to Evaluate the Oxidative-Reductive Status of the Upper Aquifer

In an aquifer that is in a reduced state (i.e., minerals present are in a reduced rather than oxidized form), there may be competition for the use of oxygen added to the aquifer for remedial purposes. The reduced minerals may compete for available oxygen with the microorganisms accomplishing the degradation of organic contaminants; thus, the time required for remediation will be much longer than estimated based on oxidation of organic contaminants present, as well as more expensive, especially when oxidants such as hydrogen peroxide are used. In a reduced aquifer, ground-water samples would be expected to have lower concentrations of electron acceptors, such as oxygen, nitrates, and sulfates, and higher concentrations of electron donors, such as reduced manganese (II) and iron (II), and sulfides. Conversely, ground-water samples from an oxidized aquifer should have higher levels of electron acceptors and lower levels of electron donors.

5.1.2.1 *Experimental Approach and Methods for the Evaluation of the Oxidative-Reductive Status of the Upper Aquifer*

Ground-water samples were collected in October 1991 for analysis of iron (II), manganese (II), and dissolved oxygen (D.O.) during the testing period for the push/pull injection experiments. Three to four samples were collected over a 10 to 24 hour period; results are presented as the average of the replicate samples. During a sampling trip in April 1992, ground-water samples were collected for analysis of iron (II), manganese (II), D.O., nitrate (NO_3^-), and sulfate (SO_4^{-2}).

Wells sampled in October 1991 included: Well Nos. 3014.1 and 3034 (located outside the contaminated plume) and Well Nos. 3003.2, 3010.1, and 3017.2 (located within the contaminated plume). In April 1992, the following wells inside the contaminated plume were sampled: Well Nos. 3002.1, 3003.1, 3008.1, 3010.1, 3013.1, 3017.1, and 3018.1. The wells outside the contaminated plume included: Well Nos. 3011.1, 3014.1, 3014.2, 3021, 3027, 3033, 3034, 3036, and 3037. were analyzed in the field immediately after collection for ferrous iron (Fe^{2+}) using a procedure modified from Lovely and Phillips (1987, 1988). Forty mL of ground water were placed in a commercially pre-cleaned jar containing 0.5 mL of a 0.5 N HCl solution. After mixing, 0.2 mL of this solution was added to 5 mL of a buffered ferrozine solution. The ferrozine solution was prepared by dissolving 0.5 g of ferrozine in 500 mL of a 50 mM HEPES buffer, which had been prepared by dissolving 13.02 g of HEPES (N-[2Hydroxyethyl]piperazine-N'-[2-ethanesulfonic acid]) in approximately 800 mL distilled, deionized water (DDW) and diluted to 1 L. The solution with the ferrozine solution was mixed for 15 seconds. The concentration of Fe^{2+} was determined by measuring the absorbance at 562 nm.

Manganese in the ground-water samples was analyzed at the Utah Water Research Laboratory (UWRL) by inductively coupled atomic emission spectroscopy (ICP) using U.S EPA Method 6010 (U.S. EPA, 1986b). The instrument used for the analysis was a Perkin-Elmer ICP/6000 Inductively Coupled Arc Plasma system. Nitrates and sulfates were analyzed using ion chromatography (Dionex Ion Chromatograph/HP 3396A Integrator) according to U.S. EPA Method 300.0: *The Determination of Inorganic Ions in Water by Ion Chromatography* (Pfaff et al., 1989).

Dissolved oxygen measurements were performed at the wellhead. Analyses for dissolved oxygen were performed using a YSI Dissolved Oxygen instrument (YSI, Inc., Yellow Springs, Ohio).

5.1.2.2 *Results of the Evaluation of the Oxidative-Reductive Status of the Upper Aquifer*

Results of both sampling trips indicate that aquifer materials located in both contaminated and uncontaminated areas are in a chemically reduced condition (as indicated by the presence of reduced iron and manganese)

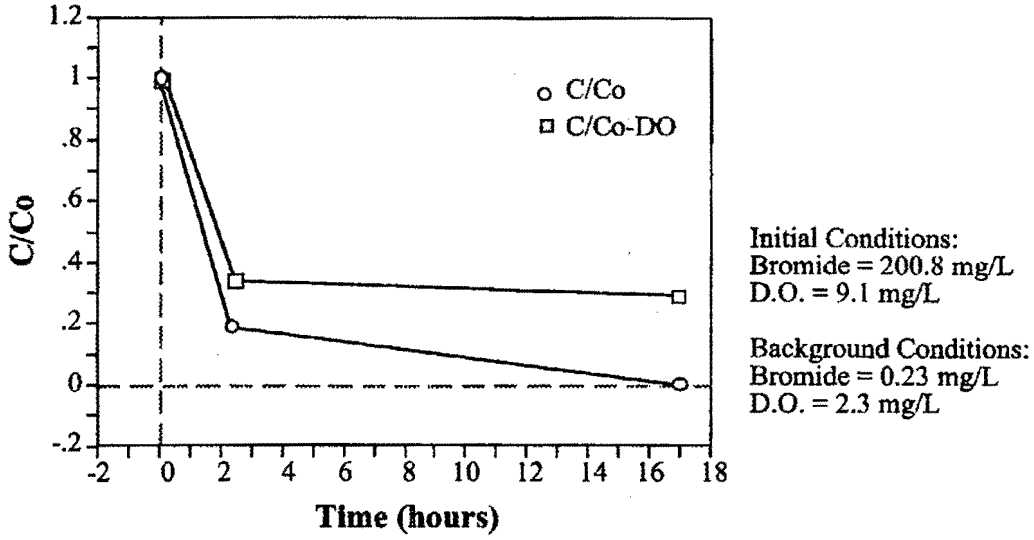


Figure 5.3. Bromide Tracer Push/Pull Test for Well No. 3003.2: October, 1991.

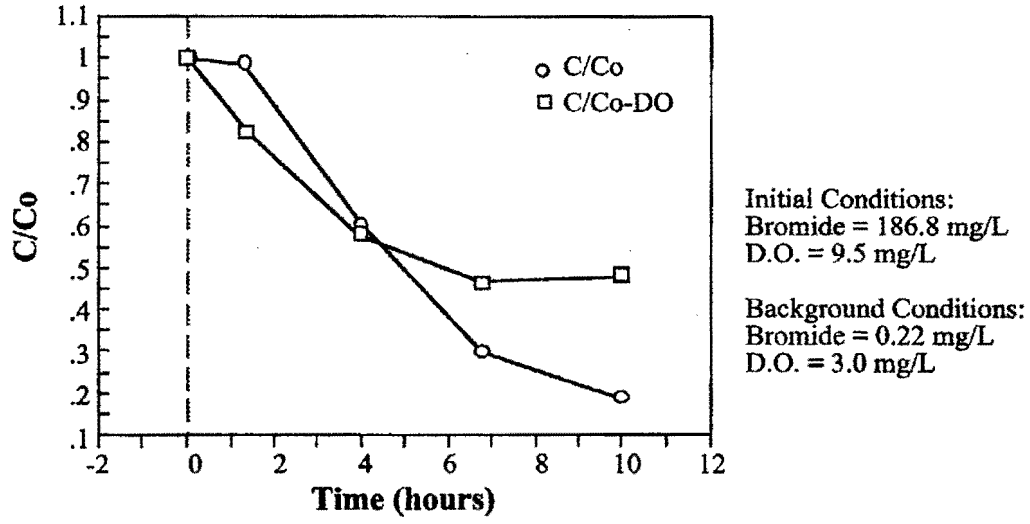
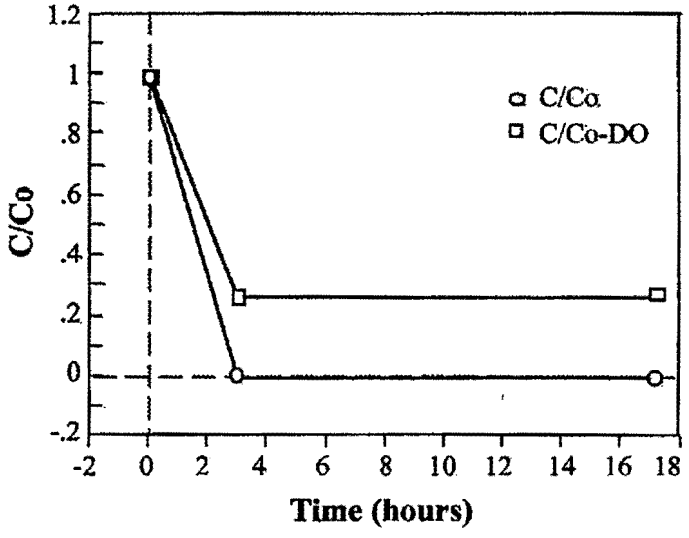


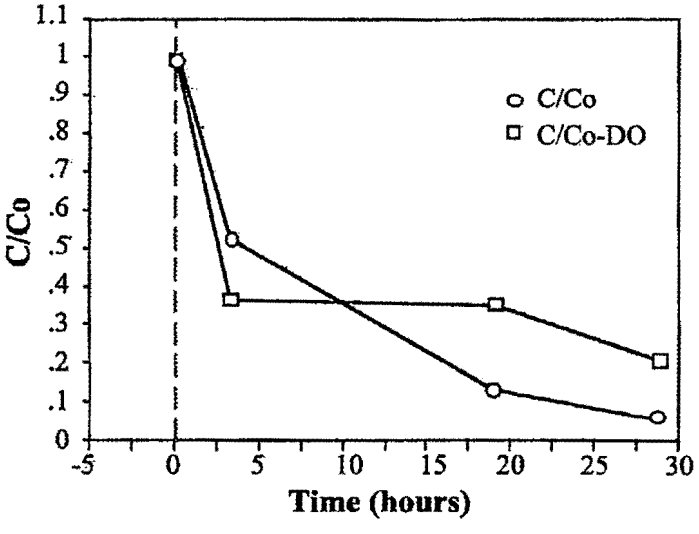
Figure 5.4. Bromide Tracer Push/Pull Test for Well No. 3010.1: October, 1991.



Initial Conditions:
Bromide = 208.5 mg/L
D.O. = 9.1 mg/L

Background Conditions:
Bromide = 0.20 mg/L
D.O. = 1.9 mg/L

Figure 5.5. Bromide Tracer Push/Pull Test for Well No. 3017.1: October, 1991.



Initial Conditions:
Bromide = 203.7 mg/L
D.O. = 8.6 mg/L

Background Conditions:
Bromide = 0.36 mg/L
D.O. = 2.4 mg/L

Figure 5.6. Bromide Tracer Push/Pull Test for Well No. 3014.1: October, 1991.

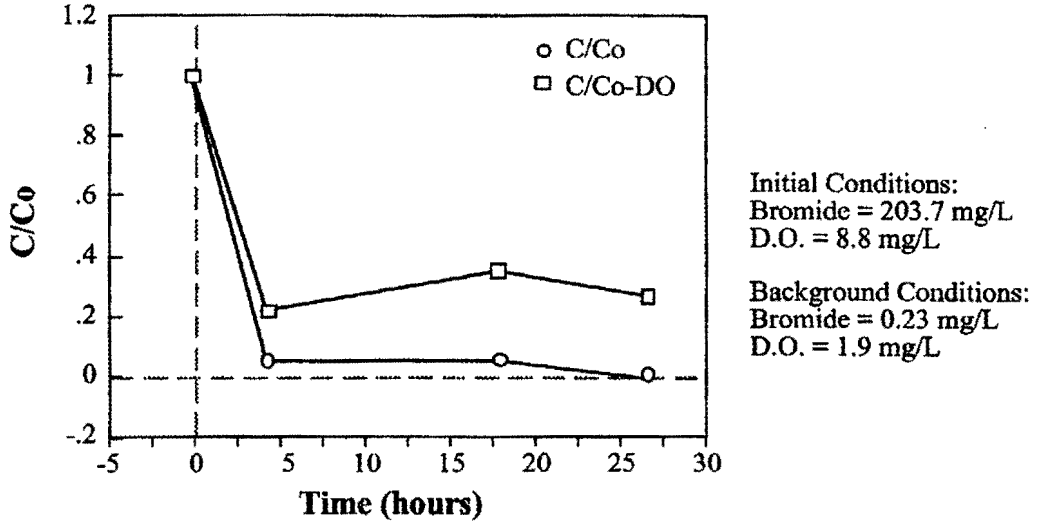


Figure 5.7. Bromide Tracer Push/Pull Test for Well No. 3034: October, 1991.

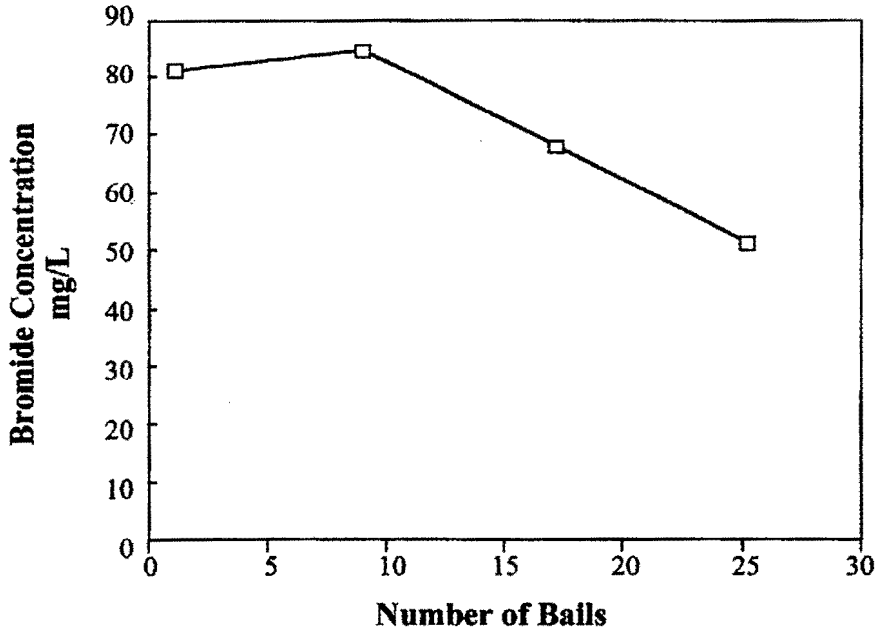


Figure 5.8. Number of bailings required to achieve a constant Bromide concentration in Well No. 3010.1: October, 1991.

(Tables 5.1 and 5.2); therefore, the site has an abiotic oxygen demand in addition to the biological oxygen demand of the organic contamination. In general, concentrations of reduced chemicals were inversely related to dissolved oxygen concentrations. The presence of the abiotic oxygen demand presents challenges with respect to the evaluation of uptake of oxygen due to microbial activity. Due to this abiotic oxygen demand, the calculation of ratios of electron acceptors (oxygen-demanding substances) to electron donors (organic contaminants) regarding biological activity is not possible. Since both abiotic and biotic demands are occurring simultaneously, the amount of oxygen available for microbial degradation of organic contaminants is reduced.

5.2 *Phase II - Performance of a Field Evaluation to Assess the Performance of Remediation Activities with Regard to Removal of Contaminants Associated with the Subsurface Solid Particles and Oily Materials.*

The effectiveness of remedial activities was evaluated by performing the following tasks:

(1) collection of aquifer core samples from background areas and from contaminated areas undergoing treatment with hydrogen peroxide and nutrients for use in laboratory studies and for analysis for residual contamination;

(2) analysis of dissolved oxygen concentrations and temperature in selected ground-water wells;

(3) analysis of ground-water samples collected from selected wells to determine hydrogen peroxide concentrations;

(4) analysis of soil gas at selected sites near an injection well to determine concentration of oxygen in the soils above the site of injection of hydrogen peroxide in order to assess whether degassing of hydrogen peroxide from the aquifer was occurring;

(5) analysis of ground-water samples collected from selected wells for the presence of compounds that indicate the oxidative-reductive status of the aquifer;

(6) determination of aqueous phase concentrations of PAH compounds and PCP in ground-water samples collected from wells within and not within the influence of the intermediate injection area and from a well in an uncontaminated background area;

(7) determination of nonaqueous phase concentrations of PAH compounds, PCP, and TPH in a NAPL sample collected from a well downgradient from the intermediate injection area; and

(8) determination of solid phase concentrations of PAH compounds, PCP and TPH in aquifer core samples in contaminated areas receiving nutrients and oxygen and in a background uncontaminated aquifer core sample.

Table 5.1. *Concentrations of Compounds that Indicate the Oxidative-Reductive Status of the Upper Aquifer: October, 1991.*

Well No.	Iron (II) (mg/L)	Mn (II) (mg/L)	D.O. (mg/L)
Wells Outside the Plume			
3014.1	nd	3.02	2.4
3034	4.89	6.62	1.9
Wells Inside the Plume			
3003.2	1.07	2.13	2.3
3010.1	0.56	2.76	3.0
3017.1	9.54	6.17	1.9

[1] nd = non-detectable

Table 5.2. *Concentrations of Compounds that Indicate the Oxidative-Reductive Status of the UpperAquifer: April, 1992.*

Well No.	Iron (II) (mg/L)	Mn (II) (mg/L)	SO_4^{-2} (mg/L)	NO_3^{-1} (mg/L)	D.O. (mg/L)	(mg/L)
Wells Outside the Plume						
3011.1	nd[1]		nd	1.9	nd	3.6
3014.1	nd		nd	11.2	nd	3.2
3014.2	nd		0.7	8.4	nd	6
3021	nd		nd	2.7	nd	3.7
3027	nd		nd	10.3	nd	2.5
3033	nd		0.6	8.5	nd	1.4
3034	5.8		0.5	5.1	nd	1.4
3036	1.2		6.0	9.6	nd	1.7
3037	2.0		2.7	13.7	nd	1
Wells Inside the Plume						
3002.1	nd		nd	6.9	nd	5.3
3003.1	5.2		1.0	1.3	nd	1.3
3008.1	10.3		3.1	nd	nd	2.3
3010.1	1.1		0.1	3.5	nd	1.2
3013.1	nd		1.2	10.4	nd	1.5
3017.1	10.7		1.8	nd	nd	1.7
3018.1	nd		nd	6.3	nd	3.3

[1] nd = non-detectable

5.2.1 Task 1: Collection of Aquifer Core Samples from Background Areas and from Contaminated Areas Undergoing Treatment with Hydrogen Peroxide and Nutrients for Use in Laboratory Studies and for Analysis for Residual Contamination

5.2.1.1 *Experimental Approach and Methods for Aquifer Core Sampling*

Core samples were collected in November 1992, in the following areas: (1) control area (upgradient); and (2) contaminated areas downgradient of injection wells (Figure 5.9; Table 5.3). This strategy was designed to allow evaluation of the effect of injection of nutrients and hydrogen peroxide on the biodegradation of PAH compounds, PCP, and total petroleum hydrocarbons (TPH) associated with aquifer core materials. Groundwater monitoring data from Well No. 3025 during the pilot-scale study had indicated that contaminants may have still been present in the pilotscale study area, so the downgradient cores were specifically located within that area. Collection of a second set of cores was initially planned to evaluate changes in contaminant concentrations as a function of time, but due to results from the initial sampling in November 1992, the collection of additional cores was not conducted.

The depth of sampling was approximately 20-30 feet bgs. The method of drilling used was air rotary with casing hammer, a technique that has been used at the Libby Site by a local contractor, B&B Drilling. B&B Drilling performed all drilling for this field evaluation. A sampling procedure developed at the U.S. EPA Robert S. Kerr Environmental Research Laboratory was used to obtain aquifer core samples (Leach et al., 1988). A 5-foot long, 4-inch diameter core barrel equipped with a retainer basket and plunger seal was attached to the drill stem, lowered into the cased hole and driven into the subsurface. The core barrel was extracted from the hole and a 2-foot section of the core was extruded using a hydraulic jack. The core was laid out on a preparation table (aluminum foil-lined PVC half pipe) and halved over the length of the core (i.e., split sample). One-half was quartered and composited into a glass container. The sampling intervals began near the water table and proceeded at selected depths for approximately 20-30 feet. The core barrel was rinsed off with tap water between samples, and the water was disposed of in the above-grade bioreactor system. Large rocks and boulders often hindered penetration of the sampler. These rocks were crushed by the drill hammer to form cuttings. Cuttings and ground water produced during drilling were contained in a diverter. The diverter was periodically emptied using a forklift. Each core hole was carefully plugged after drilling to prevent cross-contamination of the aquifer.

Vertical profiles of each core were characterized on site by Lowell E. Leach, a geological engineer associated with the RSKERL. Subsamples of each core were taken with depth. Aquifer core (i.e., undisturbed) samples were taken in unconsolidated sediments, while at depths where large rocks were present, aquifer cuttings samples (which represented disturbed samples) were taken. Samples were not collected below the area of influence of the injection wells (Figure 5.10). Injection well 9500 is screened at the base of the Upper Aquifer from 45 to 65 feet bgs. Samples were placed and sealed in appropriately labeled, pre-cleaned (rinsed with solvent and distilled water and autoclaved) 1-quart Mason jars.

After all samples had been collected, the sample jars were wrapped in newspaper and placed in a cooler with "blue ice." The coolers were secured with filament tape and shipped by express services to the UWRL in Logan, Utah, for analysis.

All personnel involved in core sample extraction, handling, and packing had received the *Hazardous Waste Operations and Emergency Response* training required under OSHA 1910.120. Personnel in the drilling and core handling areas wore appropriate protective clothing (i.e., Level C).

5.2.1.2 *Results of Aquifer Core Sampling*

Boring logs were prepared for the boreholes drilled where the samples were collected and are presented in Figures 5.11 through 5.14. One hole was drilled in an uncontaminated area, while three holes were drilled in the intermediate injection area where nutrients and hydrogen peroxide were introduced to the aquifer to stimulate

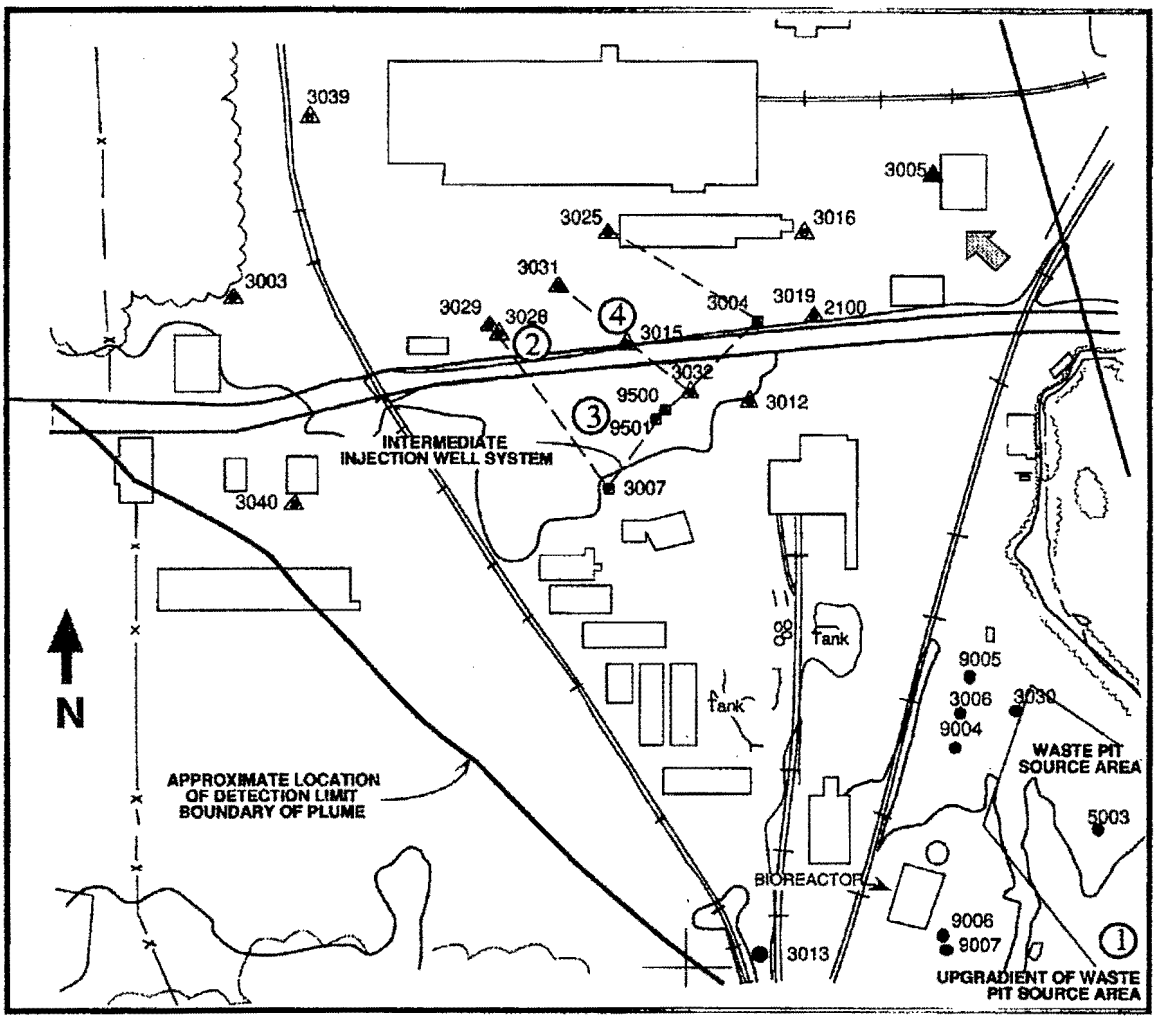


Figure 5.9. Schematic of Site showing locations of Injection Wells, Monitoring Wells, and Aquifer Drilling Core locations.

microbial activity for *in situ* bioremediation of target PAH compounds and PCP. Samples taken from the boreholes revealed a highly heterogeneous, rocky formation. Very little finer-grained soil materials, as represented by the sand, silt, and clay size fractions, were present in the samples. Unconsolidated material (cores) and consolidated material (aquifer cuttings) were subsampled in the field and placed and sealed in glass jars for measurement of contaminant concentrations and for the performance of laboratory evaluation of microbial metabolic potential to transform the target compounds, including PCP and the PAH compound, phenanthrene.

Table 5.3. Aquifer Core Drilling Locations: November 1992.

Core No.	Comments	Rationale
1	Background: upgradient from the waste pit area (200 feet south of land treatment units and approximately 600 yards south of Core # 3)	Background PCP/PAHs/TPH
2	Downgradient from injection wells in the intermediate injection area (pilot study area) (~ 31 feet southeast of the axis between Injection Site 3007 [~5 yr operation] and Monitoring Well 3026)	PCP/PAHs/TPH upgradient from monitoring wells & downgradient from injection wells of the intermediate injection system
3	Downgradient from injection wells in the intermediate injection area (~ 58 feet northwest of Injection Well No.3007 directly towards Well No. 3026)	Same as Core # 2, but closer to injection wells (Core # 2 had exhibited visual evidences of contamination, so a core closer to injection wells was selected)
4	Downgradient from injection wells in the intermediate injection area (~ 51 feet north of Injection Wells No. 9500/9501 [~ 3 yr operation] directly towards Well No. 3015.1)	Same as Cores # 2 and # 3, but closer to injection wells and towards the of the center of the zone of influence of the intermediate injection system

5.2.2 Task 2: Analysis of Dissolved Oxygen Concentrations and Temperature in Selected Ground-water Wells

5.2.2.1 *Experimental Methods for Measurement of Temperature and Dissolved Oxygen Concentrations*

Dissolved oxygen measurements were performed at the wellhead. Ground-water samples were collected using either a bladder pump or an air lift evacuation pump connected to a sampling bladder. Analyses for dissolved oxygen and temperature were performed using a YSI Dissolved Oxygen instrument (YSI, Inc., Yellow Springs, Ohio). Two to three pore volumes of the well were purged prior to performing the analysis. Monitoring wells within the influence of the intermediate injection system sampled included: Nos. 3026, 3032, 3029, 3015.1, and 3025. Monitoring wells outside the influence of the intermediate injection system sampled included: Nos. 3012.1 and 3016.1. If LNAPL was present in a well, it was measured during this sampling event using an ORS Interface Probe.

5.2.2.2 *Results of Measurement of Temperature and Dissolved Oxygen Concentrations*

Results of measurements of temperature and dissolved oxygen concentrations for water from selected wells are presented in Table 5.4. The average temperature of the wells was 9.2° C. In Well No. 3026, the

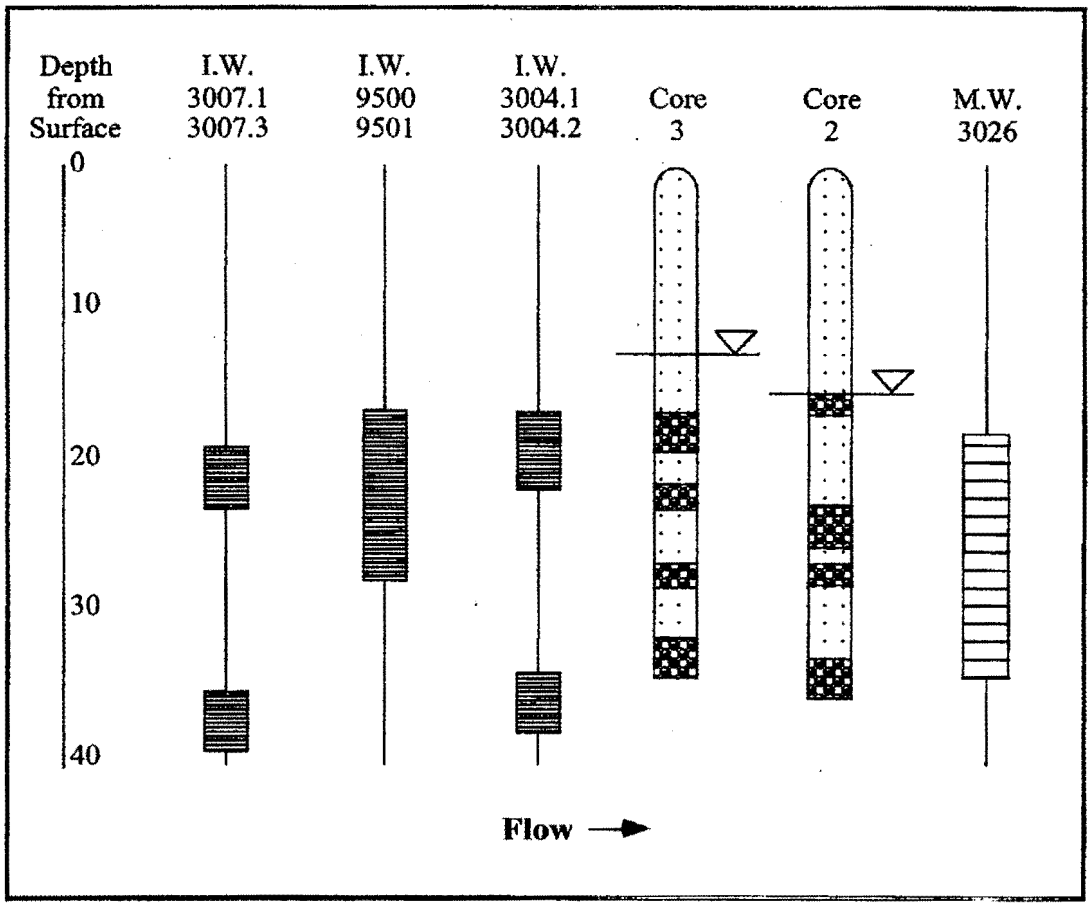


Figure 5.10. Location of Core Nos. 2 and 3 and depths of Injection Well Screens (I.W. = Injection Well and M.W. = Monitoring Well).

average yearly temperature in 1992, based on monthly measurements, was 9.9° C (data provided by Champion International). The monthly measurements were:

1/92: 7.0° C (estimated)
2/92: 6.0° C
3/92: 5.8° C
4/92: 6.3° C
5/92: 8.1° C
6/92: 9.3° C
7/92: 11.6° C
8/92: 14.1° C
9/92: 14.1° C
10/92: 15.8° C
11/92: 11.8° C
12/92: 9.0° C (estimated).

Seasonal fluctuations in temperature over the year are also evident the data presented above.

Drilling Log

Project: Champion International Corp., Libby, Montana	Date Drilled: 11-21-92
Hole No: #1 (Background)	Bot. Hole Depth: 20' 5"
Location: ~600 yd. south of hole #3. 200' S of land treatment units	No. Of Samples: 1 Core
Type of Drill: Air Rotary with Casing Hammer	Depth to W.T.: 18' 3"
Size of Bit: 5 1/2" Carbide Tip	Driller: B & B Drilling, Libby, MT., Dave Iliff
Size of Casing: 6" I.D. Welded	Log Prepared By: Lowell Leach
Type of Sampler: 4" O.D. Thinwall Barrel with Piston	Consulting Engineer, OK, PE 6951

Depth Scale Ft	Description	Geol Symbol	Remarks
	Tan to yellow silty sandstone chips with 10% grey angular limestone up to 1/2". 2 to 3% black granitic chips		0 – 5' drill cuttings
5	50% grey and 50% tan angular chips. Sandstone and limestone gravels		5' – 9' drill cuttings
10	Material continuous mixture of tan sandstone and grey limestone chips grading to higher % limestone with depth		9' 0" – 19' 4" drill cuttings
15			First moisture 15' 10"
			18' 3" water table
20	Tan and grey medium round sand and limestone		19 4" to 20' 5" core sample to refusal. 6" recovery
	Gravels 1/4 to 3/4" diameter		Bottom of Hole 20' 5" No evidence of Pentachlorophenol
25			
30			✱ Core Samples

Figure 5.11. Drilling Log for Core No. 1 (Background).

Drilling Log

Project: Champion International Corp., Libby, Montana	Date Drilled: 11-18-92
Hole No: #2	Bot. Hole Depth: 33' 8"
Location: Approximately 31' SE of Well 3026	No. Of Samples: 4 Cores
Type of Drill: Air Rotary with Casing Hammer	Depth to W.T.: 16'
Size of Bit: 5 1/2 Carbide Tip	Driller: B & B Drilling, Libby, MT. Dave Iliff
Size of Casing: 6" I.D. Welded	Log Prepared By: Lowell Leach
Type of Sampler: 4" O.D. Thinwall Barrel with Piston	Consulting Engineer, OK, PE 6951

Depth Scale Ft	Description	Geol Symbol	Remarks
	Tan silty sand with few 1/2" diameter elongated moderately rounded gravels. Approx. 10% gravels		0 – 5' drill cuttings
5	Tan weathered limestone silty texture with green and black gravels varying in size from BB to 1/2". Granules 20% tan and 10% black and green. Very angular		5 – 10' drill cuttings
10	Gray angular limestone with light orange brown clay balls (<10%)		10 – 12' drill cuttings
	Weathered tan limestone, subangular with pea size clay balls		12 – 13' drill cuttings
			First Odor of Pentachlorophenol
15	Tan to yellow sandstone. Medium soft with gravels shot size to 1/4" well ground		13 – 16' drill cuttings
			16' — W.T. on drill rod
	Red/gray/green mixture of 1/4" to 3/4" semiround gravel. 90% gravel 10% silt		16' 1" – 16' 7" core sample #1 to refused
20	Grey/green/black angular gravel 18' to 23' 6" tan very angular limestone shot size to 1/2" mixed with black angular granitic chips		16' 7" – 23' 6" drill cuttings
25	Well rounded green to black limestone cobbles 1" - 3" diameter <10% fines		23' 6" – 24' 9" core sample recover 13 1/2" sample
	Brown/pink grey angular gravels		24' 9" – 26' 6" drill cuttings
	1/2 to 1 1/2" grey-green wellround limestone		26' 0" – 26' 6" core sample
30	Tan silty sand 10%, 40% grey/red/green angular gravels		29' 6" – 31' 0" drill cutting sample
	50% course angular gravels. 1/2" to 3/4" dark grey limestone		31' 0" – 32' 6" cuttings sample 32' 0" – 33' 8" core sample
	10% tan silty sand, 50% semiangular cobbles 1/2" to 3" grey limestone		Bottom of Hole 33' 8"

✱ Core Samples

Figure 5.12. Drilling Log for Core No. 2 (31 feet SE of Monitoring Well No. 3026).

Drilling Log

Project: Champion International Corp., Libby, Montana	Date Drilled: 11-19-92
Hole No: #3	Bot. Hole Depth: 32' 6"
Location: Approximately 58' NW of Injection Well 3007	No. Of Samples: 4 Cores
Type of Drill: Air Rotary with Casing Hammer	Depth to W.T.: 13' 6"
Size of Bit: 5 1/2" Carbide Tip	Driller: B & B Drilling, Libby, MT., Dave Iliff
Size of Casing: 6" I.D. Welded	Log Prepared By: Lowell Leach
Type of Sampler: 4" O.D. Thinwall Barrel with Piston	Consulting Engineer, OK, PE 6951

Depth Scale Ft	Description	Geol Symbol	Remarks
5	Soft tan silty sandstone with 10% grey angular limestone gravels up to 1/4" diameter		0 – 6' drill cuttings
10	50/50 mixture of tan sandstone and grey angular limestone gravels, BB to 1/2" size. 10% silty sand		6 – 11' drill cuttings
	Tan sandstone chips. BB top 1/2" angular		11' - First moisture *12' First Odor of Pentachlorophenol* 1 – 13' drill cutting *Water Table ~ 13' 4"*
15	Grey to green mixture of 1/4" to 3/4" limestone gravels. 90% gravel with 10% tan silty sand. Well rounded		16' 5" – 18' 0" core sample
20	Tan very angular limestone chips Shot size to 1/2" with black chips		18' 5" – 20' 0" cutting sample
	Tan & grey angular chips of limestone 1/4" to 3/4". About 10% silty sand		20' 0" – 21' 5" cuttings sample
	1/4" to 3" gray limestone cobblers, angular 10%. Fine silty sand.		22' 4" – 23' 3" core sample
25	Green to black limestone chips. 1/4" to 1/2" angular. 10% fines		23' 3" – 24' 9" cutting sample
	Course well rounded grey limestone gravel 1/4" to 1 1/2". 10% fine tan silts		25' 10" – 26' 8" core sample *Noted oily sheen on sample*
	Grey and green limestone chips. 1/2/4" to 3/4"		26' 8" – 27' 6" cutting sample
30	Tan silty sand 10%, grey/red/green angular gravels. 1/2" to 3/4"		27' 6" – 29' cutting sample
	BB to 3/4" angular and well rounded pebbles grey and black limestone & granite		29' – 30' 10" drill cuttings *Strong penta odor*
	10% tan silty sand, 50% semiangular cobbles 1/2" to 2" grey limestone		30' 10" – 32' 6" core sample *Bottom of Hole 32' 6"*
			✱ Core Samples

Figure 5.13. Drilling Log for Core No. 3 (58 feet NW of InjectionWell No. 3007).

Drilling Log

Project: Champion International Corp., Libby, Montana	Date Drilled: 11-20-92
Hole No: #4	Bot. Hole Depth: 31' 6"
Location: Approx. 51' N of Injection Well 9500/9501	No. Of Samples: 3 Cores
Type of Drill: Air Rotary with Casing Hammer	Depth to W.T.: 8' 6"
Size of Bit: 5 1/2" Carbide Tip	Driller: B & B Drilling, Libby, MT., Dave Iliff
Size of Casing: 6" I.D. Welded	Log Prepared By: Lowell Leach
Type of Sampler: 4" O.D. Thinwall Barrel with Piston	Consulting Engineer, OK, PE 6951

Depth Scale Ft	Description	Geol Symbol	Remarks
5	Tan silty sand with few angular grey limestone chips <1/2". 10% black/grey granitic chips. Small gravels well rounded		0 – 7' drill cuttings
10	Grey angular limestone chips with tan to yellow sandstone. 1/4" to 3/4".		First moisture in cuttings @ 10' Water table at 8' 6" 13' 8" to 15' 0" core sample Recovery 8"
15	Grey to green mixture of 1/4" to 1 1/2" well rounded limestone gravels 10% tan silty sand.		
	1/8" to 1/2" gray limestone chips, few pink granitic & white xlts. <5%.		15' 0" to 16' 6" cuttings sample
	Grey & green 1/4 to 1" angular limestone chips. 10% silty sand.		17' 2" to 18' 8" cuttings sample
20			18' 8" to 19' 0" core sample immediate refusal no recovery
25	Mixture of 1/8 – 1/2" angular chips grey to tan limestone with 5% red and black granitic chips.		18' 6" to 25' 0" 2-cuttings samples. material same.
30	BB to 3/4" angular grey/brown and few red and green chips. Approximately 80% limestone mixed with granitic chips.		25' 0" to 30' 10" drill cuttings
	10% silty sand. 1/2 to 2" grey limestone cobbles		30' 10" to 31' 6" core sample Recovery 8" Bottom Hole - 31' 6"
			✱ Core Samples

Figure 5.14. Drilling Log for Core No. 4 (51 feet N of Injection Well Cluster 9500/9501).

Table 5.4. Temperature, Oxygen, and Hydrogen Peroxide Measurements for Ground Water from Selected Wells: November 19, 1992.

Well No.	Temperature (°C)	D.O. (mg/L)	H_2O_2 (mg/L)
Injection Wells:			
3004.1	-	-	108
3004.2	-	-	96
3007.1	-	-	97
3007.3	-	-	123
9500	-	-	110
9501	-	-	112
Monitoring Wells Within the Influence of the Intermediate Injection System			
3026	11.4	>20	2.0
3032	5.8	>20	3.4
3029	7.4	>20	-
3015.1	9.7	2.7	-
3025	10.0	2.8	-
Monitoring Wells Outside the Influence of the Intermediate Injection System			
3012.1	9.5	0.7	5.0
3016.1	10.5	0.7	-

Dissolved oxygen concentrations ranged from 0.68 to greater than 20 mg/L, where the higher D.O. concentrations indicate the influence of hydrogen peroxide injection. In Well No. 3025, a 0.1 foot layer of LNAPL was measured on the surface of the water table.

5.2.3 Task 3: Analysis of Hydrogen Peroxide Concentrations in Ground-Water Samples Collected from Selected Wells

5.2.3.1 *Experimental Method for Measurement of Hydrogen Peroxide Concentrations*

Hydrogen peroxide analyses were performed using a titanium sulfate acid colorimetric procedure modified from the procedure developed by Boltz and Howell (1978). A field spectrophotometer was used to measure absorbance (ABS) at 407 nanometers. One mL of titanium sulfate/H_2SO_4 reagent was added to ten mL of sample. A calibration curve was prepared using a Spectronic 20 spectrophotometer in the on-site laboratory. Linear regression analysis (for 0 to 40 mg/L H_2O_2) was performed; the regression parameters were as follows:

$r^2 = 0.999$
x coefficient = 0.022232
y intercept = 0
ABS = 0.0222 $[H_2O_2]$ or $[H_2O_2]$ = 45.05 ABS

5.2.3.2 *Results of Measurement of Hydrogen Peroxide Concentrations*

Results of measurement of hydrogen peroxide concentrations for water from selected wells are presented in Table 5.4. Hydrogen peroxide concentrations in the injection wells were approximately 100 mg/L, the target concentrations. Hydrogen peroxide concentrations were low in Monitoring Well Nos. 3026, 3032, and 3012.1, where loss of hydrogen peroxide may have been due to utilization by microorganisms and also to reactions with reduced inorganic chemicals such as ferrous iron and manganous manganese. Hydrogen peroxide may also degas upon reaction with mineral surfaces of the subsurface. Well No. 3032 is located 30 to 35 feet laterally to the 9500/9501 injection cluster. The low hydrogen peroxide concentration may indicate that a significant rate of hydrogen peroxide decomposition is occurring in a relatively small area away from these wells.

5.2.4 Task 4: Analysis of Soil Gas at Selected Sites Near an Injection Well to Determine Concentration of Oxygen in the Soils Above the Site of Injection of Hydrogen Peroxide in Order to Assess Whether Degassing of Hydrogen Peroxide from the Aquifer was Occurring

5.2.4.1 *Experimental Method for the Analysis of Soil Gas to Assess Degassing of Hydrogen Peroxide*

Soil gas samples were collected in the vicinity of Injection Well Cluster 9500/9501. Soil gas samples were obtained using a series of (0.5 inch O.D.) galvanized pipe that were coupled together and driven into the subsurface to the desired depth(s). Several depths were measured to evaluate vertical concentrations of oxygen within the vadose zone near the Injection Well Cluster 9500/9501. A hand-held, positive displacement pump was used to pump gas into the sample vessel containing an oxygen detector.

5.2.4.2 *Results of the Analysis of Soil Gas to Assess Degassing of Hydrogen Peroxide*

Results of the measurement of soil gas at selected sites near Injection Well Cluster 9500/9501 are presented in Table 5.5.

Results of soil gas sampling show that hydrogen peroxide was degassing near the injection wells and entering the overlying vadose zone. The degassing was observed while dissolved oxygen concentrations in wells 3026, 3032, and 3029 were in excess of 20 mg/L. This degassing represents an abiotic pathway for loss of oxygen in the subsurface; this pathway accounts for part of the decrease in hydrogen peroxide concentrations within the water phase as peroxide moves from an injection well to a monitoring well within the subsurface at the site.

5.2.5 Task 5: Analysis of Ground-Water Samples Collected from Selected Wells for the Presence of Compounds that Indicate the Oxidative-Reductive Status of the Upper Aquifer

5.2.5.1 *Experimental Methods for the Analysis of Compounds that Indicate the OxidativeReductive Status of the Upper Aquifer*

Ground-water samples were collected from monitoring wells within the influence of the intermediate injection area, Well Nos. 3015.1, 3025, 3029, and 3032; wells outside the influence of the intermediate injection area, Well Nos. 3012.1 and 3016.1; and a background well, Well No. 3001. The methods used for the analysis of iron, manganese, nitrate, and sulfate are presented in Section 5.1.2.1.

Table 5.5. Chemical Analysis of Soil Gas for Oxygen Concentrations Near Injection Well Cluster 9500/9501: November 21, 1992.

Sample Location Relative to Injection Well Cluster 9500/9501	Depth (Feet)	Oxygen Gas Content (%)
10.4 Feet NW	1	20.2
10.4 Feet NW	2	36.8
13 Feet W	2.6	19.4
13 Feet W	5.0	21.9
13 Feet W	7.4	53.8
10.6 Feet SE	2.6	20.9
10.6 Feet SE	5.0	48.2
13 Feet E	2.1	12.1

5.2.5.2 *Results of Analyses for the Presence of Compounds that Indicate the Oxidative-Reductive Status of the Upper Aquifer*

Results of ground-water analyses for inorganic chemicals, including iron, manganese, sulfate, and nitrate, are presented in Table 5.6. Results indicated that reduced iron and manganese were present in the ground water, with the highest concentrations associated with Well Nos. 3012.1 and 3016.1. These wells are outside the influence of the intermediate injection system and therefore, outside of the influence of the oxidation source, i.e., hydrogen peroxide. Water from these wells also had the lowest D.O. concentrations, indicating reducing conditions in the ground water. Conversely, reduced iron and manganese concentrations were lowest in ground water under the influence of the intermediate injection system, where a more oxidizing environment was present, indicated by elevated levels of D.O. due to the injection of hydrogen peroxide. Reduced iron and manganese may exert an abiotic oxygen demand on the ground-water environment at the site. Oxidized manganese (IV) has been shown to react abiotically with intermediates of PAH degradation to transform the intermediates and result in the reduction of manganese IV to manganese II (Whelan, 1992; Whelan and Sims, 1995; Whelan and Sims, 1995).

Although reduced compounds were present, reducing conditions were not sufficient to transform sulfate to hydrogen sulfide.

Table 5.6. Concentrations of Compounds that Indicate the Oxidative-Reductive Status of the Upper Aquifer: November, 1992.

Well No.	Iron (II) (mg/L)	Mn (II) (mg/L)	SO_4^{-2} (mg/L)	NO_3^{-1} (mg/L)	D.O. (mg/L)
Wells Within the Influence of the Intermediate Injection System					
3029	1.07	3.10	1.994	0.032	>20
3032	0.93	nd[1]	2.542	1.560	>20
3015.1	1.61	0.10	2.918	0.766	2.7
3025	2.49	0.33	2.173	0.443	2.8
Wells Outside the Influence of the Intermediate Injection System					
3012.1	4.25	2.72	1.073	nd	0.7
3016.1	2.50	4.45	0.209	nd	0.7
Well In Background Area					
3001	0.54	nd	4.336	0.097	——[2]

[1] nd = non-detectable
[2] not measured

5.2.6 Task 6: Determination of Aqueous Phase Concentrations of PAH Compounds and PCP in Ground-Water Samples Collected from Wells Within and Not Within the Influence of the Intermediate Injection Area and from a Well in an Uncontaminated Background Area

5.2.6.1 *Experimental Methods for the Analysis of Ground-Water Samples for PAH Compounds and PCP*

Ground-water samples were collected from two wells under the influence of the intermediate injection system, Well Nos. 3015.1 and 3025; from two wells outside the influence of the intermediate injection system, Well Nos. 3012.1 and 3016.1; and from a well in an uncontaminated background area, Well No. 3001. Well Nos. 3015.1 and 3016.1 were sampled before and after purging. Well Nos. 3001, 3025, and 3012.1 were sampled only after purging. A peristaltic pump was used to obtain the ground-water samples. Water removed during well evacuation was disposed in the above-ground bioreactor. The samples were extracted and analyzed for PAH compounds and PCP using the methods presented in Appendix B.

5.2.6.2 *Results of the Analysis of Ground-Water Samples for PAH Compounds and PCP*

Concentrations of PAH compounds and PCP found in the aqueous phase in selected samples from the Upper Aquifer are presented in Table 5.7.

Table 5.7. Concentrations of PCP and Pah Compounds in Ground Water: November, 1992.

Compound	Concentrations (μg/L) in Samples Collected from Well No.:		
	3015.1 (Prepurge)	3015.1 (Postpurge)	3025 (Postpurge)
Naphthalene	<0.63	<0.63	<0.63
Acenaphthylene	<1.58	<1.58	<1.58
Acenaphthalene	<1,15	<1.15	<1.15
Fluorene	<0.07	<0.07	<0.07
Phenanthrene	<0.06	<0.06	<0.06
Anthracene	<0.04	<0.04	<0.04
Fluoranthene	<0.30	<0.30	118.94
Pyrene	<0.15	<0.15	46.25
Benzo(a)anthracene	<0.07	<0.07	<0.07
Chrysene	<0.05	<0.05	<0.05
Benzo(b)fluoranthene	<0.11	<0.11	6.28
Benzo(k)fluoranthene	<0.21	<0.21	<0.21
Benzo(a)pyrene	<0.10	<0.10	<0.10
Dibenzo(a,h)anthracene	<0.27	<0.27	<0.27
Benzo(g,h,i) perylene	<0.28	<0.28	<0.28
Indeno(1,2,3-cd) pyrene	<2.11	<2.11	<2.11
Pentachlorophenol	10	1	14

Compound	Concentrations (μg/L) in Samples Collected from Well No.:			
	3016.1 (Prepurge)	3016.1 (Postpurge)	3012.1 (Postpurge)	3001 (Postpurge)
Naphthalene	13.65	<0.63	680.04	<0.63
Acenaphthylene	<1.58	<1.58	<1.58	<1.58
Acenaphthalene	<1,15	<1.15	<1.15	<1.15
Fluorene	57.98	185.16	82.57	<0.07
Phenanthrene	53.47	660.86	171.29	<0.06
Anthracene	0.91	27.98	20.54	<0.04
Fluoranthene	33.16	422.52	91.54	<0.30
Pyrene	16.28	244.87	46.28	<0.15
Benzo(a)anthracene	6.17	123.12	15.48	<0.07
Chrysene	1.09	26.32	<0.05	<0.05
Benzo(b)fluoranthene	<0.11	16.82	<0.11	<0.11
Benzo(k)fluoranthene	<0.21	<0.21	<0.21	<0.21
Benzo(a)pyrene	<0.10	<0.10	<0.10	<0.10
Dibenzo(a,h)anthracene	<0.27	<0.27	<0.27	<0.27
Benzo(g,h,i) perylene	<0.28	<0.28	<0.28	<0.28
Indeno(1,2,3-cd) pyrene	<2.11	104.61	<2.11	<2.11
Pentachlorophenol	58	98	446	<3

In Well No. 3015.1, downgradient of the intermediate injection system, concentrations of PAH compounds were low (below detectable limits), and there was little difference between prepurge and postpurge results. The concentration of PCP was found to decrease after purging. In Well No. 3025, which is farther downgradient of the injection system than Well No. 3015.1, concentrations of three PAH compounds, fluoranthene, pyrene, and benzo(b)fluoranthene, and PCP were higher than in Well No. 3015.1.

Concentrations of PAH compounds and PCP were also evaluated in wells where the ground water was not under the influence of the intermediate injection system. In Well No. 3016.1, downgradient but outside the influence of the injection system, concentrations of PAH compounds and PCP were high. There was a trend towards increasing concentrations of PAH compounds from prepurge to postpurge for nine PAH compounds in Well No. 3016.1. In Well No. 3012.1, which is upgradient of the intermediate injection system and within the contaminated plume, concentrations of PAH compounds and PCP were also high.

No contamination was evident in water collected from a background well located upgradient from the source area and the contaminated ground-water plume, Well No. 3001. Therefore, in the water phase as evaluated through the analysis of ground water for the presence of target contaminants, nondetectable concentrations of PAH compounds and PCP were associated with ground water under the influence of the intermediate injection system.

5.2.7. Task 7: Determination of Concentrations of PAH Compounds and PCP in an LNAPL Sample Collected from a Well Downgradient from the Intermediate Injection Area

5.2.7.1 *Experimental Methods for the Analysis of PAH Compounds and PCP in an LNAPL Sample*

Using an ORS Interface Probe, a layer of LNAPL measuring 2.15 ft. deep was detected in Monitoring Well No. 3031, located within the vicinity, and assumed to be within the influence, of the intermediate injection system. The top of the LNAPL layer was measured at 16.85 ft. from the top of the well casing. A sample of the LNAPL was collected and shipped to the U.S. EPA RSKERL in Ada, Oklahoma, for analysis by GC/MS using modifications of U.S. EPA Method 8270A ((U.S. EPA, 1986b) - see Appendix B-5).

5.2.7.2 *Results of the Determination of PAH Compounds and PCP in an LNAPL Sample from a Ground-Water Monitoring Well*

Both PAH compounds and PCP were found in high concentrations in the LNAPL from Monitoring Well No. 3031, as shown in Table 5.8. The intermittent presence of LNAPL at the Libby site has been report for over eight years (Piotrowski, personnel communication). These results indicate that there is contamination of the Upper Aquifer remaining in the form of a pure product phase, which represents long-term continual significant potential contamination by transfer of contaminants from the NAPL phase to the water phase.

Table 5.8. Concentrations of PAH Compounds and PCP in LNAPL Collected from Monitoring Well No. 3031: November 1992.

Compound	Concentration (mg/L)
Acenaphthylene	400[1]
Fluorene	5,080
Phenanthrene	10,080
Anthracene	2,230
Pyrene	3,040
Benzo(a)anthracene	700
Chrysene	720
Benzo(b)fluoranthene	440
Benzo(k)fluoranthene	1,160
Benzo(a)pyrene	830
Indeno(1,2,3-c,d)pyrene	41
Dibenzo(a,h)anthracene	36
Benzo(g,h,i)perylene	38
PCP	1,342

[1] Results are mean of two duplicate analyses.

5.2.8 Task 8: Determination of Solid Phase Concentrations of PAH Compounds, PCP, and TPH in Aquifer Core Samples in Contaminated Areas Receiving Nutrients and Oxygen

5.2.8.1 *Experimental Methods for the Determination of the Vertical Distribution of PAH Compounds, PCP, and TPH in Aquifer Core Samples*

Extraction and analytical methods used for samples of aquifer solids from Borehole Nos. 2, 3, and 4 (collected as described in Section 5.2.1.1) are described in Appendix B for: (1) extraction of samples (U.S. EPA Method 3550 (U.S. EPA, 1986b)) and moisture determinations for the aquifer solids (B-1); (2) analysis of PCP (U.S. EPA Method 8040 (U.S. EPA, 1986b)) using gas chromatography (B-2); (3) analysis of PAH compounds using high performance liquid chromatography (HPLC) (U.S. EPA Method 8310 (U.S. EPA, 1986b)) (B-3); and (4) analysis of TPH using gas chromatography (B-4). The UWRL Environmental Quality Laboratory is certified by the State of Utah Department of Health, Division of Laboratory Services, for analyses pertaining to environmental compliance monitoring required by the Resource Conservation and Recovery Act.

5.2.8.2 *Results of the Determination of the Vertical Distribution of Contamination*

Vertical profiles of chemical contaminants associated with the aquifer solids for Borehole No. 2 are presented in Figure 5.15 for TPAH compounds, in Figure 5.16 for PCP, and in Figure 5.17 for TPH. Numerical values for each sample are provided in Appendix C. TPAH concentrations ranged from 25 to 416 mg/kg, PCP concentrations ranged from 0.1 to 1.3 mg/kg, and TPH concentrations ranged from

184 to 2,910 mg/kg. The highest values for all these contaminants within Borehole No. 2 occurred at 23.5 - 24.8 feet bgs (7.5 - 8.8 feet below the water table). Profiles for TPAH, PCP, and TPH indicate the heterogeneous distribution of contaminants over a relatively short distance (16 feet) within the aquifer in Borehole No. 2. Comparison of contaminant profiles indicates that the contaminants are highly correlated with each other.

Vertical profiles of chemical contaminants associated with the aquifer solids for Borehole No. 3 are presented in Figure 5.18 for TPAH, in Figure 5.19 for PCP, and in Figure 5.20 for TPH. Numerical values for each sample are provided in Appendix C. TPAH concentrations ranged from 5.2 to 687 mg/kg and, therefore, demonstrated a greater spread in TPAH concentrations than that observed for Borehole No. 2. The highest TPAH concentration (687 mg/kg) was observed in the sample at 26.7 - 27.5 feet bgs. Samples containing over 400 mg/kg were also present at depths of 23.3 - 24.8 feet (404 mg/kg) and at 27.5 - 29 feet (443 mg/kg). PCP concentrations ranged from 0.1 mg/kg to 3.2 mg/kg, and TPH concentrations ranged from 258 to 1,924 mg/kg. Profiles for TPAH, PCP, and TPH indicate a heterogeneous distribution of contaminants over a 15 foot depth from the water table within Borehole No. 3. Comparison of contaminant profiles indicated that the contaminants were highly correlated with each other, and that the most contaminated interval sampled occurred at 26.7 - 27.5 feet bgs (13.4 - 14.2 feet below the water table) within Borehole No.3.

Vertical profiles of chemical contaminants associated with the solid matrix for Borehole No. 4 are presented in Figure 5.21 for TPAH, in Figure 5.22 for PCP, and in Figure 5.23 for TPH. Numerical values for each sample are provided in Appendix C. TPAH concentrations ranged from 5.8 to 216 mg/kg, with the highest value sample occurring at the sample depth of 17.2 - 18.7 feet bgs. PCP concentrations ranged from 0.1 to 7.9 mg/kg, with the high value sample occurring at 15 - 16.5 feet bgs. TPH concentrations ranged from 70 to 2525 mg/kg, with the highest value also occurring at 15 - 16.5 feet bgs. Profiles for TPAH, PCP, and TPH indicate a heterogeneous distribution of contaminants over a 17 foot interval from the water table within Borehole No. 4 at the site. Comparison of contaminant profiles indicates that the contaminants are highly correlated with each other, and that the most contaminated interval sampled occurred between 15 and 18.7 feet bgs (6.5 - 10.2 feet below the water table) within Borehole No. 4.

Comparison of results among Borehole Nos. 2, 3, and 4 indicates that concentrations and ranges of chemical contaminants in each borehole were similar, and that there was no trend of decreasing contaminant concentrations with increasing proximity to the injection system (i.e., from Borehole No. 2 to No. 3 to No. 4) (Table 5.9). Site vertical physical heterogeneity was associated with a heterogeneous vertical distribution of the contaminants, as shown in Figures 5.15 to 5.23. Preferential pathways of flow may have resulted in differences in treatment in the subsurface, with some areas more hydrodynamically connected to the intermediate injection system and some more hydrodynamically isolated from the injection system. However, even where subsurface areas were hydrodynamically connected and, therefore, received oxygen and nutrients from the injection system, the presence of immiscible NAPL in these areas (as identified in the drilling logs (Figures 5.12, 5.13, and 5.14)) results also in the presence of NAPL-associated contaminants (i.e., TPAH, PCP, and TPH) that are less susceptible to the influence of the injection system than contaminants present in the water phase or sorbed to the surface of rock particles. Therefore, reductions in concentrations of contaminants were not observed in a borehole as related to the distance of the borehole from the injection system, but rather differences in contaminant concentrations were found to be more closely related to distances below the water table.

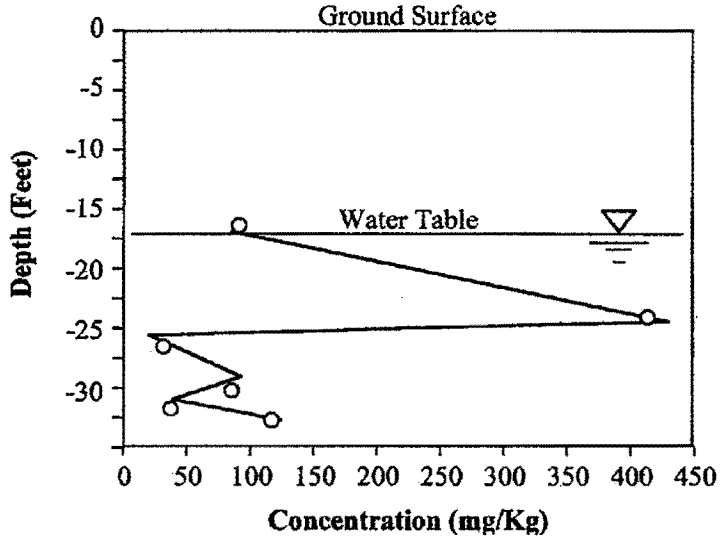


Figure 5.15. Total Poycylic Aromatic HydrocarbonConcentrations with depth in Borehole 2.

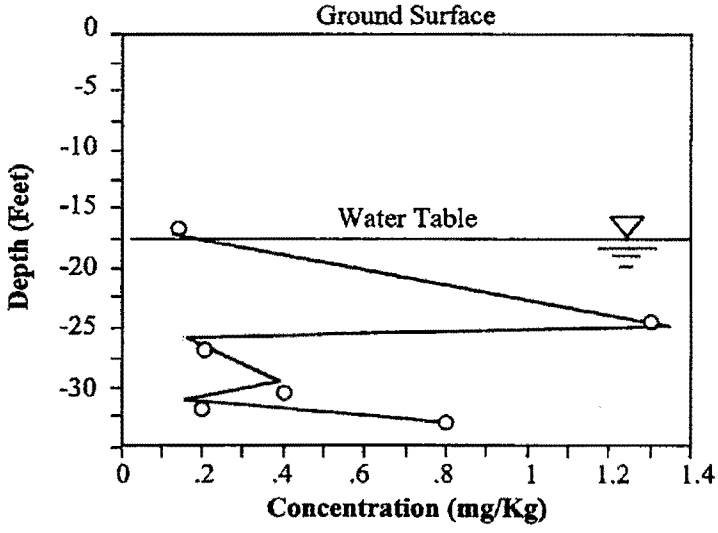


Figure 5.16. Pentachlorophenol Concentrations with depth in Borehole 2.

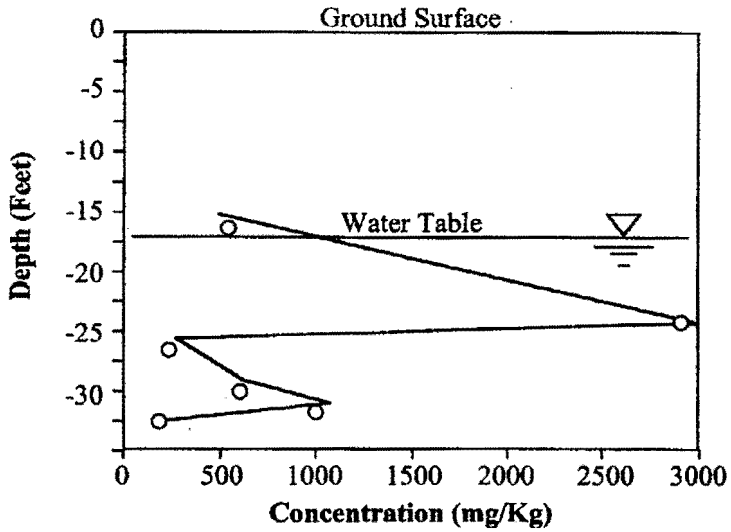


Figure 5.17. Total Petroleum HydrocarbonConcentrations with depth in Borehole 2.

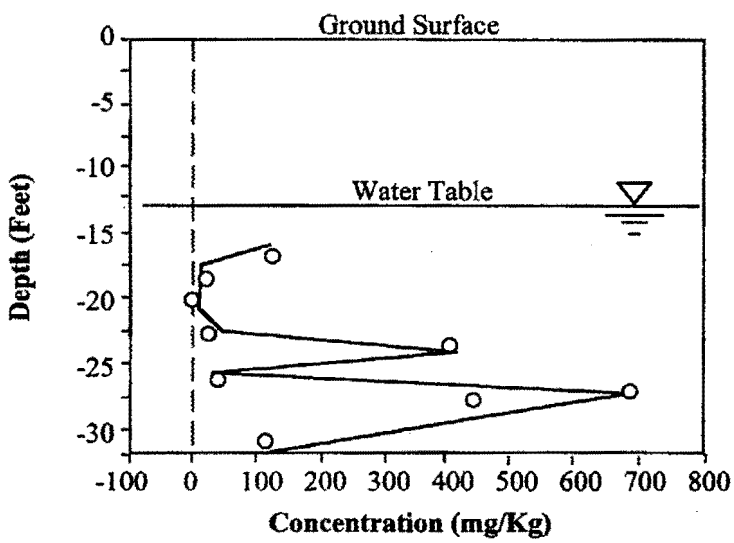


Figure 5.18. Total Polycyclic Aromatic HydrocarbonConcentrations with depth in Borehole 3.

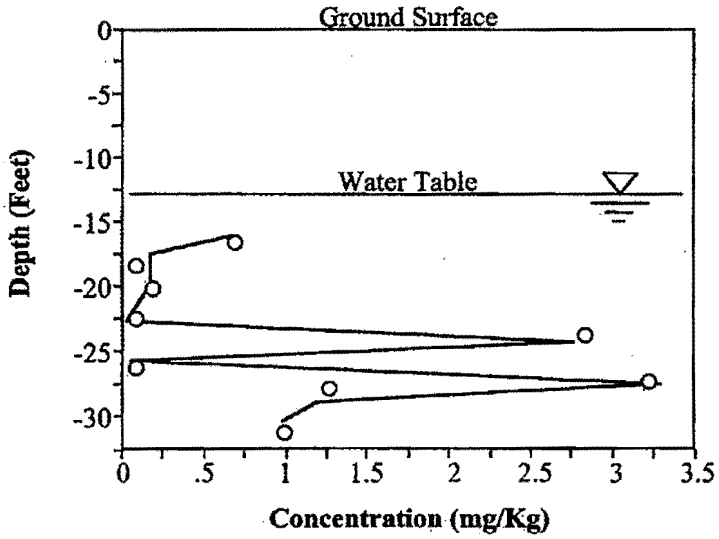


Figure 5.19. Pentachlorophenol Concentrations with depth in Borehole 3.

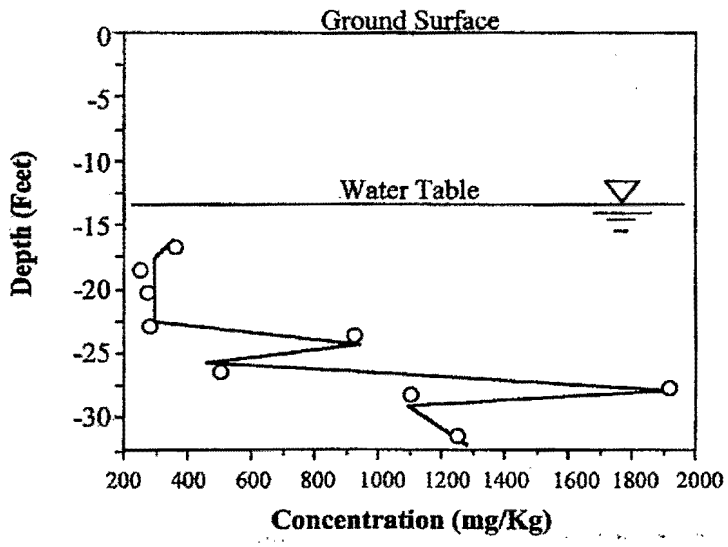


Figure 5.20. Total Petroleum Hydrocarbon Concentrations with depth in Borehole 3.

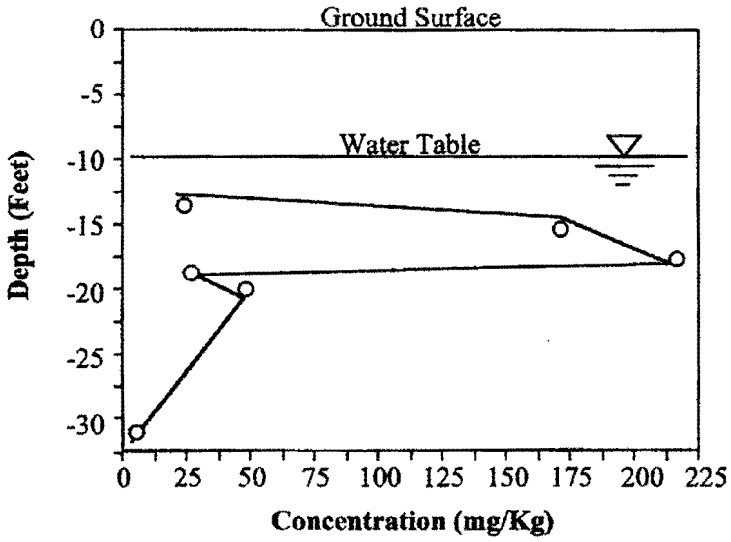


Figure 5.21. Total Polycyclic Aromatic Hydrocarbon Concentrations with depth in Borehole 4.

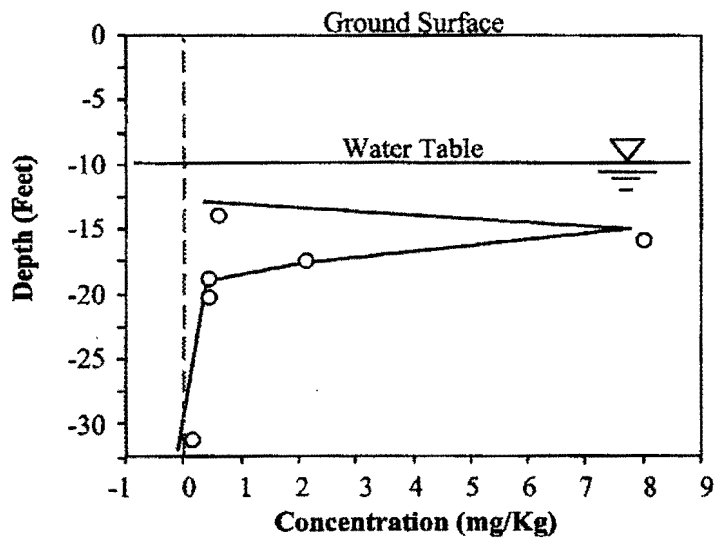


Figure 5.22. Pentachlorophenol Concentrations with depth in Borehole 4.

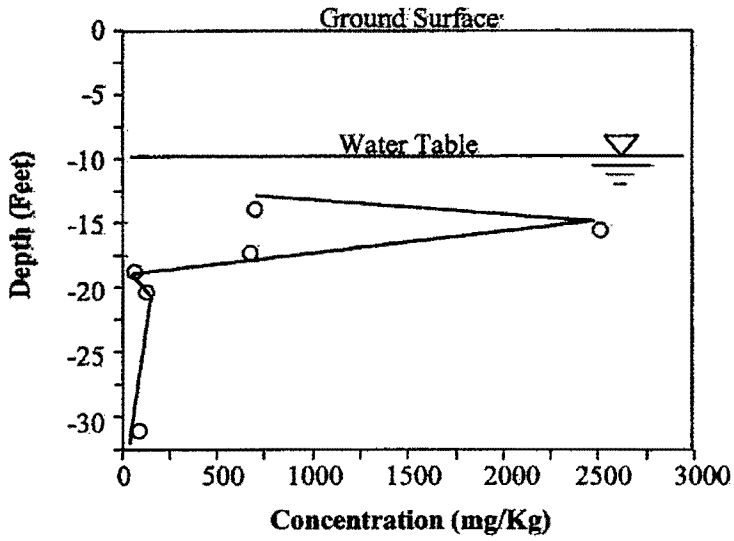


Figure 5.23. Total Petroleum HydrocarbonConcentrations with depth in Borehole 4.

Table 5.9. *Ranges of Concentrations of Contaminants Associated with Aquifer Solids: November 1992.*

Chemical Contaminant	Concentrations of Contaminants in Borehole No.: (mg/Kg)		
	2	3	4
TPAH	25 - 416	5.2 - 687	5.8 - 216
PCP	0.1 - 0.3	0.1 - 3.2	0.1 - 7.9
TPH	184 - 2,910	258 - 1,924	70 - 2,525

5.3 *Phase III - Performance of a Field Evaluation to Investigate the Role of Preferential Flow Pathways in the Intermediate Injection Area of the Upper Aquifer*

5.3.1 Purpose of Investigation

Results from analyses of ground-water samples and aquifer solids, as well as visual inspections of the aquifer cores during core acquisition, indicated that the effectiveness of bioremediation in the aquifer materials may be affected by the presence of preferential flow pathways that may be conveying relatively large volumes of injected water; these layers (or layer) may be responsible for enhanced flow but may not necessarily coincide with zones with high degrees of contamination. When ground-water samples from a well are collected, two to three well volumes are typically purged from the well before sampling; this purging may result in the sampling of water that represents a relatively large volume of ground water from a highly permeable, low contaminated zone and only a small volume of water from a slowly permeable, highly contaminated zone.

Therefore, in Phase III of the field performance evaluation, an investigation of the role of preferential flow pathways in the intermediate injection area by means of sampling and analysis of discrete levels of the ground water was conducted. Data were collected to evaluate effects of preferential flow pathways on delivery of hydrogen peroxide and nutrients and on the concentrations of contaminant concentrations in downgradient monitoring wells.

5.3.2 Experimental Methods and Materials

Sampling was conducted in March 1993 by personnel from the U.S. EPA RSKERL. Three monitoring wells in the intermediate injection area were used in the investigation: Well Nos. 3025, 3026, and 3032. Well No. 3025 is a 5 inch (inner diameter (I.D.)) cased well with a 20 foot stainless steel (4 inch I.D., #30 wire-wrapped, 0.03 inch opening) screen welded to the casing extending from 14 to 34 feet bgs. Well No. 3026 is an 5 inch (I.D.) cased well with a 15 foot stainless steel (4 inch I.D., #30 wire-wrapped, 0.03 inch opening) screen welded to the casing extending from 18 to 33 feet bgs. Well No. 3032 is a 2 inch (I.D.) well with a 10 foot stainless steel slotted (0.02 inch) screen extending from 10.5 to 20.5 feet bgs. Well construction details are presented in Table 5.10. The depths of these wells were calculated based on measurements taken during the Phase III sampling trip and do not necessarily correlate with the depths of the screened intervals provided by Champion International.

Table 5.10. *Details of Construction for Well Nos. 3025, 3026, and 3032.*

Well No.	Elevation of T.O.C.[1] (feet)	Elevation of Ground Surface (feet)	Height of Pipe[2] (feet)	Screen Interval[3] (feet)	Total Depth[4] (feet)	Depth bgs[5] (feet)
3025	2101.9	2097.4	4.49	14-34	32.1	27.6
3026	2101.6	2097.4	4.20	18-33	35.6	31.4
3032	2104.7	2101.2	3.51	10.5-20.5	24.5	20.99

[1] Elevation of top of casing (T.O.C.)

[2] Height = (elevation of top of casing - elevation of ground surface)

[3] Below ground surface (bgs)

[4] Total depth of well from T.O.C.

[5] Total depth of well from ground surface

The following assumptions were used to determine an appropriate sampling rate in order to collect ground-water samples from discrete levels within the wells: Assuming the ground-water seepage velocity was greater than 100 feet/day in the injection area (Piotrowski, 1991), the flow of ground water through a one-foot screened interval (assuming 30% open screen area) was 200 mL/min in a 4 inch (I.D.) well; and 82 mL/min in a 2 inch (I.D.) well (assuming 25% open screen area). Assuming there was no ambient flow within the well, slow-rate sampling below these rates should provide ground-water samples from discrete levels within the wells.

Therefore, slow-rate, discrete level ground-water sampling was conducted using a peristaltic pump attached to Teflon® tubing. The average flow rate of ground-water sampling was 200, 184, and 91 mL/min in Well Nos. 3025, 3026, and 3032, respectively. The end of the Teflon® tube was modified with a weighted T-joint to encourage horizontal ground-water flow so as to collect samples representative of the interval from which they were obtained. The volume of water in the tubing was removed prior to sample collection. Ground-water samples were collected at one-foot intervals in Well Nos. 3026 and 3032 and at three-foot intervals in Well No. 3025 (Figure 5.24). In addition, samples of the fire pond water amended with nutrients and hydrogen peroxide and used for injection into Well Nos. 9500 and 9501 were collected from the pipework inside the injection "houses" prior to injection. Ground water was also collected from Injection Well Nos. 9500 and 9501.

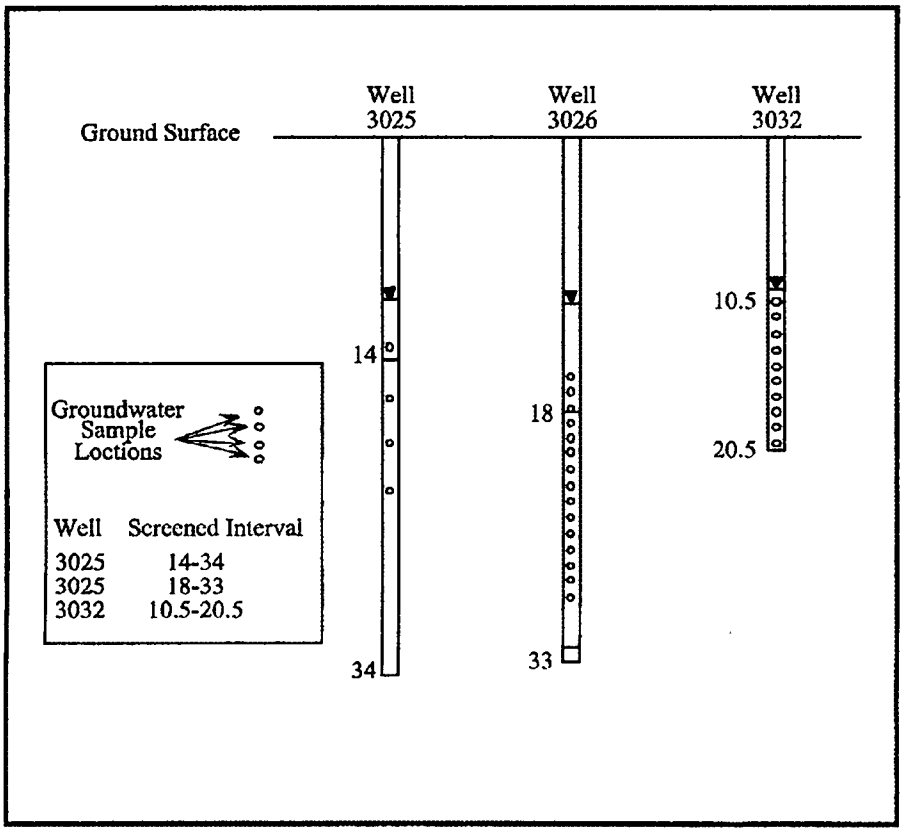


Figure 5.24. Screened Intervals and Sampling Depths for Well Nos. 3025, 3026, and 3032.

The ground-water samples were analyzed for temperature, dissolved oxygen (D.O.), hydrogen peroxide, nutrients (total phosphorus, ammonia, and nitrate-nitrite), chlorides, PAH compounds, and PCP. Injection water sampled prior to injection was analyzed for nutrients, D.O., temperature, and hydrogen peroxide (H_2O_2). Temperature, D.O., and hydrogen peroxide measurements were performed at the wellhead, using procedures described in Sections 5.2.2.1 and 5.2.3.1. Samples analyzed for nutrients and chlorides were acidified in the field and analyzed at the U.S. EPA RSKERL in Ada, Oklahoma. Ammonia (NH_3-N), nitrate/nitrite (NO_3^-/NO_2^-), chloride (Cl^-), and total phosphorus (total P) were analyzed using U.S. EPA Method Nos. 350.1, 353.1, 325.2, and 365.4, respectively (U.S. EPA, 1979). Samples used for analysis of organic compounds (PAH compounds and PCP) were collected and sealed in 1 L amber glass bottles, stored on ice, and shipped to the U.S. EPA RSKERL for extraction (using U.S. EPA Methods 3500 and 3510 (U.S. EPA, 1986b)) and analysis by GC/MS (using modifications of U.S. EPA Method 8270A (U.S. EPA, 1986b) - see Appendix B-5).

5.3.3 Results of the Investigation of the Role of Preferential Flow Pathways in the Intermediate Injection Area

5.3.3.1 *Inorganic Compounds as Indicators of Preferential Flow Pathways*

Results of the analyses for inorganic compounds in the fire pond injection water are shown in Table 5.11. These data represent only one point in time; during on-going injection operations, concentrations of the compounds vary with time.

Table 5.11. *Inorganic Compounds in Injection Water: March 1993.*

Well No.	D.O. (mg/L)	Temperature (°C)	NO_3^-/NO_2^- (mg/L)	NH_3-N Cl^- (mg/L)	Total P (mg/L)	H_2O_2 (mg/L)	(mg/L)
9500	5.1	12.1	0.26	3.32	8.24	1.21	84.4
9501	5.1	12.1	0.26	3.11	8.00	1.40	93.2

Results of analyses for inorganic compounds are shown in Figures 5.25 to 5.30 and in Appendix Table C-4. The D.O. and nitrate/nitrite concentrations at the second sampling depth in Well No. 3025 (Figures 5.25 and 5.27) indicate the presence of a possible preferential flow pathway. However, in general, the inorganic nutrient data do not conclusively indicate the presence of preferential flow pathways in the intermediate injection area. This observation is based on the absence of a clear, consistent pattern of vertical profiles of the measured inorganic compounds in downgradient wells. Variability in the data collected, as well as transformations of some of the compounds in the subsurface, also complicated the evaluation of flow pathways.

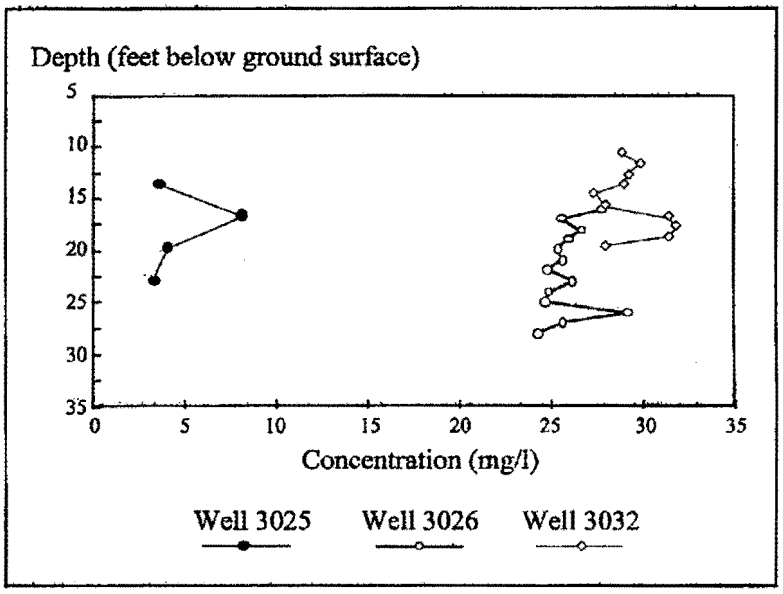


Figure 5.25. Vertical Profile of Dissolved Oxygen in the Ground Water: March, 1993.

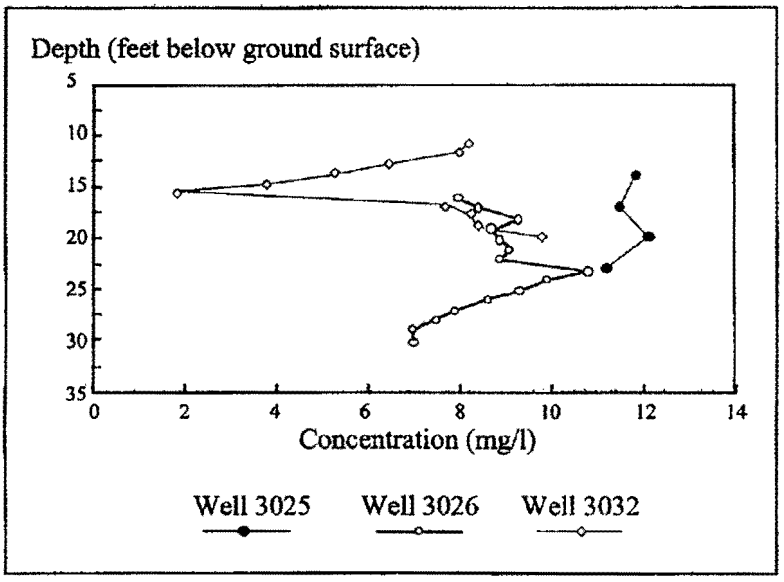


Figure 5.26. Vertical Profile of Ground Water Temperature: March, 1993.

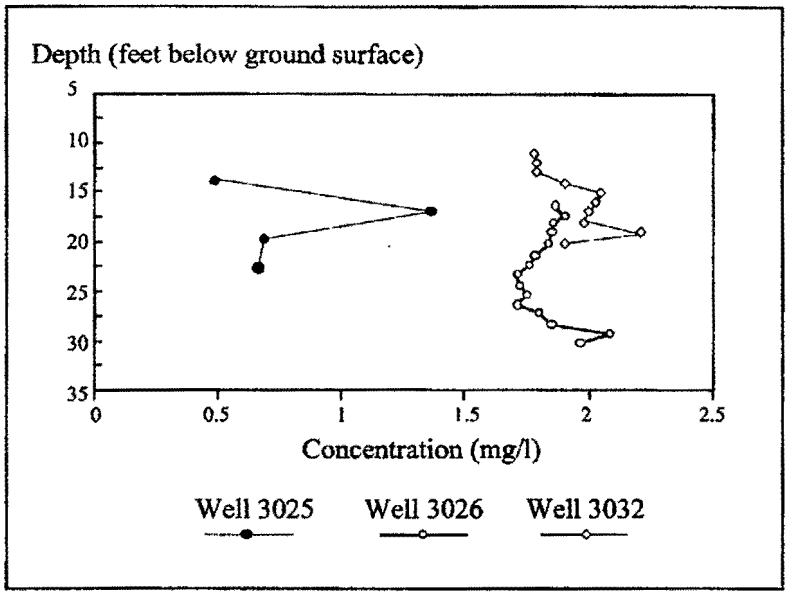


Figure 5.27. Vertical Profile of Nitrate/Nitrite in the Ground Water: March, 1993.

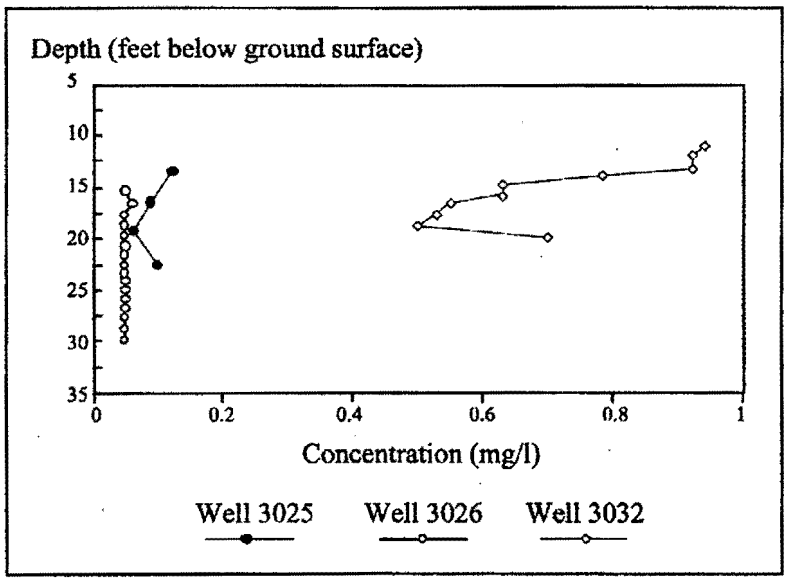


Figure 5.28. Vertical Profile of Ammonia in the Ground Water: March, 1993.

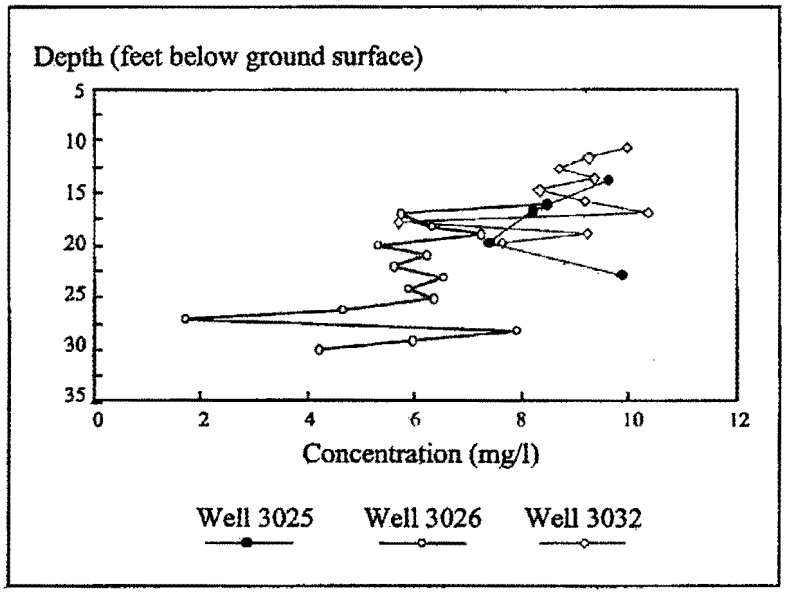


Figure 5.29. Vertical Profile of Chloride in the Ground Water: March, 1993.

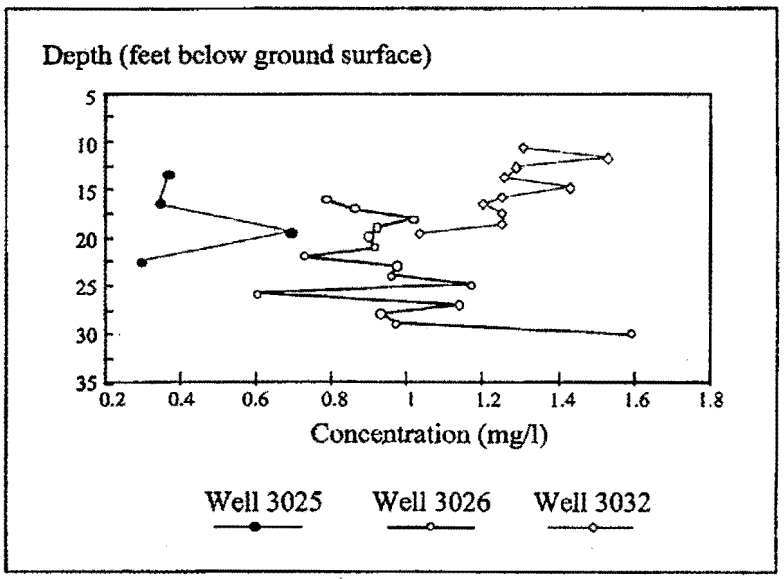


Figure 5.30. Vertical Profile of Total Phosphorus in the Ground Water: March, 1993.

Hydrogen peroxide was not detected in Well Nos. 3025 and 3026, indicating that no preferential pathway was present that allowed rapid transport of hydrogen peroxide. Hydrogen peroxide is likely to be unstable in the subsurface and decomposes rapidly, as indicated for Well No. 3032 in Table 5.12. In this well, hydrogen peroxide concentrations were less than 4 mg/L, representing greater than 95 percent decomposition within only approximately 25 feet from the injection wells. Although Well No. 3032 is located slightly upgradient under non-injection conditions, the ground-water mounding resulting from injection into Well Nos. 9500 and 9501 result in Well No. 3032 becoming a downgradient well. The presence of a preferential pathway to Well No. 3032 is not apparent from the data.

Due to hydrogen peroxide decomposition, with the associated oxygen gas generated from the decomposition, the concentration of D.O. in the ground water is greater than the concentration at saturation at 1 atmosphere. The D.O. data indicate the relative impact of the injection system on nearby wells. D.O. concentrations decrease with increasing distance from the injection wells (i.e., Well No. 3025 is located at a greater distance from the injection wells than Well Nos. 3026 and 3032.)

Measurement of the temperature of the ground water is shown in Figure 5.26. Decreasing temperature with depth for the six upper depths in Well No. 3032 may have been due to formation of ice inside the sampling line; the line had been left in the well overnight. Therefore, some of the temperature measurements may not have been representative of actual ground-water temperatures.

Nutrient and chloride data are also inconclusive with regard to identifying the presence of preferential flow pathways (Figures 5.27 to 5.30). Several sinks and sources affect the concentrations of the nutrients and chloride in the aquifer; a more complex analysis would be required to more thoroughly assess their fate and transport in this aquifer.

5.3.3.2 *Organic Compounds as Indicators of Preferential Flow Pathways*

A primary objective of this investigation was to account for the discrepancies between routine ground-water analyses, which do not show evidences of ground-water contamination remaining after *in situ* treatment, and the results of soil core analyses obtained in Phase II of this study, which showed both physical and analytical evidences of residual contamination. Groundwater samples were obtained without purging three well volumes prior to collection, in contrast to normal collection procedures, in order to see if purging results in dilution of contaminated water from aquifer layers of low conductivity.

Table 5.12. *Hydrogen Peroxide Concentrations in Well No. 3032: March 1993.*

Sample Depth (ft. bgs)	H_2O_2 Concentration (mg/L)
10.5	3.8
11.5	3.8
12.5	3.6
13.5	3.6
14.5	——
15.5	2.4
16.5	2.8
17.5	3.8
18.5	3.6
19.5	3.6

However, in Well Nos. 3026 and 3032, PCP and PAH compounds were not detected in the ground water. The detection limit of the GC/MS method used for analysis was less than 1 mg/L (or 1 ppb). The discrepancy between field observations of visibly contaminated aquifer core materials (oily appearance, dark color, and hydrocarbon odor) obtained 30 ft. upgradient from Monitoring Well No. 3026 during the November 1991 sampling trip and the lack of ground-water contamination in Well No. 3026 still exists. One possible explanation for the discrepancy is that boring #2 did not access aquifer sediments directly under the influence of the injection system (M. Piotrowski, personnel communication).

PCP and 10 of the 16 PAH compounds were detected in the ground-water samples collected from Well No. 3025 (Table 5.13). No consistent trend was observed in the concentration of the compounds with depth. Detection of PAH compounds and PCP in this well may be due to the presence of a thin film (approximately 0.01 ft.) of LNAPL in the water table in the well.

Therefore, this investigation did not definitely identify any preferential flow pathways. However, preferential pathways may exist in the aquifer, but, if present, their role in influencing contaminant concentrations in downgradient monitoring wells is not known.

Table 5.13. *Concentrations of PCP and PAH Compounds in Ground Water Collected from Well No. 3025: March 1993.*

Compound	Concentrations (μg/L) in Samples Collected from Depth (bgs)			
	13.5 ft.	16.5 ft.	19.5 ft.	22.5 ft.
Acenaphthylene	2	1	1	1
Acenaphthalene	33	2	11	<1 ppb
Fluorene	13	1	8	N.F.[1]
Phenanthrene	3	N.F.	18	N.F.
Anthracene	2	<1 ppb	5	<1 ppb
Fluoranthene	6	N.F.	15	N.F.
Pyrene	5	3	16	1
Benzo(a)anthracene	1	<1 ppb	2	N.F.
Chrysene	<1 ppb	<1 ppb	2	N.F.
Benzo(b)fluoranthene	<1 ppb	<1 ppb	<1 ppb	N.F.
Benzo(k)fluoranthene	N.F.	<1 ppb	<1 ppb	N.F.
Benzo(a)pyrene	<1 ppb	<1 ppb	1	N.F.
Indeno(1,2,3-cd) pyrene	N.F.	N.F.	N.F.	N.F.
Dibenzo(a,h)anthracene and Indenopyrene	N.F.	N.F.	N.F.	N.F.
Benzo(g,h,i) perylene	N.F.	N.F.	N.F.	N.F.
Pentachlorophenol	40	26	43	34

[1] N.F. = Not found

Chapter 6
Laboratory Performance Evaluation of *In Situ* Bioremediation of the Upper Aquifer

6.0 BFI Study Objective 3: Laboratory Evaluation to Assess Performance of In Situ Bioremediation of the Upper Aquifer

The third objective of this BFI-sponsored study was to perform a laboratory evaluation to assess the microbial metabolic potential of subsurface aquifer materials to accomplish bioremediation of target chemicals under various conditions. This laboratory study to provide additional information concerning *in situ* bioremediation of the Upper Aquifer is consistent with the intent of the U.S. EPA Bioremediation Field Initiative. While the laboratory study involved tests on aquifer samples *ex situ*, it provided direct evidence of biodegradation *in situ*. Results from the study are used to evaluate the role of nutrient amendments, abiotic losses/transformations, and abiotic oxygen demand in the subsurface. Measurement of mineralization of radiolabeled PCP and phenanthrene in aquifer material allowed the evaluation of biodegradation by indigenous microorganisms. While analyses of ground water and aquifer material yield information on the presence of important components to biodegradation in the subsurface, the laboratory study yielded information indicating that indigenous microorganisms have the metabolic capability to biodegrade the compounds of interest. Numerous biotic and abiotic processes affect the concentration of contaminants and dissolved oxygen in ground water. In an effort to more clearly identify the relative role of biotic processes, it is necessary to understand both processes.

The approach used in the laboratory study was to estimate the rate and extent of contaminant removal in aquifer core materials in laboratory microcosms using a chemical mass balance approach (Sims, 1990). By performing a chemical mass balance, the fraction of contaminants: 1) biodegraded; 2) sorbed to organic solids; 3) humified (i.e., irreversibly bound); and 4) mineralized was estimated. In order to accomplish a chemical mass balance, contaminated aquifer cores were spiked with ^{14}C-PCP and ^{14}C-phenanthrene in the laboratory microcosms.

Since biodegradation potential of a chemical may vary depending on temperature, oxygen availability, and nutrient availability, the influence of these factors on the rate and extent of mineralization, volatilization and soil incorporation was also investigated. Contaminant biodegradation at 10° and 20° C, with and without nutrient addition, and with and without atmospheric oxygen, was evaluated. The lower temperature was selected to simulate the average ground-water temperature at the site (see Section 5.2.2.2), while the higher temperature was selected to ensure that temperature was not a limiting factor in biodegradation in order to evaluate the effects of the other variables. Nutrients were added in the form of ammonium chloride. Poisoned microcosms were also evaluated to separate the effects of biological metabolism from abiotic reactions. Poisoning was accomplished by adding a mercuric chloride solution to the microcosms. Aerobic microcosms were aerated periodically to maintain oxygen in the headspace atmosphere. Anaerobic microcosms were flushed with an oxygen-free atmosphere. Volatile traps were used to capture compounds removed by volatilization. Carbon dioxide traps were used to evaluate mineralization of the compounds to carbon dioxide. The aquifer sediment slurries from the microcosms were analyzed at the end of the incubation period to determine the distribution of the parent compounds and/or their degradation products.

6.1 Objectives of Laboratory Study

The specific objectives of the laboratory study were to:

(1) determine the rate and extent of biodegradation of ^{14}C-phenanthrene and ^{14}C-PCP in contaminated aquifer materials as affected by temperature, oxygen, and nutrient addition in two different core samples; and

(2) determine the fate of ^{14}C-phenanthrene and ^{14}C-PCP in the aquifer materials (solvent- extractable and bound residue) and air (mineralization and volatilization) phases using a chemical mass balance approach.

6.2 Experimental Design, Materials, and Methods

A complete factorial design approach was used for the investigation of the effects of temperature and biotic/abiotic conditions on degradation of PCP and phenanthrene in two borehole samples, with every factor at two levels (2^k design) and with duplicate sets of each treatment (referred to as the Temperature Effects Study). A substudy was conducted using one borehole sample to investigate the effects of oxygen, nutrients, and biotic/abiotic conditions on the degradation of PCP, with each factor at two levels and with duplicate sets of each treatment (referred to as the Oxygen/Nutrient Effects Study). The treatments used in the laboratory studies are summarized in Table 6.1 and graphically presented in Figures 6.1 and 6.2. The borehole samples used in the experiments were collected as described in Section 5.2.1.1.

Table 6.1. Experimental Variables in the Laboratory Studies.

(a) Temperature Effects Study

Variable	Levels of Treatment
Compounds	PCP and phenanthrene
Temperature	10° C and 20° C
Sample	Sample # 1: Borehole No. 2 at 20-foot depth Sample # 2: Borehole No. 2 at 29-foot depth
Poisoned	Yes (Abiotic) and No (Biotic)
Nutrients	Yes
Oxygen	Yes

(b) Oxygen/Nutrient Study

Variable	Levels of Treatment
Compound	PCP
Temperature	10° C
Sample	Sample # 2: Borehole No. 2 at 29-foot depth
Poisoned	Yes (Abiotic) and No (Biotic)
Nutrients	Yes and No
Oxygen	Yes and No

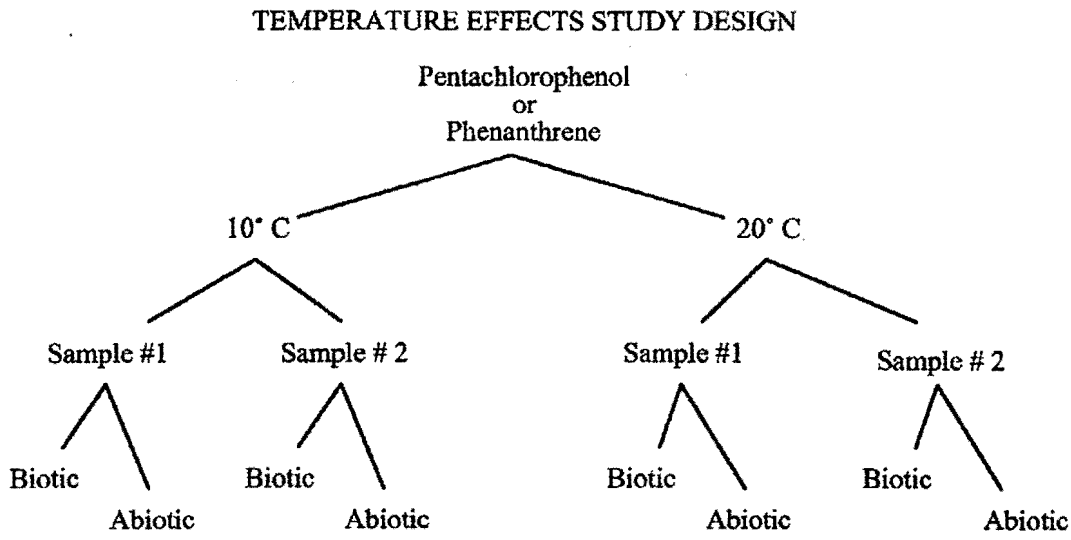


Figure 6.1. Temperature Effects Study Design (Both samples are from Borehole No. 2. Sample #1 is from 20 feet deep and Sample #2 is from 29 feet deep. Duplicate microcosms were used for each Biotic and Abiotic treatment).

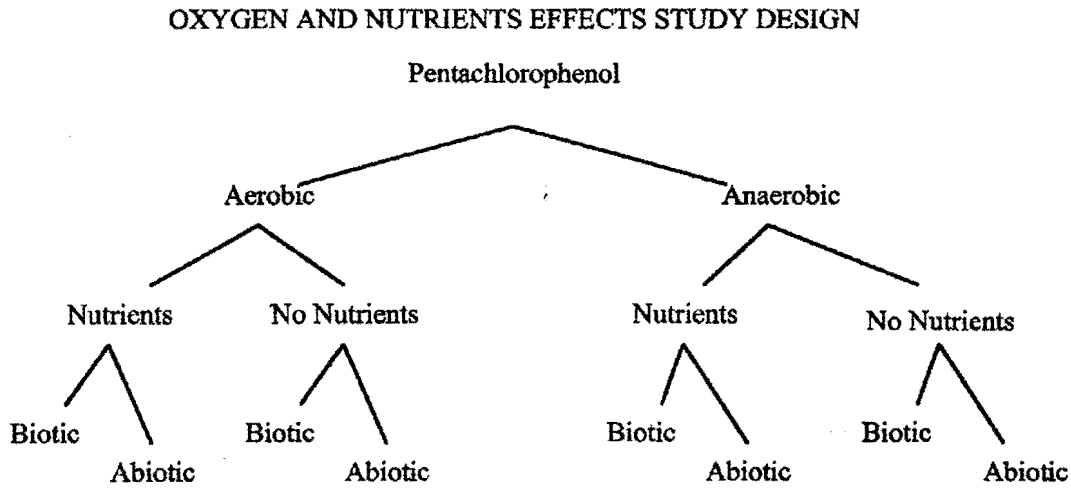


Figure 6.2. Oxygen/Nutrient Effects Study Design (A sample from Borehole No. 2: 29-foot depth was used for all of the microcosms. Incubation temperature was 10° C. Duplicate microcosms were used for each Biotic and Abiotic treatment).

This design resulted in the use of 32 microcosms (2 contaminants x 2 temperatures x 2 samples x 2 poisoned levels x 2 replicates = 32) for the Temperature Effects Study.

The Oxygen/Nutrient Effects Study consisted of 16 microcosms (2 oxygen levels x 2 nutrients x 2 poisoned levels x 2 replicates = 16). Only 12 additional microcosms were set up for this study as 4 microcosms in the Temperature Effects Study had the same treatment factors (i.e., the treatments for Sample 2, PCP,10° C, biotic and abiotic, with nutrients, were used in both studies).

Concentrations of PAH compounds and PCP in the borehole samples used in this study are shown in Table 6.2.

Table 6.2. *Concentrations of PAH Compounds and PCP in Borehole Samples Selected for the Laboratory Studies.*

Compound	Sample Location Borehole No. 2: 20 foot depth	Borehole No. 2: 29 foot depth
Naphthalene	40.26[1]	8.92
Acenaphthylene	15.35	3.29
Acenaphthene	99.05	21.91
Fluorene	45.14	4.5
Phenanthrene	66.37	6.35
Anthracene	27.07	3.12
Fluoranthene	98.76	16.75
Pyrene	71.36	6.33
Benzo(a)anthracene	31.62	4.82
Chrysene	15.09	2.33
Benzo(b)fluoranthene	7.12	0.51
Benzo(k)fluoranthene	6.47	0.81
Benzo(a)pyrene	nd[2]	nd
Total PAH Compounds	523.66	79.64
Pentachlorophenol	0.137	2.26

1 All concentrations are in mg/kg
2 nd = non-detectable

There was not enough water in the samples collected from the field to keep the solid materials submerged in the microcosms, so a solution containing approximately the same concentration of major cations and anions as the site ground water was added to ensure that the solid material was submerged. This addition was done to simulate the aquifer environment at the Libby Site. Analysis of water from the sample, Borehole No. 1: 19 feet 3 inches depth, to determine principal cations was conducted using inductively coupled arc plasma (ICP) by the Utah State University Soils Testing Laboratory. Chloride, sulfate, and phosphate were determined by the Utah Water Research Laboratory using ion chromatography. Bicarbonate was determined by titration with standard acid. Data from these analyses and the principal ion composition of the artificial aquifer water are presented in Table 6.3.

Table 6.3. Principal Cations and Anions in a Libby Aquifer Sample and the Artificial Aquifer Water.

Ion	Natural sample concentration (mg/L)	Artificial water concentration (mg/L)[1]
Na	27	27.1
K	19	19.0
Ca	39	38.7
Mg	14	13.6
Cl	13	13.2
SO_4	10	10.3
PO_4-P	15	15.2
HCO_3	197	155.5

[1] Concentration calculated from composition.

Table 6.4 shows the concentrations of various salts added to deionized water to prepare the artificial aquifer water. The salts were brought into solution by bubbling the suspension with CO_2. The final pH was adjusted to 7.4 using dilute NaOH.

Table 6.4. Salts Used to Prepare Simulated Water.

Salt	Concentration (mg/L)
NaCl	21.8
$MgSO_4$	12.9
KH_2PO_4	21.8
$NaHCO_3$	67.7
$KHCO_3$	32.6
$MgCO_3$	38.1
$CaCO_3$	96.6

Microcosms were constructed using 250 mL Erlenmeyer flasks with a two-holed rubber stopper. Teflon® tubing through this stopper provided an inlet and an outlet (Figure 6.3). The outlet and inlet were closed using one-way stopcocks, equipped with male Luer Lock adapters. Each microcosm received 13 grams of the sample slurry material and 12 mL of artificial aquifer water.

Nutrients used in the full-scale field system at the Libby Site are ammonium chloride and dibasic potassium phosphate. The analysis of the water from Borehole No. 1: 19 feet 3 inches indicated that the ground water contained 15 mg/L PO_4 -P. The artificial ground water added to the microcosms was prepared to contain approximately this concentration (Table 6.3). This unexpectedly high concentration of available phosphorus was considered to be adequate to support biodegradation of the contaminants present in the aquifer materials, so no additional phosphorus was added. Ammonium chloride solution was added to all the microcosms in the Temperature Effects Study and to the "nutrient " microcosms in the Oxygen/Nutrient Effects Study to increase the concentration of the aqueous phase by 2.4 mg of NH_4-N per L.

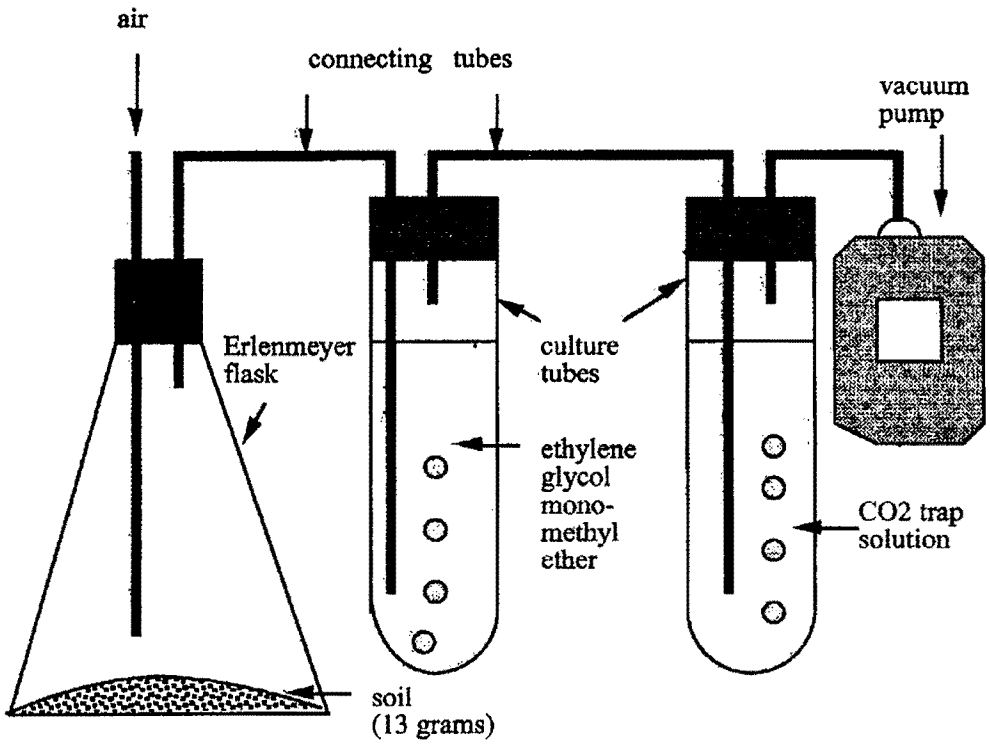


Figure 6.3. Schematic of a Laboratory Microcosm and Gas Trapping Apparatus.

"Abiotic" microcosms were prepared by adding 1.25 mL of a 5.2 mg/mL solution of $HgCl_2$ to the appropriate microcosms to achieve a concentration of approximately 2 mM $HgCl_2$ per Kg dry weight of aquifer materials, as recommended by Wolf et al. (1989).

Uniformly labeled ^{14}C-pentachlorophenol (250 μL; 1.16 x 10^5 DPM) or ^{14}C-phenanthrene (250 μL; 1.38 x 10^4 DPM) was added into the appropriate microcosms. Each radiolabeled compound was prepared by dissolving the compound in 50 mL of DDW (distilled, deionized water). The solutions were agitated for 24 hours and then filtered through a 45 μm filter before use. Triplicates of the same volume of spiking solutions were prepared and measured on a liquid scintillation counter (Beckman Corporation, Models LS1701 or LS6000 SE) to obtain a measurement of the total amount of ^{14}C spiked into the microcosms. These measured values were used to calculate the mass balance obtained in the experiments.

Aerobic microcosms were placed on shaker tables and gently shaken at 100 rpm to ensure effective mass transfer of oxygen from the atmosphere. Anaerobic microcosms were incubated at 10° C in an anaerobic glove box with an atmosphere of 95 percent N_2 and 5 percent H_2. They were not placed on a shaker table, but were shaken by hand. To achieve temperature control, microcosms were incubated in constant temperature rooms at either 10 ± 2° C or 20 ± 2° C.

The headspace of the aerobic microcosms was simultaneously purged and aerated once every four days by applying a vacuum at the outlet of the CO_2 trap (Figure 6.3). The anaerobic microcosms were purged with a vacuum pump using the gas in the glove box. At the time of purge, the outlet was connected to a volatile organics trap and a CO_2 trap. The outlet of the organic trap was connected to the inlet of the CO_2 trap, as shown in Figure 6.3. Gas traps were constructed from 150 mm long gas washing tubes. The first trap contained 15 mL of ethylene glycol monomethyl ether (EGME) for the collection of organic compounds. The carbon dioxide trap contained 15 mL of a solution containing 50 percent Ready Gel™ (Beckman), 40 percent methanol and 10 percent monoethanolamine.

The purge rate was slow (<60 mL/min) to keep air bubbles small to effect a greater trapping efficiency. Each purge lasted 15 minutes. A 1 mL sample from the CO_2 trap or the volatile organics trap was counted in the Beckman liquid scintillation counter after mixing the solution with Ready Gel™. The maximum counting time used was 10 minutes and the maximum counting error allowed was 10 percent.

At the end of the incubation period, residual phenanthrene and PCP in the solid phase were extracted using sonication (U.S. EPA Method 3550 (U.S. EPA, 1986b) - see Appendix B-1). The solvent used for extraction was a 1:1 mixture of methylene chloride and acetone (Baxter HPLC grade). The aquifer solids from each microcosm were transferred to a beaker. The microcosms were rinsed twice with about 10 mL of the solvent. The solvent slurry was sonicated using an ultrasonic processor (Sonicator® Heat Systems, Model XL 2020) after addition of 100 mL of solvent. Pulsed sonication was applied to the sample for two minutes with the output control maintained at position 5 and the duty cycle at 50. The sonicator was tuned before starting the extractions and was subsequently checked after every five extractions. The probe was cleaned with solvent in between extractions. After sonication, the supernatant was decanted into a drying column filled to three-fourth of its height with crystalline, oven-dried anhydrous sodium sulfate. The remaining solids were rinsed with 10 mL of solvent; this solvent was also passed through the drying column. The solvent was collected in a Kuderna-Danish (KD) flask by applying pressure to the top of the drying column. Two to three boiling stones were added to the KD flask, and a Snyder column was fitted to the top. The KD flask was heated over a water bath to concentrate the sample to about 2 to 4 mL. The concentrate was transferred to a 10 mL volumetric flask; acetonitrile was added to bring the solution to volume. A 1 mL sample was removed and added to scintillation cocktail. The sample was then measured for radioactivity using the Beckman liquid scintillation counter.

Soil-bound ^{14}C was determined by combusting the solids after extraction in a Biological Oxidizer (R.J. Harvey Instruments) and trapping the resulting CO_2 in the carbon dioxide trap. After extraction, the aquifer solids were air dried under a hood for 24 hours. The solids were then hand-ground in a porcelain dish. Duplicate 1 g samples of these solids were then combusted in the biological oxidizer. The temperature of the catalyst zone was 670°-690° C; the temperature of the combustion zone was about 900° C. The flow of the oxygen and nitrogen gases through the oxidizer was maintained at 350 mL/min. Evolved $^{14}CO_2$ was trapped in a CO_2 trapping solution. Ready Gel™ was added to the trapping solution, and the samples were counted in the liquid scintillation counter for 10 minutes. The maximum error allowed was 2 percent. The quench limits were set at a low of 3.8 and a high of 319.3

For quality control, duplicates of a 1.00 g aquifer solid sample were spiked with 250 μL of the radiolabeled solutions. The samples were allowed to dry for 30 minutes in a hood and then combusted for four minutes. The amount of activity recovered was calculated on a percentage basis. Recoveries were 94 percent and 97 percent.

A mass balance was calculated based on the total ^{14}C-chemical added to the microcosms. The following equation was evaluated for all microcosms:

Total amount of ^{14}C-chemical spiked = [amount of ^{14}C mineralized] + [amount ^{14}C volatilized] + [amount of ^{14}C solvent extractable] + [amount ^{14}C soil bound]

Statistical analyses were conducted using the JMP® software package (SAS Institute, Inc.) on a Macintosh computer. Repeated measures analysis of variance (ANOVA) was used to analyze mineralization and volatilization data, with sampling day as the repeated measure. The solventextractable and solid-bound data were analyzed with ANOVA. Differences among results were considered to be significant at the 95 percent confidence level.

6.3 Results of the Laboratory Evaluation to Assess Performance of In Situ Bioremediation of the Upper Aquifer

6.3.1 *Mineralization of Phenanthrene*

Cumulative phenanthrene mineralization in biotic microcosms over the 56-day Temperature Effects Study ranged from 11.18 to 20.12 percent of the added ^{14}C. The mean and standard deviation of the percent mineralization in the duplicate microcosms in this experiment are shown in Table 6.5.

Phenanthrene mineralization was significantly affected by the interaction of temperature with the sample and biotic/abiotic treatment. The nature of this interaction is illustrated in Figure 6.4. Averaged across the period of the experiment, the highest mineralization occurred in the microcosms using the Borehole No. 2: 29-foot depth sample, without poison, at 10° C. In the Borehole No. 2: 20-foot depth sample, mineralization was significantly lower than that in the Borehole No. 2: 29-foot depth sample, but phenanthrene mineralization at 10° C was higher in both samples than it was at 20° C. At 20° C, there was no significant difference between mineralization in Borehole No. 2: 20-foot depth and Borehole No. 2: 29-foot depth samples.

Average mineralization in the abiotic microcosms was low in comparison to the biotic microcosms. There was no significant difference in mineralization between temperatures or samples. This low level of activity may have been due to the incomplete destruction of microbial activity by the $HgCl_2$ poison or may be due to non-biological chemical reactions.

There was a significant difference in average phenanthrene mineralization activity over time between the biotic and abiotic microcosms from the beginning of the experiment (Figure 6.5).

These data indicate that mineralization of phenanthrene in the Libby aquifer material is microbiologically mediated and that the microorganisms responsible for the mineralization activity are adapted to the lower temperatures of the aquifer. There is no indication that artificially raising the temperature of the contaminated zone would result in higher rates of mineralization.

6.3.2 Mineralization of Pentachlorophenol

In the Temperature Effects Study, cumulative $^{14}CO_2$ evolved from microcosms amended with ^{14}C-pentachlorophenol ranged from 0.44 to 1.16 percent. The averages and standard deviations of the cumulative percent pentachlorophenol mineralized from duplicate microcosms are shown in Table 6.6. The average cumulative PCP mineralized in microcosms in the Oxygen/Nutrient Effects Study did not exceed 0.46 percent of the added radiolabeled carbon (Table 6.7).

The rates of PCP mineralization in the Libby aquifer material, under aerobic or anaerobic conditions, were very slow. Assuming first order degradation kinetics and 1 percent mineralization in 56 days, the half life for mineralization of PCP would be approximately 10 years.

Table 6.5. *Mean and Standard Deviation of Cumulative Percent ^{14}C-Phenanthrene Mineralization in Duplicate Experimental Microcosms During the Temperature Effects Study.*

Temp. (°C)	Sample/Type		Day 4	8	12	16	20	24	28	35	42	49	56
			$^{14}CO_2$ (^{14}C Mineralized, Cumulative %)										
20	20 ft./Biotic												
		Mean	0.81	1.70	1.71	2.33	2.50	2.91	3.73	6.42	6.80	6.82	11.77
		Std. Dev.	0.40	0.31	0.31	0.71	0.69	1.28	1.22	4.50	5.00	5.01	11.13
10	20 ft./Biotic												
		Mean	2.95	3.64	3.67	4.67	5.55	6.36	9.88	12.03	12.24	12.24	14.90
		Std. Dev.	2.68	3.37	3.40	4.43	5.47	6.37	4.25	6.67	6.88	6.88	9.21
20	20 ft./Abiotic												
		Mean	0.18	0.24	0.25	0.29	0.31	0.43	1.19	1.50	1.55	1.55	2.44
		Std. Dev.	0.05	0.05	0.05	0.00	0.03	0.14	0.09	0.21	0.20	0.19	0.10
10	20 ft./Abiotic												
		Mean	0.29	0.38	0.39	0.63	0.79	0.88	3.12	3.70	3.75	3.76	5.36
		Std. Dev.	0.03	0.06	0.06	0.00	0.22	0.10	0.97	1.02	1.05	1.05	2.37
20	29 ft./Biotic												
		Mean	0.45	0.56	0.57	1.11	1.41	1.93	3.43	6.48	6.78	6.80	11.18
		Std. Dev.	0.37	0.39	0.39	0.18	0.60	1.33	1.49	5.17	5.47	5.49	9.37
10	29 ft./Biotic												
		Mean	7.44	10.05	10.11	10.83	11.55	12.25	13.40	15.44	15.72	15.74	20.12
		Std. dev.	7.44	10.70	10.72	11.09	11.58	11.88	12.14	12.65	12.83	12.83	15.00
20	29 ft./Abiotic												
		Mean	0.38	0.56	0.57	0.66	0.74	0.74	1.76	2.06	2.08	2.09	2.70
		Std. Dev.	0.28	0.18	0.19	0.06	0.05	0.05	0.70	0.69	0.70	0.70	0.99
10	29 ft./Abiotic												
		Mean	0.46	0.82	0.82	0.94	1.05	1.17	1.46	1.72	1.88	1.89	4.51
		Std. Dev.	0.20	0.28	0.28	0.32	0.39	0.43	0.52	0.58	0.56	0.56	0.18

6.3.3 *Volatilization of Phenanthrene and Pentachlorophenol*

In the Temperature Effects Study, volatilization in ^{14}C-phenanthrene microcosms ranged from 1.32 percent in abiotic Borehole No. 2: 20-foot depth samples incubated at 10° C to 3.26 percent in biotic Borehole No. 2: 20-foot depth samples incubated at 10° C (Table 6.8). Repeated measures analysis of variance revealed that there was a significant effect of the interaction of temperature with sample and biotic/abiotic treatment on volatilization of radiolabeled compound(s) from these microcosms (Figure 6.6). The highest average volatilization occurred in the biotic Borehole No. 2: 20-foot depth microcosms at both 10° and 20° C. Average volatilization was significantly higher at 10° C than at 20° C in these microcosms. Volatilization in the abiotic microcosms (generally limited to less than or equal to 1%) of the same sample was significantly lower than in either the 10° or 20° C biotic microcosms (generally less than 3%).

Average PCP volatilization in the Temperature Effects experiment did not exceed 0.4 percent in any microcosm. The average percent volatile radiolabeled carbon recovered from each of the treatments in this experiment is shown in Table 6.9. Similarly, the volatilization of PCP in the Oxygen/Nutrient Study was very low, averaging not more than 0.09 percent (Table 6.10). These very small amounts of PCP, or its degradation products, lost through volatilization would not be expected to affect the treatment of the contaminated aquifer material.

6.3.4 *Soil Incorporation of Phenanthrene*

The final distribution and mass balance of ^{14}C-phenanthrene, or its degradation products, in the microcosms in the Temperature Effects Study are shown in Table 6.11. Both the fraction of phenan-

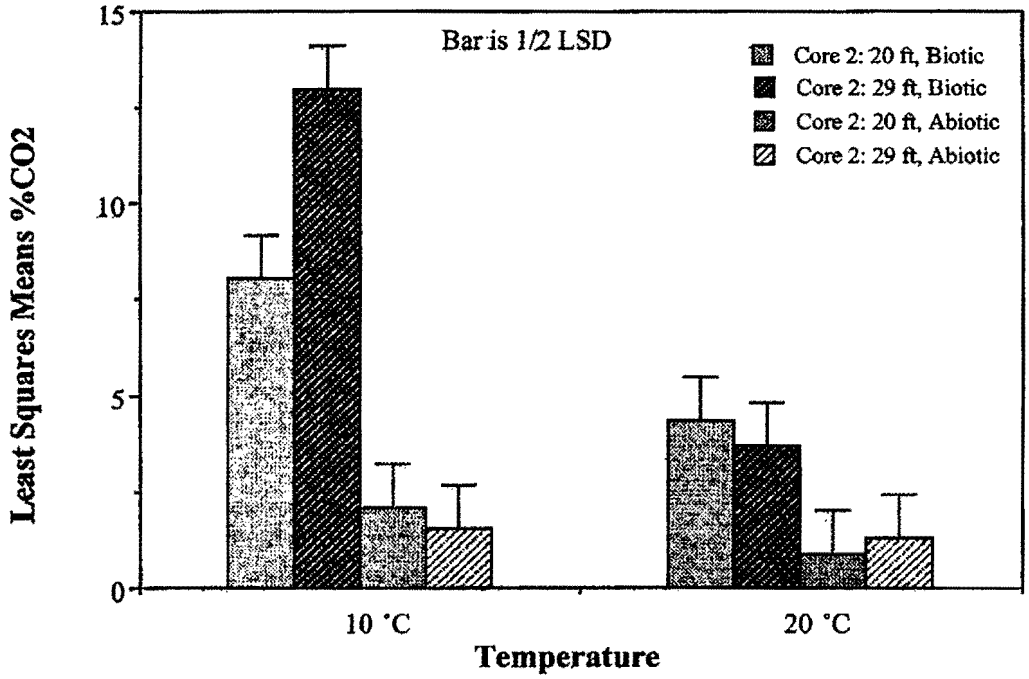


Figure 6.4. Interaction of Temperature, Aquifer Material Sample, and Biotic/Abiotic Treatment on the Time-Averaged, Cumulative Mineralization of 14^{C}-Phenanthrene in the Laboratory Microcosms.

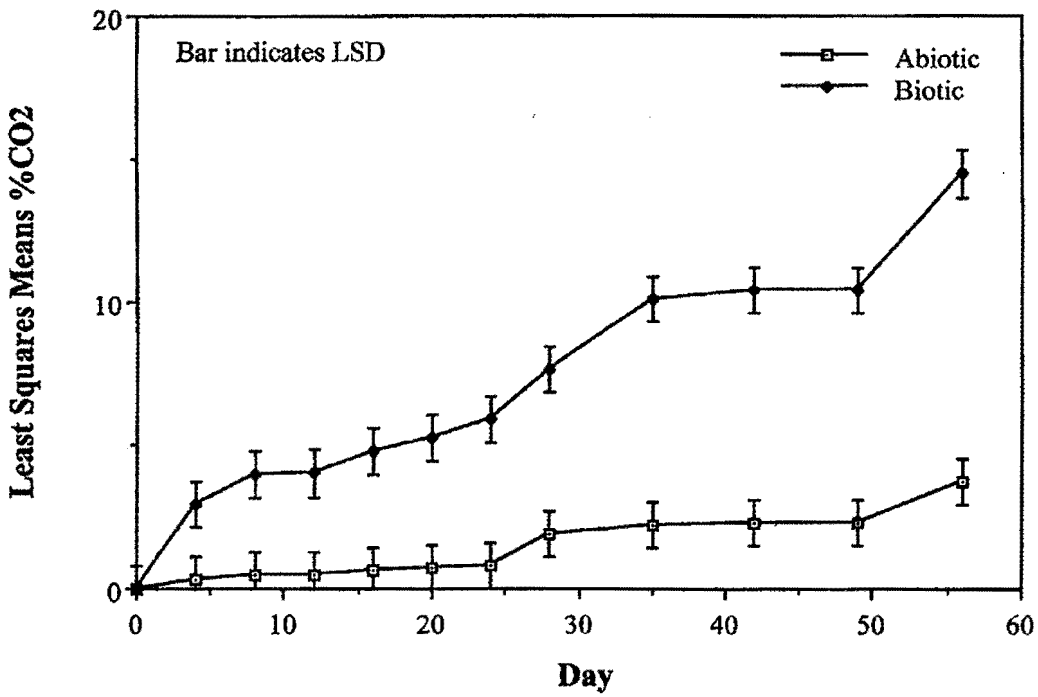


Figure 6.5. Effects of the Interaction of Poisoning and Incubation Time on the Average Cumulative $^{14}CO_2$ Evolved from the Mineralization of ^{14}C-Phenanthrene in the Laboratory Microcosms.

Table 6.6. Mean and Standard Deviation of Cumulative Percent ^{14}C-Pentachlorophenol Mineralization in Duplicate Microcosms During the Temperature Effects Study.

Temp. (°C)	Sample/Type		Day 4	8	12	16	20	24	28	35	42	49	56
			$^{14}CO_2$ (^{14}C Mineralized, Cumulative %)										
20	20 ft./Biotic												
		Mean	0.08	0.12	0.13	0.18	0.22	0.28	0.45	0.63	0.82	0.85	0.85
		Std. Dev.	0.04	0.07	0.07	0.11	0.17	0.25	0.31	0.45	0.60	0.60	0.60
10	20 ft./Biotic												
		Mean	0.02	0.05	0.06	0.10	0.15	0.22	0.39	0.47	0.54	0.54	0.54
		Std. Dev.	0.00	0.01	0.01	0.01	0.01	0.02	0.15	0.18	0.20	0.21	0.21
20	20 ft./Abiotic												
		Mean	0.02	0.03	0.03	0.14	0.24	0.39	0.64	0.81	1.13	1.15	1.16
		Std. Dev.	0.01	0.01	0.01	0.13	0.28	0.46	0.64	0.65	0.54	0.53	0.54
10	20 ft./Abiotic												
		Mean	0.02	0.04	0.04	0.08	0.15	0.19	0.45	0.57	0.70	0.71	0.72
		Std. Dev.	0.00	0.00	0.00	0.01	0.05	0.10	0.03	0.02	0.08	0.08	0.09
20	29 ft./Biotic												
		Mean	0.04	0.05	0.06	0.15	0.25	0.30	0.52	0.76	1.09	1.12	1.12
		Std. Dev.	0.01	0.02	0.02	0.06	0.07	0.13	0.15	0.17	0.26	0.26	0.26
10	29 ft./Biotic												
		Mean	0.03	0.06	0.07	0.09	0.11	0.17	0.31	0.38	0.43	0.44	0.44
		Std. Dev.	0.00	0.01	0.02	0.01	0.02	0.04	0.00	0.01	0.02	0.02	0.02
20	29 ft./Abiotic												
		Mean	0.03	0.04	0.05	0.09	0.12	0.16	0.29	0.39	0.46	0.48	0.48
		Std. Dev.	0.00	0.01	0.01	0.02	0.07	0.13	0.12	0.20	0.25	0.25	0.25
10	29 ft./Abiotic												
		Mean	0.02	0.03	0.06	0.07	0.18	0.25	0.45	0.51	0.57	0.58	0.58
		Std. Dev.	0.00	0.00	0.02	0.03	0.08	0.05	0.09	0.09	0.09	0.10	0.10

threne extractable with solvent and the fraction tightly bound to the soil (combustible) were significantly affected by the interaction of temperature with the effects of poisoning and the aquifer material samples used in the microcosms (Figures 6.7 and 6.8). The highest average soil-bound and the lowest average solvent-extractable phenanthrene was observed in the Borehole No. 2: 20-foot depth sample, without poison, incubated at 10° C. The next highest, but significantly lower, average amount of soil-bound phenanthrene was observed in Borehole No. 2: 20-foot depth sample microcosms, without poison, incubated at 20° C. The lowest average soil binding and the highest average solvent-extractability of phenanthrene was observed with the Borehole No. 2: 29-foot depth sample, poisoned, and incubated at 20° C. This suggests that the characteristics of the aquifer materials, in combination with temperature and microbial activity, may be important in immobilizing phenanthrene and its degradation products on the aquifer materials. Apparently, soil incorporation, as well as mineralization of phenanthrene in the aquifer material is microbiologically mediated.

6.3.5 *Soil Incorporation of Pentachlorophenol*

The distribution and mass balance of ^{14}C-PCP in the Temperature Effects experimental microcosms after 56 days of incubation are shown in Table 6.12. The solvent-extractability of PCP, or its degradation products, from the aquifer material incubated at either 10° or 20° C, ranged between 51 and 89 percent in all of the treatments. Table 6.13 contains the mass balance data for the Oxygen/Nutrient Study. Solvent extractability in the Oxygen/Nutrient Study ranged from 50 to 86 percent.

Table 6.7. Mean and Standard Deviation of Cumulative Percent ^{14}C-Pentachlorophenol Mineralization in Duplicate Microcosms in the Oxygen/Nutrient Effects Study.

Oxygen/Type Nitrogen Status		Day 4	8	12	16	20	24	28	35	42	49	56
		^{14}C Mineralized (Cumulative%)										
No Oxygen/Biotic Nitrogen	Mean	0.02	0.03	0.03	0.03	0.03	0.03	0.03	0.04	0.04	0.04	0.04
	Std. Dev.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Oxygen/Biotic Nitrogen	Mean	0.03	0.06	0.07	0.07	0.08	0.08	0.09	0.11	0.13	0.15	0.15
	Std. Dev.	0.00	0.01	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Oxygen/Biotic No Nitrogen	Mean	0.03	0.05	0.06	0.07	0.08	0.09	0.14	0.17	0.21	0.25	0.26
	Std. Dev.	0.01	0.02	0.02	0.02	0.02	0.03	0.06	0.05	0.04	0.01	0.01
No Oxygen/Biotic No Nitrogen	Mean	0.02	0.03	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.05
	Std. Dev.	0.00	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.03
No Oxygen/Abiotic Nitrogen	Mean	0.02	0.19	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.21
	Std. Dev.	0.00	0.21	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22
Oxygen/Abiotic Nitrogen	Mean	0.02	0.03	0.06	0.06	0.06	0.07	0.08	0.10	0.12	0.15	0.16
	Std. Dev.	0.00	0.00	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.05	0.05
Oxygen/Abiotic No Nitrogen	Mean	0.02	0.05	0.06	0.07	0.24	0.25	0.26	0.32	0.37	0.45	0.46
	Std. Dev.	0.01	0.00	0.00	0.01	0.02	0.01	0.01	0.02	0.05	0.11	0.13
No Oxygen/Abiotic No Nitrogen	Mean	0.01	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.04
	Std. Dev.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

There were no significant temperature effects on soil incorporation of ^{14}C-PCP, or its degradation products into the aquifer materials in the microcosms of these experiments. There was, however, a significant effect of the interaction of incubation temperature with biotic/abiotic treatment on the extractability of ^{14}C-PCP with the 20° C, abiotic treatment exhibiting a significantly higher solvent-extraction yield than other treatment combinations (Figure 6.9). The narrow range of response to these combinations suggests that the differences among these effects should probably not be major considerations in the management and treatment of the Libby aquifer contamination.

There was a significantly larger average concentration of ^{14}C-PCP bound to Borehole No. 2: 20-foot depth aquifer materials during the 56 days of the Temperature Effects Study than was bound to Borehole No. 2: 29-foot depth materials (Figure 6.10). This result demonstrates the spatial variability of factors potentially affecting soil incorporation of ^{14}C-PCP in the contaminated aquifer at Libby. The effect of biotic/abiotic treatment was also significantly different between the samples (Figure 6.11). A larger average concentration of ^{14}C-PCP was extractable from those microcosms where the poisoned, Borehole No. 2: 29-foot depth sample was used. This observation supports the finding that PCP binding in Borehole No. 2: 29 foot depth materials was lower than in the Borehole No. 2: 20-foot depth sample.

Significantly more ^{14}C-PCP was bound to aquifer material under anaerobic conditions than under aerobic conditions in the Oxygen/Nutrient Study (Figure 6.12). There was also a significant three-way interaction effect of the biotic/abiotic treatment, nitrogen addition, and oxygen on the extractability of ^{14}C-PCP in this experiment (Figure 6.13). The average amount of ^{14}C-PCP extractable from the abiotic,

nitrogen-amended aquifer material in aerobic microcosms was much lower than that from other treatments. The range of ^{14}C-PCP extractability responses to other three-way interactions of this kind was less than 10 percent. The influence of these differences on the full-scale treatment process would not be expected to be important.

Table 6.8. *Mean and Standard Deviation of Cumulative Percent ^{14}C-Phenanthrene Volatilization During the Temperature Effects Study.*

Temp. (°C)	Sample/Type		Day 4	8	12	16	20	24	28	35	42	49	56
			^{14}C Volatilized (Cumulative %)										
20	20 ft./Biotic	Mean	0.44	0.68	0.68	0.71	0.71	1.41	2.29	2.53	2.70	2.73	2.73
		Std. Dev.	0.07	0.15	0.15	0.11	0.11	0.72	1.93	2.02	2.01	2.06	2.06
10	20 ft./Biotic	Mean	2.12	2.49	2.50	2.50	2.55	2.55	2.72	3.02	3.26	3.26	3.26
		Std. Dev.	2.51	2.73	2.74	2.74	2.80	2.80	3.04	2.96	2.87	2.87	2.87
20	20 ft./Abiotic	Mean	0.27	0.41	0.43	0.43	0.54	0.54	0.67	0.96	1.31	1.35	1.35
		Std. Dev.	0.08	0.04	0.04	0.04	0.20	0.20	0.03	0.10	0.06	0.06	0.06
10	20 ft./Abiotic	Mean	0.24	0.32	0.33	0.44	0.44	0.44	0.76	1.14	1.32	1.32	1.32
		Std. Dev.	0.03	0.02	0.03	0.13	0.13	0.13	0.58	0.87	1.00	0.99	0.99
20	29 ft./Biotic	Mean	0.34	0.53	0.54	0.55	0.55	0.65	1.30	1.52	1.72	2.39	2.39
		Std. Dev.	0.08	0.03	0.04	0.05	0.05	0.09	0.48	0.47	0.36	0.19	0.19
10	29 ft./Biotic	Mean	0.27	0.59	0.63	0.71	0.71	0.71	1.45	1.82	2.12	2.62	2.62
		Std. Dev.	0.12	0.37	0.34	0.44	0.44	0.44	0.40	0.33	0.47	0.31	0.31
20	29 ft./Abiotic	Mean	0.32	0.49	0.50	0.57	0.57	0.63	1.25	1.46	1.70	1.82	1.82
		Std. Dev.	0.03	0.06	0.05	0.16	0.16	0.24	0.11	0.09	0.03	0.06	0.06
10	29 ft./Abiotic	Mean	0.17	0.29	0.30	0.48	0.48	0.48	1.31	1.62	1.94	2.08	2.08
		Std. Dev.	0.07	0.02	0.02	0.28	0.28	0.28	0.06	0.03	0.09	0.04	0.04

The results from these laboratory experiments indicate that temperature and nitrogen enrichment effects on the incorporation of PCP into the aquifer material are minor. More PCP may be incorporated into the aquifer material under anaerobic conditions than under aerobic conditions. There was no evidence of a significant role of microbial activity in PCP incorporation into the solid phase aquifer material.

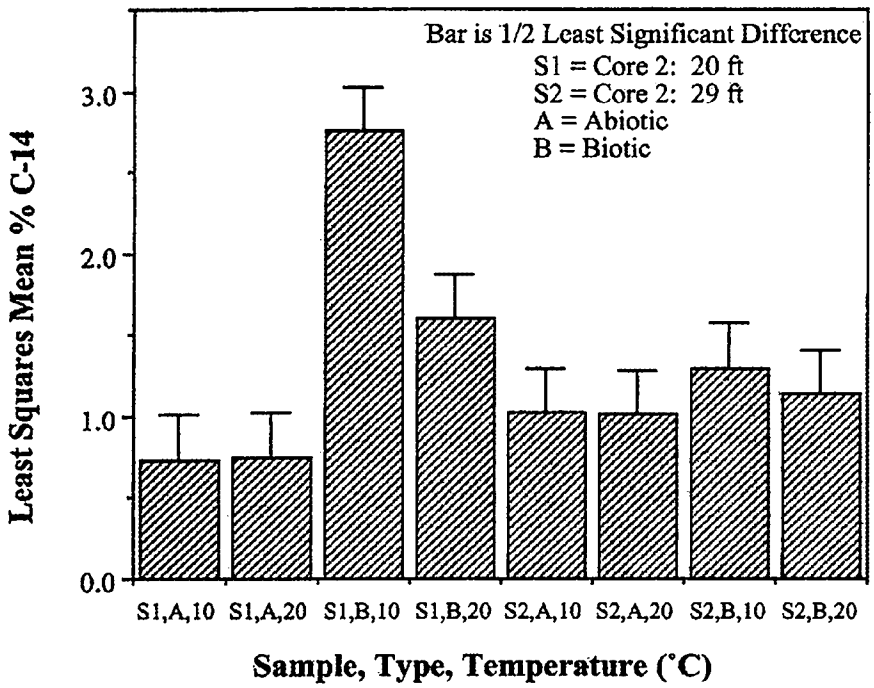


Figure 6.6 Effects of the Interaction of Sample, Biotic/Abiotic Treatment, and Temperature on the Volatilization of ^{14}C-Phenanthrene in the Temperature Effects Study.

Table 6.9. *Mean and Standard Deviation of Cumulative Percent ^{14}C-Pentachlorophenol Volatilization in Duplicate Microcosms in the Temperature Effects Study.*

Temp. (°C)	Sample/Type		Day 4	8	12	16	20	24	28	35	42	49	56
			^{14}C Volatilized (Cumulative %)										
20	20 ft./Biotic	Mean	0.04	0.07	0.07	0.07	0.07	0.07	0.09	0.13	0.16	0.16	0.16
		Std. Dev.	0.02	0.01	0.00	0.00	0.00	0.00	0.02	0.03	0.04	0.04	0.04
10	20 ft./Biotic	Mean	0.03	0.05	0.07	0.07	0.07	0.07	0.09	0.12	0.16	0.16	0.16
		Std. Dev.	0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.01	0.01	0.0
20	20 ft./Abiotic	Mean	0.02	0.05	0.05	0.05	0.05	0.07	0.13	0.18	0.23	0.23	0.23
		Std. Dev.	0.01	0.00	0.00	0.00	0.00	0.03	0.06	0.06	0.05	0.05	0.05
10	20 ft./Abiotic	Mean	0.02	0.03	0.04	0.04	0.04	0.04	0.10	0.13	0.17	0.17	0.17
		Std. Dev.	0.00	0.00	0.00	0.01	0.01	0.01	0.08	0.08	0.09	0.09	0.09
20	29 ft./Biotic	Mean	0.03	0.06	0.07	0.07	0.07	0.07	0.10	0.13	0.17	0.17	0.17
		Std. Dev.	0.01	0.00	0.00	0.00	0.00	0.00	0.04	0.03	0.04	0.04	0.04
10	29 ft./Biotic	Mean	0.02	0.03	0.04	0.04	0.05	0.05	0.05	0.10	0.12	0.12	0.12
		Std. Dev.	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.03	0.03	0.03	0.03
20	29 ft./Abiotic	Mean	0.03	0.05	0.06	0.10	0.11	0.14	0.19	0.22	0.28	0.28	0.28
		Std. Dev.	0.00	0.01	0.01	0.05	0.07	0.10	0.16	0.15	0.18	0.18	0.18
10	29 ft./Abiotic	Mean	0.02	0.03	0.04	0.04	0.05	0.05	0.07	0.11	0.12	0.13	0.13
		Std. Dev.	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.04	0.03	0.03	0.03

Table 6.10. *Mean and Standard Deviation of Cumulative Percent ^{14}C-Pentachlorophenol Volatilization in Duplicate Microcosms in the Oxygen/Nutrient Effects Study.*

Oxygen/Type Nitrogen Status		Day 4	8	12	16	20	24	28	35	42	49	56
		^{14}C Volatilized (Cumulative %)										
No Oxygen/Biotic	Mean	0.03	0.05	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
Nitrogen	Std. Dev.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Oxygen/Biotic	Mean	0.02	0.03	0.04	0.04	0.04	0.04	0.04	0.06	0.07	0.07	0.07
Nitrogen	Std. Dev.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01
Oxygen/Biotic	Mean	0.04	0.05	0.06	0.06	0.06	0.06	0.07	0.08	0.09	0.09	0.09
No Nitrogen	Std. Dev.	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
No Oxygen/Biotic	Mean	0.03	0.05	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
No Nitrogen	Std. Dev.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No Oxygen/Abiotic	Mean	0.03	0.06	0.06	0.06	0.06	0.06	0.06	0.07	0.07	0.07	0.07
Nitrogen	Std. Dev.	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00
Oxygen/Abiotic	Mean	0.02	0.03	0.04	0.04	0.04	0.04	0.05	0.06	0.06	0.08	0.08
Nitrogen	Std. Dev.	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.03	0.03
Oxygen/Abiotic	Mean	0.02	0.03	0.04	0.04	0.04	0.04	0.05	0.06	0.07	0.07	0.07
No Nitrogen	Std. Dev.	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.01	0.01	0.01	0.01
No Oxygen/Abiotic	Mean	0.03	0.04	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
No Nitrogen	Std. Dev.	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01

Table 6.11. *^{14}C-Phenanthrene Mass Balance for each of the Temperature Effects Experimental Microcosms after 56 Days of Incubation.*

Temperature (°C)	Sample/ Type	^{14}C Volatilized (%)	Mineralized (%)	Solvent-Extractable (%)	Soil-Bound (%)	Total Recovery (%)
20	Core 2: 20 ft/ Biotic	4.13	19.64	17.95	59.36	101.07
20	Core 2: 20 ft/ Biotic	1.27	3.90	13.04	46.45	64.66
10	Core 2: 20 ft/ Biotic	5.29	21.42	11.19	70.24	108.13
10	Core 2: 20 ft/ Biotic	1.23	8.39	10.70	60.48	80.81
20	Core 2: 20 ft/ Abiotic	1.39	2.37	31.52	40.06	75.34
20	Core 2: 20 ft/ Abiotic	1.30	2.52	18.08	44.58	66.48
10	Core 2: 20 ft/ Abiotic	0.63	7.03	37.16	35.35	80.16
10	Core 2: 20 ft/ Abiotic	2.02	3.68	49.79	29.60	85.09
20	Core 2: 29 ft/ Biotic	2.26	17.81	35.41	40.07	95.55
20	Core 2: 29 ft/ Biotic	2.52	4.56	41.71	42.49	91.28
10	Core 2: 29 ft/ Biotic	2.40	9.51	44.96	29.38	86.25
10	Core 2: 29 ft/ Biotic	2.84	30.72	32.62	44.72	110.91
20	Core 2: 29 ft/ Abiotic	1.78	2.00	82.04	34.80	120.62
20	Core 2: 29 ft/ Abiotic	1.87	3.40	88.43	25.85	119.55
10	Core 2: 29 ft/ Abiotic	2.11	4.38	31.05	42.20	79.74
10	Core 2: 29 ft/ Abiotic	2.05	4.64	30.01	40.19	76.89
					Average Total	90.16
					Standard Deviation	17.58

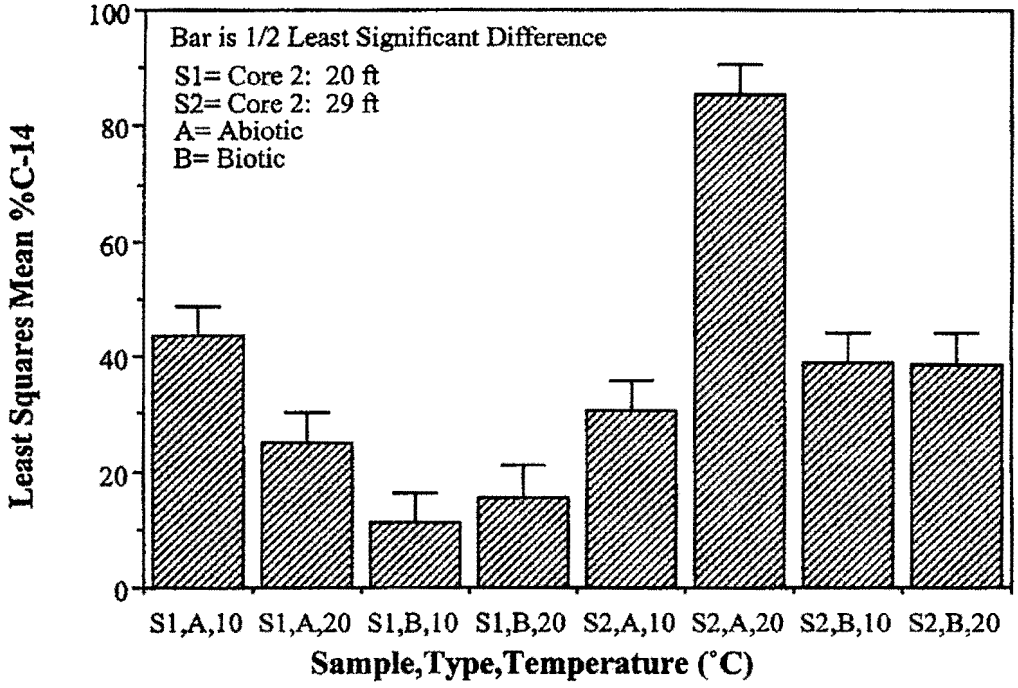


Figure 6.7. Effects of the Interaction of Temperature, Sample, and Biotic/Abiotic Treatment on the Amount of Solvent-Extractable ^{14}C-Phenanthrene from the Aquifer Materials used in the Temperature Effects Study.

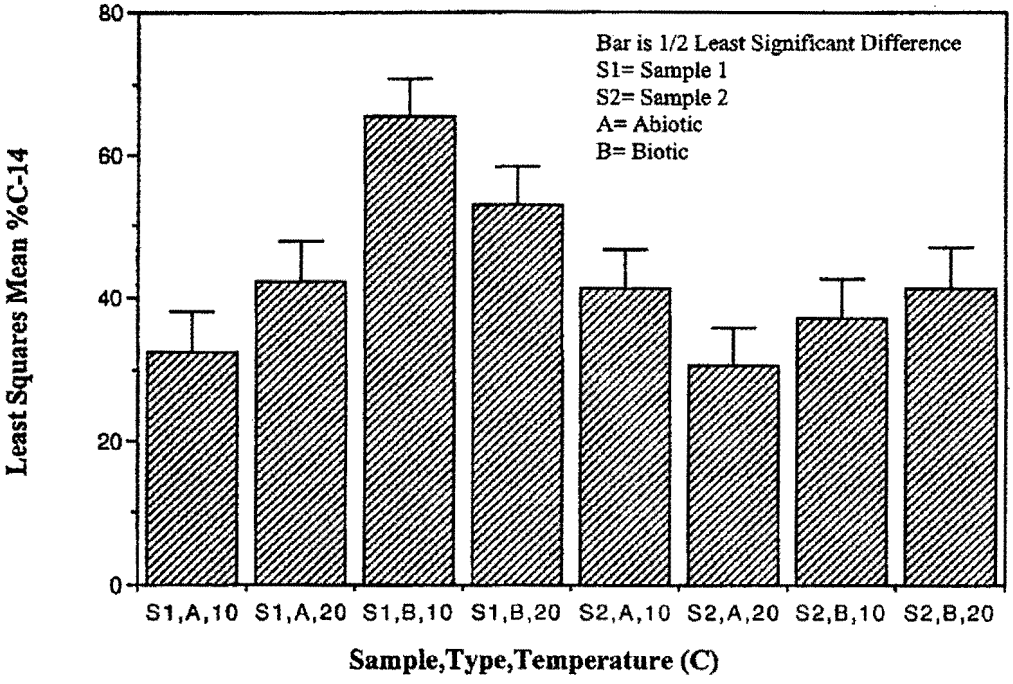


Figure 6.8. Effects of the Interaction of Temperature, Sample, and Biotic/Abiotic Treatment on the Soil-Binding of ^{14}C-Phenanthrene in the Temperature Effects Study.

Table 6.12. *^{14}C-Pentachlorophenol Mass Balance for each of the Temperature Effects Experimental Microcosms after 56 Days of Incubation.*

Temperature (°C)	Sample/ Type	^{14}C Volatilized (%)	Mineralized (%)	Solvent-Extractable (%)	Soil-Bound (%)	Total Recovery (%)
10	Core 2: 20 ft/ Biotic	0.19	0.43	61.83	26.96	89.40
10	Core 2: 20 ft/ Biotic	0.14	1.28	65.96	27.55	94.92
20	Core 2: 20 ft/ Biotic	0.17	0.40	78.18	14.15	92.89
20	Core 2: 20 ft/ Biotic	0.15	0.69	70.89	28.57	100.30
10	Core 2: 20 ft/ Abiotic	0.27	0.78	68.77	29.91	99.72
10	Core 2: 20 ft/ Abiotic	0.19	1.54	62.18	27.00	90.93
20	Core 2: 20 ft/ Abiotic	0.11	0.65	52.20	37.71	90.68
20	Core 2: 20 ft/ Abiotic	0.24	0.78	51.16	32.58	84.75
10	Core 2: 29 ft/ Biotic	0.15	1.30	62.11	29.39	92.95
10	Core 2: 29 ft/ Biotic	0.20	0.93	58.75	18.94	78.82
20	Core 2: 29 ft/ Biotic	0.10	0.45	67.61	19.01	87.18
20	Core 2: 29 ft/ Biotic	0.14	0.42	68.41	15.70	84.67
10	Core 2: 29 ft/ Abiotic	0.15	0.65	89.32	17.71	107.83
10	Core 2: 29 ft/ Abiotic	0.41	0.31	82.09	22.59	105.39
20	Core 2: 29 ft/ Abiotic	0.11	0.65	72.80	18.19	91.75
20	Core 2: 29 ft/ Abiotic	0.15	0.51	74.42	17.70	92.77
					Average Total	92.81
					Standard Deviation	7.62

Table 6.13. *^{14}C-Pentachlorophenol Mass Balance for Each of the Oxygen/Nutrient Effects Experimental Microcosms after 56 Days of Incubation.*

Nitrogen Added	Oxygen Status	^{14}C Volatilization (%)	Mineralization (%)	Solvent-Extractable (%)	Soil-Bound (%)	Total Recovery (%)
Yes	No Oxygen	0.06	0.04	76.31	10.49	86.90
Yes	No Oxygen	0.06	0.04	86.04	6.42	92.56
Yes	Oxygen	0.06	0.15	67.61	19.01	86.83
Yes	Oxygen	0.07	0.16	68.41	15.70	84.34
No	Oxygen	0.09	0.26	73.49	15.68	89.51
No	Oxygen	0.10	0.25	69.83	13.12	83.30
No	No Oxygen	0.06	0.04	88.40	8.55	97.04
No	No Oxygen	0.05	0.07	72.25	21.66	94.03
Yes	No Oxygen	0.07	0.36	80.27	8.99	89.69
Yes	No Oxygen	0.06	0.05	71.05	5.38	76.55
Yes	Oxygen	0.10	0.20	72.80	18.19	91.29
Yes	Oxygen	0.06	0.12	74.42	17.70	92.30
No	Oxygen	0.08	0.37	51.65	16.62	68.71
No	Oxygen	0.07	0.55	50.38	17.78	68.78
No	No Oxygen	0.04	0.04	75.06	15.40	90.54
No	No Oxygen	0.05	0.04	80.30	4.99	85.38
					Average Total	86.11
					Standard Deviation	8.33

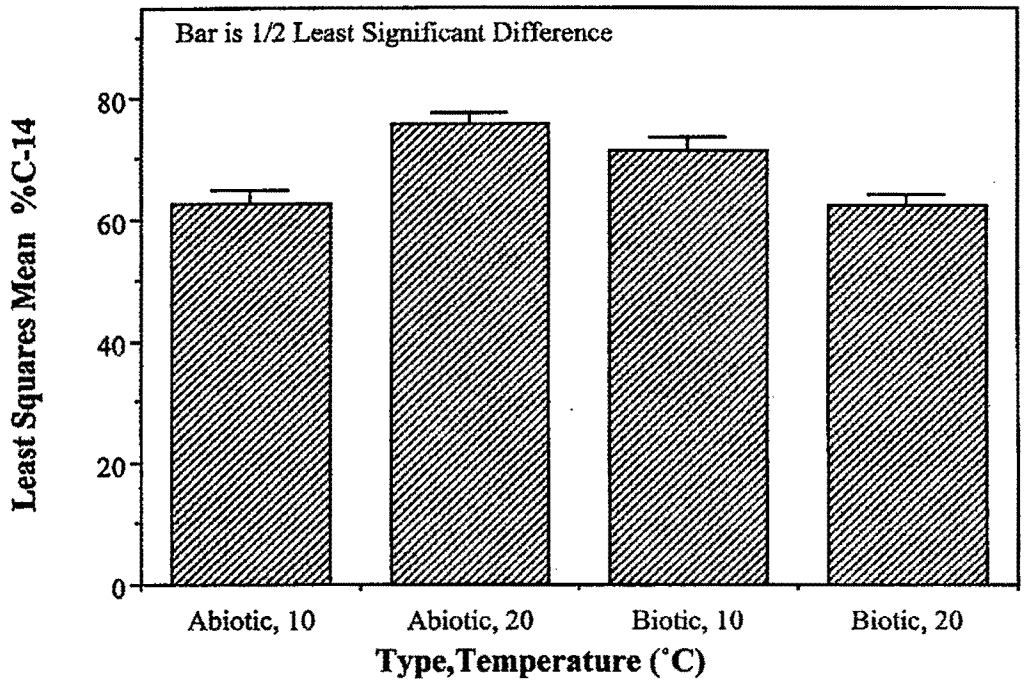


Figure 6.9. Temperature x Biotic/Abiotic Treatment Interaction Effects on the Solvent- Extractability of ^{14}C-PCP Following 56 Days Incubation in the Temperature Effects Study.

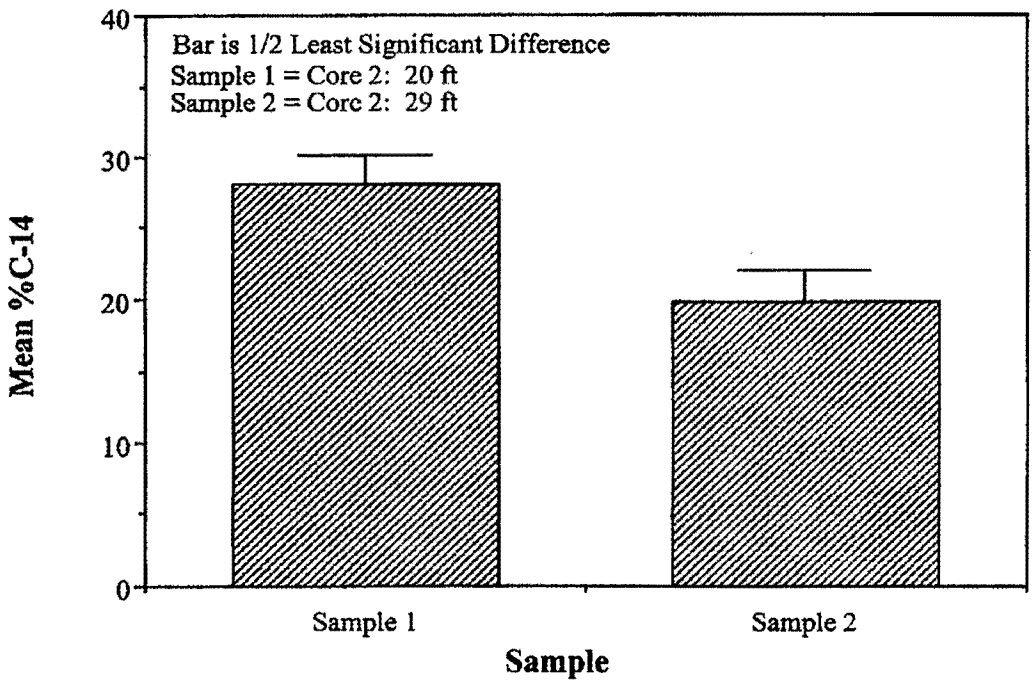


Figure 6.10. ^{14}C-PCP Bound to Aquifer Materials Following 56 Days of Incubation in the Temperature Effects Study

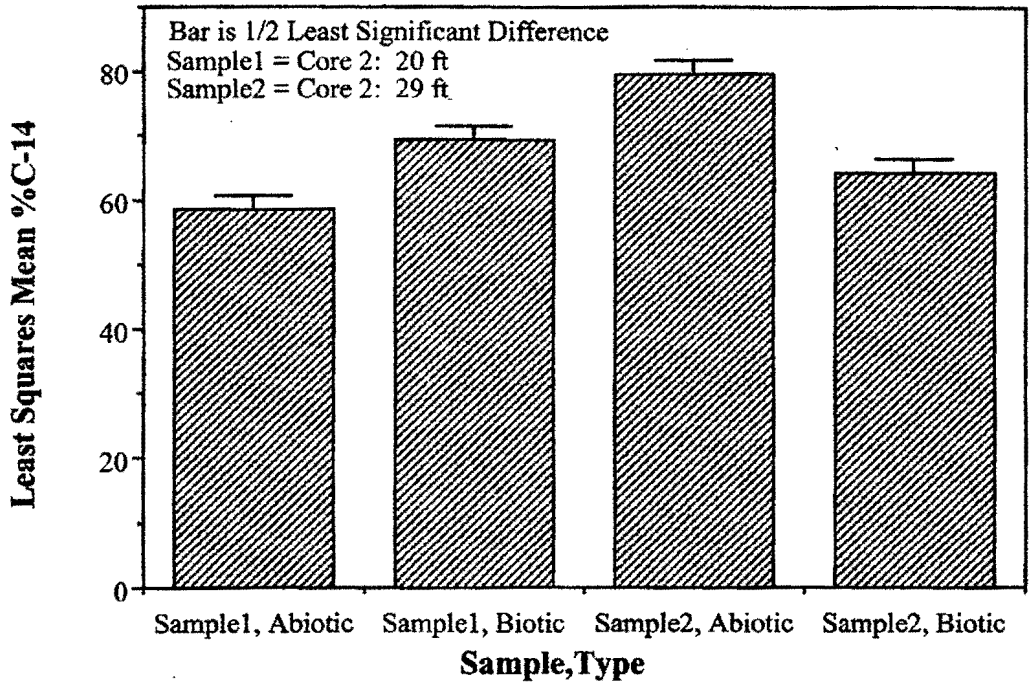


Figure 6.11. Sample x Biotic/Abiotic Treatment Interaction Effects on the Solvent Extractability of ^{14}C-PCP Following 56 days of Incubation in the Temperature Effects Study.

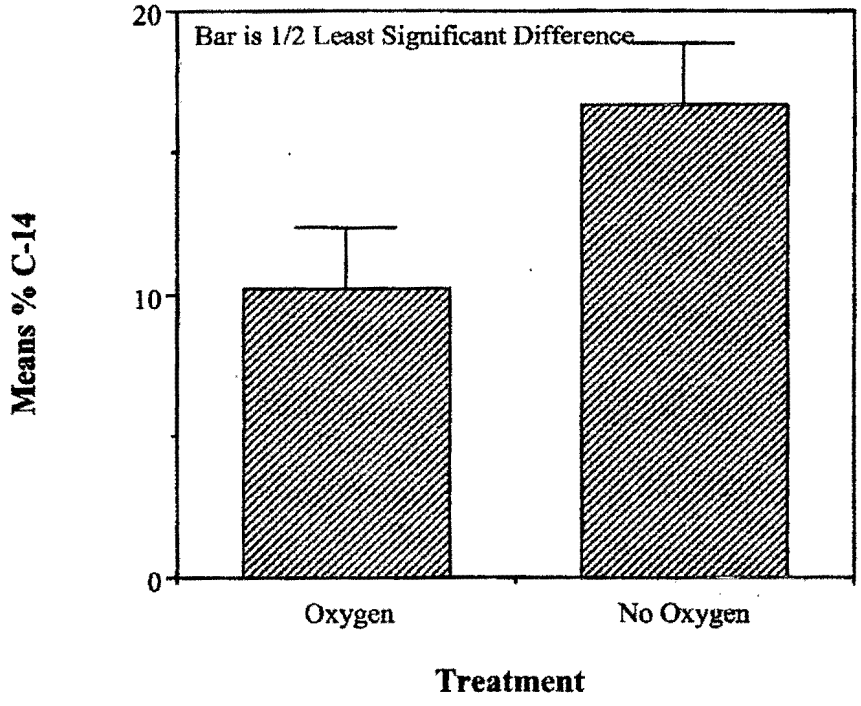


Figure 6.12. Effects of Oxygen on Soil-Binding of ^{14}C-PCP Following 56 days of Incubation in the Oxygen/ Nutrient Study.

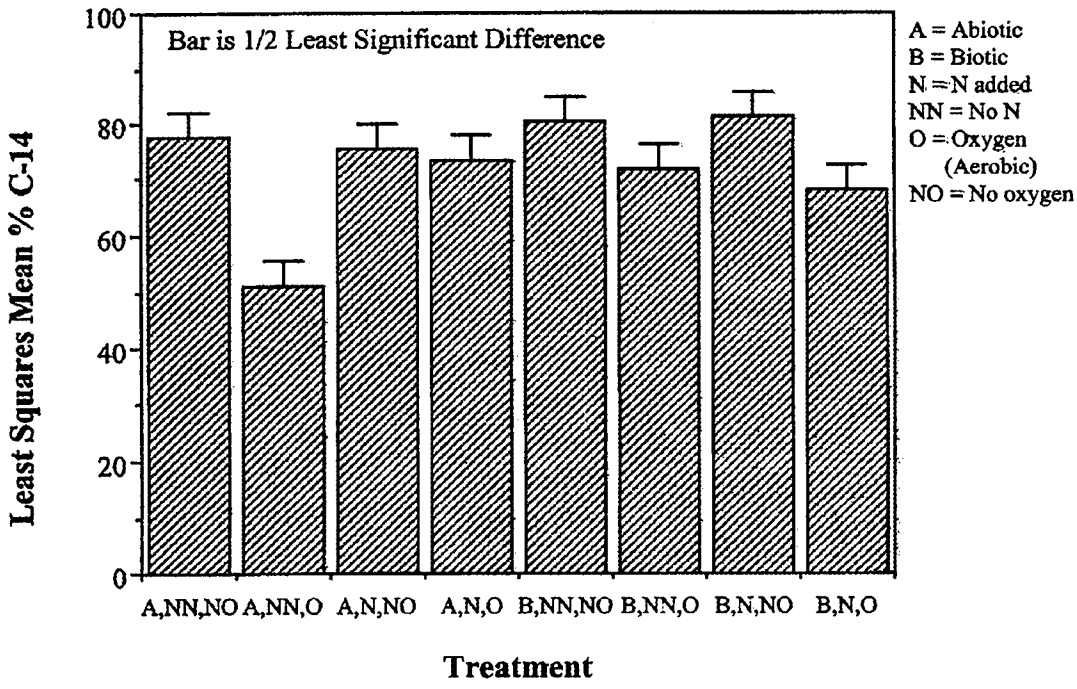


Figure 6.13. Effects of the Interaction of Biotic/Abiotic Conditions, Nitrogen Addition, and Oxygen on the Solvent-Extractability of ^{14}C-PCP Following 56 Days of Incubation in the Oxygen/Nutrient Study.

Chapter 7
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7.0 References

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Appendix A

Preliminary Cost Estimates for the *In Situ* Bioremediation Program for the Upper Aquifer (Woodward-Clyde Consultants, 1990)

A-1. Cost Estimate Assumptions

Costs for the entire *in situ* remediation system are included, although the program may be phased in over more than one year.

Lower contaminant concentrations at the Downgradient System (Station 2) allow the use of an air compressor and oxygen generator for the oxygen supply. The existing peroxide system will be used at the Intermediate System (Station 1) and a peroxide system will be installed at the Source Area System (Station 3).

The only piece of major purchased equipment required to upgrade the Intermediate System at Station 1 is a 2,500 gal. storage tank for peroxide. This tank will be housed in a separate structure with a concrete berm to provide secondary containment. Another 2,500 gal. peroxide storage tank will be installed at Station 3. This tank also will be surrounded by a concrete berm for secondary containment. These tanks will provide approximately a 2 month supply of peroxide and will allow the peroxide to be purchased at a lower bulk rate.

The piping trenches are 5-1/2 feet deep. The trenches will be benched, with a width of 2 feet for the interval 5-1/2 feet to 2-1/2 feet, and a width of 4 feet for the interval 2-1/2 feet to ground surface.

Costs for piping, valves and fittings are only included for the system from the filter out to the injection wells. Costs are not included for conveyance of fire pond water to each station. There will be no paving over the pipe trenches. All piping is PVC, except for short lengths within Station 2, as specified on the Conceptual Arrangement for that station.

Backwash water from the filters at Stations 2 and 3 will be released to a gravel drywell. The dimensions of the drywell are assumed to be 4 ft. wide x 4 ft. long x 6 ft. deep.

Nutrients are mixed in the proportion of 67 lbs. ammonium chloride to 33 lb. potassium tripolyphosphate per 600 gal. water. Nutrients are metered into the injection system at a rate of 275 mL per minute per 100 gpm of water.

At Station 2, where an oxygen generator is the oxygen source, the water will be saturated with oxygen (oxygen saturation is 40 mg oxygen per liter of water). At Stations 1 and 3, peroxide is metered into the injection well system at a rate of 70 mL per minute per 100 gpm of water.

Pipe and earthwork costs are from Means Site Work Cost Data 1990. Labor costs have been multiplied by 0.94 (per Means) for work performed in Great Falls, Montana. Costs for earthwork have been converted from $/yd^3 to $/linear foot based on cubic yard calculations for the trench benching described above.

PVC fittings and valve costs are from Harrington Plastics catalog, 7th edition. All prices are multiplied by 0.3 per the Harrington representative to provide a more realistic value.

Costs for housing are from Means Construction Cost Data 1990, and are based on a rate per cubic foot of building at this stage of the design.

CAPITAL COST

STATION 1/INTERMEDIATE SYSTEM UPGRADE

Description	Quantity Unit	Unit Price	Total Cost
Station 1 Major Purchased Equipment (MPE)			
Injection Wells	1 well	$9,990.00	$9,900
Monitoring Wells	2 well	$5,500.00	$11,000
Filter	1 each	$0.00*	$0
Air Compressor with Dryer & Filter			
0 each	$0		
Oxygen Generator	0 each		$0
Spargers	0 each		$0
Peroxide Storage Tank (2,500 gal)	1 each	$1,500.00	$1,500
Peroxide Pump	1 each	$0.00*	$0
Nutrient Storage Tank	1 each	$0.00*	$0
Nutrient Mixer	1 each	$0.00*	$0
Nutrient Pump	1 each	$0.00*	$0
Housing	1 each	$8,500.00	$8,500
Flow Meters	1 each	$0.00*	$0
Piping & Tubing			$150
Labor			
Supervisor	8 hours	$40.00	$320
Pipe Fitter	24 hours	$35.00	$840
Electrician	0 hours	$35.00	$0
Laborer	24 hours	$20.00	$480
Construction Supervisor			
Supervisor Labor	20 hours	$60.00	$1,200
Per Diem	2 day	$100.00	$200
Airfare	1 RT	$1,500.00	$1,500
SUBTOTAL STATION 1 MAJOR PURCHASED EQUIPMENT			$35,590

*Equipment exists and is currently operating

CAPITAL COST (Continued)

Description	Quantity Unit	Materials Unit Price	Materials Amount	Labor and Equipment Unit Price	Labor and Equipment Amount	Total Cost
Station 1 Pipe, Fittings, Valves						
PVC Pipe						
2 Inches	30 ft.	$1.31	$39.30	$5.69	$170.70	$210
2 1/2 Inches	500 ft.	$1.87	$935.00	$5.97	$2,985.00	$3,920
4 Inches	0 ft.	$3.28	$0.00	$6.96	$0.00	$0
PVC Tee						
2-1/2 x 2-1/2x2	3 ea.	$5.44	$16.32		$0.00	$16
4x4x2	0 ea.	$12.94	$0.00		$0.00	$0
4x4x2-1/2	0 ea.	$12.94	$0.00		$0.00	$0
PVC 45 Degree Bend						
2-1/2 inches	0 ea	$4.08	$0.00		$0.00	$0
4 inches	0 ea.	$0.30	$0.00		$0.00	$0
PVC 90 Degree Bend						
2-1/2 inches	0 ea.	4.07	$0.00		$0.00	$0
PVC Cap						
2-1/2 inches	1 ea.	$2.19	$2.19		$0.00	$2
4 inches	0 ea.	$5.45	$0.00		$0.00	$0
PVC Butterfly Valve						
2 inches	1 ea.	$34.80	$34.80		$0.00	$35
2-1/2 inches	0 ea.	$38.10	$0.00		$0.00	$0
SUBTOTAL STATION 1 PIPE, FITTINGS, VALVES			$1,027.61		$3,155.70	$4,183
Station 1 Earthwork						
Excavate	530 lf	$0.00	$0.00	$1.73	$916.90	$917
Sand Bedding	530 lf	$0.33	$174.90	$0.40	$212.00	$387
Backfill/Compact	530 lf	$0.00	$0.00	$1.57	$832.10	$832
SUBTOTAL STATION 1 EARTHWORK			$174.90		$1,961.00	$2,136
SUBTOTAL STATION 1 CAPITAL COST						$41,909

CAPITAL COST

STATION 2/DOWNGRADIENT SYSTEM

Description	Quantity Unit	Unit Price	Total Cost
Station 2 Major Purchased Equipment (MPE)			
Injection Wells	6 wells	$9,990.00	$59,400
Monitoring Wells	2 wells	$5,500.00	$11,000
Filter	1 each	$16,416.00	$16,416
Air Compressor with Dryer & Filter	1 each	$8,200.00	$8,200
Oxygen Generator	1 each	$11,680.00	$11,680
Spargers	1 each	$315.00	$315
Peroxide Storage Tank	0 each		$0
Peroxide Pump	0 each		$0
Nutrient Storage Tank (2,00 gal)	1 each	$1,500.00	$1,500
Nutrient Mixer	1 each	$5,200.00	$5,200
Nutrient Pump	1 each	$1,936.00	$1,936
Housing	1 each	$26,000.00	$26,000
Flow Meters	1 each	$1,400.00	$1,400
Piping & Tubing			$400
Labor			
Supervisor	8 hours	$40.00	$320
Pipe Fitter	40 hours	$35.00	$1,400
Electrician	16 hours	$35.00	$560
Laborer	40 hours	$20.00	$800
Construction Supervisor			
Supervisor Labor	40 hours	$60.00	$2,400
Per Diem	6 days	$100.00	$600
Airfare	1 RT	$1,500.00	$1,500
SUBTOTAL STATION 2 MAJOR PURCHASED EQUIPMENT			$151,027

CAPITAL COST (Continued)

Description	Quantity Unit	Materials Unit Price	Materials Amount	Labor and Equipment Unit Price	Labor and Equipment Amount	Total Cost
Station 2 Pipe, Fittings, Valves						
PVC Pipe						
2 Inches	10 ft.	$1.31	$13.10	$5.69	$56.90	$70
2 1/2 Inches	50 ft.	$1.87	$93.50	$5.97	$298.50	$392
4 Inches	2,200 ft.	$3.28	$7,216.00	$6.96	$15,312.00	$22,528
PVC Tee						
2-1/2 x 2-1/2x2	0 ea.	$5.44	$0		$0.00	$0
4x4x2	1 ea.	$12.94	$12.94		$0.00	$13
4x4x2-1/2	5 ea.	$12.94	$64.70		$0.00	$65
PVC 45 Degree Bend						
2-1/2 inches	0 ea	$4.08	$0.00		$0.00	$0
4 inches	1 ea.	$0.30	$0.30		$0.00	$0
PVC 90 Degree Bend						
2-1/2 inches	0 ea.	$4.07	$0.00		$0.00	$0
PVC Cap						
2-1/2 inches	0 ea.	$2.19	$0.00		$0.00	$0
4 inches	2 ea.	$5.45	$10.90		$0.00	$11
PVC Butterfly Valve						
2 inches	1 ea.	$34.80	$34.80		$0.00	$35
2-1/2 inches	5 ea.	$38.10	$190.50		$0.00	$191
SUBTOTAL STATION 2 PIPE, FITTINGS, VALVES			$7,636.74		$15,667.40	$23,304
Station 2 Earthwork						
Excavate	2,260 lf	$0.00	$0.00	$1.73	$3,909.80	$3,910
Sand Bedding	2,260 lf	$0.33	$745.80	$0.40	$904.00	$1,650
Backfill/Compact	2,260 lf	$0.00	$0.00	$1.57	$3,584.20	$3,548
Gravel Drywell	3.63 yd3	$10.55	$37.98	7.98	$28.73	$9,175
SUBTOTAL STATION 2 EARTHWORK			$783.78		$8,390.73	$9,175
SUBTOTAL STATION 2 CAPITAL COST						$183,506

A-6. Preliminary Cost Estimate for In-Situ Bioremediation Program

CAPITAL COST
STATION 3/SOURCE AREA SYSTEM

Description	Quantity Unit	Unit Price	Total Cost
Station 3 Major Purchased Equipment (MPE)			
Injection Wells	2 wells	$9,990.00	$19,800
Filter	1 each	$8,483.00	$8,483
Air Compressor with Dryer & Filter	0 each		$0
Oxygen Generator	0 each		$0
Spargers	0 each		$0
Peroxide Storage Tank	1 each	$1,500.00	$1,500
Peroxide Pump	1 each	$373.00	$373
Nutrient Storage Tank	1 each	$713.00	$713
Nutrient Mixer	1 each	$4,800.00	$4,800
Nutrient Pump	1 each	$754.00	$754
Housing	1 each	$25,500.00	
Flow Meters	1 each	$1,200.00	$1,200
Piping & Tubing			$150
Labor			
Supervisor	8 hours	$40.00	$320
Pipe Fitter	40 hours	$35.00	$1,400
Electrician	16 hours	$35.00	$560
Laborer	40 hours	$20.00	$800
Construction Supervisor			
Supervisor Labor	40 hours	$60.00	$2,400
Per Diem	6 days	$100.00	$600
Airfare	1 RT	$1,500.00	$1,500
SUBTOTAL STATION 3 MAJOR PURCHASED EQUIPMENT			$45,353

CAPITAL COST (Continued)

Description	Quantity Unit	Materials Unit Price	Materials Amount	Labor and Equipment Unit Price	Labor and Equipment Amount	Total Cost
Station 3 Pipe, Fittings, Valves						
PVC Pipe						
2 Inches	20 ft.	$1.31	$26.20	$5.69	$113.80	$140
2 1/2 Inches	1,000 ft.	$1.87	$1,870.00	$5.97	$5,970.00	$7,840
4 Inches	0 ft.	$3.28	$0.00	$6.96	$0.00	$0
PVC Tee						
2-1/2 x 2-1/2x2	2 ea.	$5.44	$10.88		$0.00	$11
4x4x2	0 ea.	$12.94	$0.00		$0.00	$0
4x4x2-1/2	0 ea.	$12.94	$0.00		$0.00	$0
PVC 45 Degree Bend						
2-1/2 inches	1 ea.	$4.08	$4.08		$0.00	$4
4 inches	0 ea.	$0.30	$0.00		$0.00	$0
PVC 90 Degree Bend						
2-1/2 inches	1 ea.	$4.07	$4.07		$0.00	$4
PVC Cap						
2-1/2 inches	1 ea.	$2.19	$2.19		$0.00	$2
4 inches	0 ea.	$5.45	$0.00		$0.00	$0
PVC Butterfly Valve						
2 inches	2 ea.	$34.80	$69.60		$0.00	$70
2-1/2 inches	0 ea.	$38.10	$0.00		$0.00	$0
SUBTOTAL STATION 3 PIPE, FITTINGS, VALVES			$1,987.02		$6,083.80	$8,071
Station 3 Earthwork						
Excavate	1,020 lf	$0.00	$0.00	$1.73	$1,764.60	$1,765
Sand Bedding	1,020 lf	$0.33	$336.60	$0.40	$408.00	$745
Backfill/Compact	1,020 lf	$0.00	$0.00	$1.57	$1,601.40	$1,601
Gravel Drywell	3.6 yd3	$10.55	$37.98	7.98	$28.73	$67
SUBTOTAL STATION 2 EARTHWORK			$374.58		$3,802.73	$4,177
SUBTOTAL STATION 3 CAPITAL COST						$57,601
TOTAL CAPITAL COST FOR ALL THREE SYSTEM						$283,016

A-8. Preliminary Cost Estimate for In-Situ Bioremediation Program

ANNUAL OPERATIONS AND MAINTENANCE (O&M) COST

Description	Quantity	Unit	Unit Price	Total Cost
STATION 1/INTERMEDIATE SYSTEM UPGRADE				
Power				$1,000
Peroxide	12,154	gal.	$3.12	$37,922
Nutrients				
Almond Chloride	5,475	lb.	$0.33	$1,807
Potassium Tripolyphosphate (PTP)	2,628	lb.	$1.19	$3,127
Maintenance and Repairs *	5% MPE of Station 3			$2,268
Operating Supplies	15% Maintenance and Repairs			$340
Well Maintenance	1	well	$200.00	$200
SUBTOTAL STATION 1 ANNUAL O&M				$46,664
STATION 2/DOWNGRADIENT SYSTEM				
Power				$10,600
Peroxide	0	gal.	$3.12	$0
Nutrients				
Ammonium Chloride	23,360	lb.	$0.33	$7,709
Potassium Tripolyphosphate (PTP)	11,680	lb.	$1.19	$13,899
Maintenance and Repairs	5% MPE of Station 2			$7,551
	15% Maintenance and Repairs			
Operating Supplies				$1,133
Well Maintenance	6	well	$200.00	$1,200
SUBTOTAL STATION 2 ANNUAL O & M				$42,092
STATION 3/SOURCE AREA SYSTEM				
Power				$1,000
Peroxide	9,709	gal.	$3.12	$30,292
Nutrients				
Ammonium Chloride	4,380	lb.	$0.33	$1,445
Potassium Tripolyphosphate (PTP)	2,190	lb.	$1.19	$2,606
Maintenance and Repairs	5% MPE of Station 3			$2,268
	15% Maintenance and Repairs			
Operating Supplies				$340
Well Maintenance	2	well	$200.00	$400
SUBTOTAL STATION 3 ANNUAL O & M				$38,351
TOTAL O & M COST FOR ALL THREE SYSTEMS				$127,107

*The percentage used for Maintenance and Repairs for Station 1 is based on the MPE cost for Station 3. This provides a more reasonable estimate for Station 1 Maintenance and Repairs because the only MPE needed to complete the Station 1 system is a new tank. The Station 3 system is of similar configuration and flow rate, so the MPE cost for the Station 3 system is similar to what the MPE would cost for Station 1 if most of the equipment for Station 1 did not already exist.

APPENDIX B

Analytical Methods and Quality Assurance/Quality Control Procedures

B-1. Extraction of Aquifer Solid and Ground-Water Samples and Moisture Determination of Aquifer Solids

Upon arrival of samples at the UWRL, the condition of samples was checked and noted. All samples were logged in by assigning each sample a UWRL log number and by entering appropriate information in the UWRL log book, including sample type, date sampled, date logged in, field ID, and type of analyses to be performed. All samples were placed in a refrigerated unit at 4° C. During sample extraction and analysis, all containers (extraction, storage, GC vials, LC vials, etc.) were labeled with the UWRL log number. After extraction and analysis, the samples were stored or archived in the 4° refrigerated unit or in a freezer at -70° C. During data management and analysis, field ID numbers were re-associated with UWRL log numbers and the concentrations of the target compounds measured in the samples.

The procedure used for the extraction of contaminated aquifer cores was based on U.S. EPA Method 3550 using sonication (U.S. EPA, 1986b); the procedure used for the extraction of ground water was based on U.S. EPA Method 3510 using a separatory funnel (U.S. EPA, 1986b). Samples were solvent-extracted with methylene chloride/acetone (in a 1:1 mixture by volume) using sonication or with methylene chloride using separation techniques. Sample extracts were passed through a funnel containing anhydrous sodium sulfate. Samples were concentrated in a Kuderna-Danish apparatus. Final volumes were adjusted, and the samples were then ready for analysis. Specifically, the procedures used included the following steps:

The aquifer core samples were prepared for extraction by weighing each sample in the jar as received using an analytical balance (Sartorius Model B120S) and recording the weight to the nearest 0.01 g. After a sample had been removed from a jar for extraction, the dry weight of the jar was obtained. The wet weight of the sample was determined by subtracting the dry weight of the jar from the total weight of the jar and sample. The sample was then transferred to a 2 L glass beaker (labeled with UWRL sample log number) for extraction. The sample jar was rinsed with solvent, and the solvent rinse was added to the sample in the beaker.

For the aquifer cuttings samples, approximately 30 g of soil sample was weighed using an analytical balance (Sartorius Model B120S) into a tared plastic, disposable weighing dish (4 cm x 4 cm), and the weight was recorded to the nearest 0.01 g. The sample was then transferred to a 125 mL glass jar with a Teflon®-lined lid (labeled with UWRL sample log number) that had been cleaned with a solvent rinse or by muffling in a muffle furnace at 550° C for 24 hours.

For the aquifer cuttings samples, at the same time as the portion used for analytical determination was removed and weighed, 5 to 10 g of the sample was removed and weighed in a tared crucible for moisture determination. The sample was dried overnight at 105° C and allowed to cool in a desiccator before re-weighing. For the aquifer core samples, the entire sample after extraction was dried to obtain the dry weight. The percent moisture of the sample was calculated using the following relationship:

$$\frac{\text{g of sample (wet weight)} - \text{g of dry sample}}{\text{g of dry sample}} \times 100 = \%\ \text{moisture (dry weight basis)}$$

For the samples used for analytical determination of contaminant concentrations, 1 mL of a tribromophenol spiking solution (5000 mg/L, prepared as pure (99% or greater; Aldrich Chemical Co.) tribromophenol in acetonitrile) was added to the aquifer materials in each extraction jar. For the aquifer cuttings samples, approximately 100 mL of solvent, 1:1 methylene chloride/acetone (pesticide quality) by volume was then added to the sample in the jar, and the sample and solvent were mixed by swirling.

The sample was then disrupted for 3 minutes with a sonicator (Tekmar Sonic Disrupter Model No. CV 17, with a 3/4 inch probe) with the output control setting at 10, pulse mode switch set "on," and percent duty cycle set at 50 %.

After sonication, the solids were allowed to settle. The supernatant (sample extract) was poured into a 100-mm funnel filled with 2-2.5 inches of anhydrous sodium sulfate and glass wool for removal of water. The anhydrous sodium sulfate (reagent grade) was prepared by drying in an oven at 105° C for 12 hours in 600 mL beaker covered with triple layer of aluminum foil, followed by storage in a desiccator until use. The dried extract was collected in a 500 mL Kuderna-Danish (K-D) flask with a 10 mL graduated concentrator tube attached (the flask was labeled with UWRL sample log number). One hundred mL of solvent were added to the sample two more times, with sonication of the sample and separation of supernatant performed after each addition of solvent. After the sample had been sonicated three times, 5-10 mL of additional solvent were added to the sample, and the sample was swirled. The solids were allowed to settle and the supernatant was poured through the funnel containing anhydrous sodium sulfate. This washing procedure of the sample was conducted four more times. The same procedures were used for the aquifer core samples, except that a total of 1 L of solvent was used for extraction, rather than 300 mL.

After the sample extract had drained from the funnel, the funnel was rinsed three times with 2-4 mL of solvent. After all the rinses had drained, the funnel was removed from the K-D flask/concentrator, and the tip of the column was rinsed with solvent into the K-D flask.

A small Teflon® boiling chip was added to the K-D flask, and a 3-ball macro Snyder column was attached. The Snyder column was prewet by adding about 1 mL of methylene chloride to the top of the column. The K-D apparatus was placed on the steam table (80°-90° C) (concentric ring electric steaming bath, Model No. 66738, Precision Scientific, Chicago, IL) so that the concentrator tube was partially immersed in the hot water, and the entire lower rounded surface of the flask was bathed with hot vapor. The vertical position of the apparatus and the water temperature, as required, were adjusted to complete the concentration in 10-15 minutes. At the proper rate of distillation, the balls of the column actively chattered, but the chambers did not flood with condensed solvent. When the volume of the liquid reached approximately 5 mL, the K-D apparatus was removed from the steam table and allowed to drain and cool for at least 10 minutes.

To accomplish solvent exchange, the Snyder column was removed and 15 - 20 mL of acetonitrile was added to the flask. The Snyder column was re-attached and the K-D apparatus was placed back on the steam table. The extract was concentrated to approximately 5 mL. The temperature of the steam table was raised as necessary to maintain the proper rate of distillation. The K-D apparatus was removed from the steam table and allowed to cool. The Snyder column was removed, and the flask and its lower joints were rinsed into the concentrator tube with 1-2 mL acetonitrile.

The final volume was adjusted to 10 mL by transferring the sample to a 10 mL volumetric flask using a clean disposable Pasteur pipette. The flask was brought to volume with acetonitrile.

Two mL of the extract was transferred to a GC vial (12 x 32 mm (OD x H)) (labeled with UWRL log number) for PCP analysis using gas chromatography (GC). One mL was transferred to a 10 mL volumetric flask and brought to volume with acetonitrile. This sample extract was filtered through a

0.2 micron filter. Two mL of this extract was transferred to a GC vial (labeled with UWRL log number) for PAH analysis using gas chromatography/mass spectrometry. The samples were stored in the dark at 4° C until analysis.

For extraction of the ground-water samples, each sample was agitated to re-suspend particulates that settled out. The sample was then filtered through glass fiber filter paper, to remove coarse materials, into a 1000 mL graduated cylinder, and the volume of the sample was recorded. The sample was then transferred to a 1000 mL separatory funnel and acidified to a pH value below 2 using a 50:50 percent sulfuric acid:water (v:v) solution. Sixty mL of methylene chloride was poured in several aliquots into the graduated cylinder to transfer quantitatively the remainder of the sample to the separatory funnel. A one mL aliquot of the tribromophenol spiking solution (5000 mg/L) was added to the sample in the separatory funnel. The sample was shook vigorously for one minute, with venting several times to release pressure. The layers were allowed to separate after shaking. If an emulsion was present, it was broken by putting a pipette through the emulsion, by adding 5 to 10 mL of saturated sodium chloride solution and agitating gently, or by transferring the emulsion to a centrifuge tube and centrifuging for 30 seconds at low speed. The lower layer (methylene chloride) was drained in a funnel filled with glass wool and two to three inches of sodium sulfate (referred to as the drying funnel), which was placed over a 250 mL serum bottle. Sixty mL of methylene chloride was added to the separatory funnel two additional times, and the extraction procedure was repeated. After the final separation, the tip of the separatory funnel was rinsed into the drying funnel with methylene chloride. The drying funnel was rinsed twice with methylene chloride, and the tip of the funnel was rinsed into the serum bottle with methylene chloride. The extract was concentrated using a K-D apparatus and prepared for analysis as described previously.

Quality control procedures utilized during the extraction procedure included:

1. Duplicate extractions: every fifteenth to seventeenth sample was extracted in duplicate to check for reproducibility of the extraction procedure. Each duplicate sample was analyzed for PCP and PAHs.

2. Procedural blanks: With each set of extractions (i.e., every 9 - 10 samples), a solvent sample (containing no soil) was run through the extraction procedure to detect contamination associated with the extraction procedure. The procedural blanks were analyzed with the set of samples with which they were extracted.

3. Spikes: With every set of extractions (i.e., every 9 - 10 samples), duplicate samples were spiked with PCP and tribromophenol. Thirty g aliquots of a sample were weighed into two containers. Before adding the solvent to the two containers, 250 mL of the PCP spiking solution, and 1 mL of the tribromophenol spiking solution were added directly to the soil. Samples in both containers were extracted. The spiked samples were analyzed and the results were recorded, including percent recovery of the spiking solutions.

Stock solutions of the compounds used for spiking the samples were prepared in the following manner:

a) PCP spiking solution: The spiking solution was prepared by dissolving 0.200 g PCP (reagent grade) into 100 mL of methanol (pesticide quality);

b) Tribromophenol spiking solution: The spiking solution was prepared at a concentration of 5000 mg/L by dissolving the appropriate amount of pure (99% or greater; Aldrich) tribromophenol in acetonitrile (pesticide quality).

After preparation, the stock spiking solutions were stored at -20° C in the dark until use.

As part of the quality assurance/quality control program, a technician certification procedure was used. Before a laboratory technician was allowed to perform extractions, he/she was required to extract duplicate spiked, clean sand samples. Recovery efficiencies of the spiked samples had to be greater than or equal to 95% and equal to or less than 105% before the technician was allowed to extract project samples.

B-2. Analysis of PCP using Gas Chromatography

An adaptation of U.S. EPA Method 8040 (U.S.EPA, 1986b) was used to determine the concentration of pentachlorophenol (PCP) in the aquifer core and cuttings sample extracts. Gas chromatography with an electron capture detector was used to detect PCP in the sample extracts. Prior to use of this method, samples were extracted using sonication as the extraction technique.

Samples were analyzed using a Shimadzu Gas Chromatograph 14A-GC with a Shimadzu Automatic Sample Injector AOC-1400, an RTX-5 column, and a Shimadzu C-R501 Chromatopac integrator (Shimadzu Instruments, Columbia, MD).

Before every analysis run, the GC column was brought to its highest allowable operating temperature for five hours. During this time, a solvent was injected every hour in order to achieve better conditioning of the column. After conditioning, without any injection, the GC was operated for twice the length of time of a normal run. If a steady baseline was not achieved, the column was re-conditioned.

The temperature program for the analysis was: initial column temperature set at 110° C, held for 2 minutes, followed by 2.5°/min temperature rise to 240° C, held for 6 minutes; a 4° C/min temperature rise to 285° C; and a 20° C/min temperature rise to 325° C, held for 4 minutes. The injector and detector temperatures were set at 270° C. Nitrogen was used as the carrier gas.

For each GC run, a log sheet was prepared containing sample identification, name(s) of persons performing the analyses, type of samples being analyzed, instrument set-up parameters, and identification of standard solutions. Also recorded on the log sheet were the date the samples were analyzed, the file name that data were stored in, and any comments specific to the samples and/or data. Also recorded were instrument operating conditions and changes (e.g., if N_2 cylinder was changed, column was reconditioned, or any changes were made in operating conditions).

Once a week, seven PCP and four tribromophenol (TBP) calibration standards were injected to prepare the linear range of the analytical system for PCP. TBP was analyzed because it had been added as an internal standard to each sample during the extraction procedure. The standard curves generated were compared to previous standard curves. During each daily run, three PCP standards and one TBP calibration standard were injected. Results had to agree within 10 % of values calculated from the weekly standard curve.

To develop the standard curves for PCP and TBP, peak areas, retention times, and corresponding calibration concentrations were transferred from the chromatograms to a spreadsheet. Regression equations were calculated based on peak areas and corresponding concentrations. Control charts were maintained for slope, y-intercept, and r^2 for PCP. A standard curve was rejected if the r^2 was less than 0.993.

For preparation of the PCP standard calibration curve, a PCP stock standard solution was prepared at a concentration of 1000 mg/l by dissolving the appropriate amount of pure (99.5% or greater) solid

PCP (Sigma) in methanol. The stock standard solution was stored at 4° C in an amber bottle to protect the solution from light. A new stock standard solution was prepared at least every four months. The PCP calibration standards (at a minimum of seven concentration levels) were prepared by dilution of the stock standard solution with acetonitrile. Concentration levels corresponded to the range of concentrations expected in samples. The calibration standards were stored at 4° C and were protected from light. New calibration standards were prepared weekly.

For preparation of the TBP standard calibration curve, a TBP stock solution was prepared at a concentration of 5000 mg/L by dissolving the appropriate amount of pure (99% or greater; Aldrich) TBP in acetonitrile. The stock solution was stored at -20° C in the dark until use. A new stock standard solution was prepared at least every four months. TBP calibration standards (at a minimum of 4 concentration levels) were prepared by dilution of stock standard solution with acetonitrile. Concentration levels corresponded to the range of concentrations expected in the samples. The calibration standards were stored at 4° C and were protected from light. New calibration standards were prepared weekly.

For each run, a solvent blank was injected, followed by the injection of 10 - 12 samples; the run was completed with the injection of another solvent blank. A typical injection volume was 1 mL. After each run, the GC glass injection sleeve was replaced with a clean sleeve. Before starting the next run, the sleeve in the injector port was heated to the maximum injection temperature allowable for one hour. The used glass sleeve was cleaned according to a procedure that utilized sulfuric acid and methanol as cleaning solutions, followed by immersion in a silonizing solution and methanol.

PCP and TBP in samples were identified by matching their respective retention times with retention times of PCP and TBP obtained using calibration standards. If the peak area exceeded the linear calibration range of the system for a sample, the extract was diluted or concentrated and re-analyzed. Using an EXCEL spreadsheet, the peak area of PCP or TBP in a sample was converted to concentration by using the slope and y-intercept of the corresponding calibration standard curve for the specific run of samples. The formula used was:

$$\text{concentration (mg/L)} = (\text{peak area} - \text{y intercept})/\text{slope}$$

The concentration was converted to mg/kg (wet weight) by dividing the concentration in mg/L by the weight of the soil extracted and then multiplying by the dilution factor. The concentration was converted to dry weight concentration by dividing the wet weight concentration by the percent dry weight x 100.

Quality control samples analyzed included:

(1) analysis of duplicate extraction samples to check reproducibility of extraction procedure (every twentieth sample was extracted in duplicate);

(2) analysis of procedural blanks to determine if any contamination was associated with the extraction procedure (procedural blanks were run through the extraction procedure every 9-10 samples);

(3) analysis of TBP in every sample to determine recovery of TBP (TBP was added to every sample before extraction);

(4) analysis of samples spiked with PCP to determine recovery of PCP in the spiked samples (duplicate samples were spiked every 9-10 samples); and

(5) analysis of solvent blanks to determine if carryover of PCP was occurring during an analytical run.

B-3. Analysis of PAH Compounds using HPLC

An adaptation of U.S. EPA Method 8310 (U.S. EPA, 1986b) was used to determine the concentration of 16 polynuclear aromatic hydrocarbons (PAHs) in water and soil samples. The 16 PAHs include:

Acenaphthene	Chrysene
Acenaphthylene	Dibenzo(a,h)anthracene
Anthracene	Fluoranthene
Benzo(a)anthracene	Fluorene
Benzo(a)pyrene	Indeno(1,2,3-cd)pyrene
Benzo(b)fluoranthene	Naphthalene
Benzo(ghi)perylene	Phenanthrene
Benzo(k)fluoranthene	Pyrene

High performance liquid chromatography (HPLC) was used to detect the PAH compounds. Prior to use of this method, the sonication extraction technique was used to prepare sample extracts for analysis.

The HPLC systems for analysis used consisted of (1) a Shimadzu SCL-6B system controller, a SIL-6B auto injector, LC-6A pumps, a Perkin-Elmer LC 90 UV spectrophotometric detector, and a CR601 Chromatopac integrator (primary system used); and (2) a Shimadzu SCL6A system controller, a SIL-6A auto injector, LC-6A pumps, an SPD-6A UV spectrophotometric detector, and a C-R3A Chromatopac integrator. The column used for analysis was a reverse phase column: Supelcolsil™ LC-PAH, 5 mm particle size diameter, in a 25 cm x 4.6 I.D. (1/4" O.D) stainless steel column (Supelco 5-8229).

Before analysis was begun for a set of samples, the column was flushed for 1.5 to 3 hours with acetonitrile/double deionized water (40:60). The acetonitrile used was HPLC grade, filtered through Costar filters manufactured by Nuclepore with a 47 mm 0.2 mm polycarbonate membrane. During analysis, the column conditions were as follows: isocratic elution for 2 minutes using acetonitrile/DDW (distilled, deionized water) (40:60) (v/v), then linear gradient elution to 70:30 acetonitrile/DDW over 15 minutes, then linear gradient elution to 100 % acetonitrile over 13 minutes, hold at 100% acetonitrile for 9 minutes, and then linear gradient elution to 40:60 acetonitrile/DDW over 6 minutes at a flow rate of 1.0 mL/min. The gradient pumping system was constant flow.

Calibration standards were injected to prepare the linear range of the analytical system for each PAH compound. The peaks of the individual compounds were labeled for each calibration standard run. The peak areas, retention times, and corresponding calibration concentrations were transferred to an EXCEL 4.0 spreadsheet. Regression equations based on peak areas and corresponding concentrations were prepared. Control charts for slope, y-intercept, and r^2 were prepared and maintained for all 16 PAH compounds.

For preparation of standard curves for each PAH compound, calibration standards at five concentration levels were prepared using volumetric pipettes and volumetric flasks through dilutions of the stock standard solution 610-M with acetonitrile (Supelco Mixture 610-M (methanol:methylene chloride used as solvent in the mixture) (Catalog no. 4-8743). Concentrations of PAHs in this mixture in mg/ml, in order of elution in HPLC analysis, are: naphthalene, 1000; acenaphthylene, 2000; acenaphthene, 1000; fluorene, 200; phenanthrene, 100; anthracene, 100; fluoranthene, 200; pyrene, 100; benzo(a)anthracene, 100; chrysene (93%), 100; benzo(b)fluoranthene, 200; benzo(a)pyrene, 100; benzo(ghi)perylene, 200; dibenzo(ah)anthracene; and indeno(1,2,3-cd)pyrene, 100). Dilutions used include 1:10, 1:50, 1:100, 1:250, and 1:500. Mixture 610-M and the calibration standards were stored at 4° C in the dark in a secured area. Standards were replaced every three months or when difficulties were observed with the linearity of the standard curve.

For each HPLC run, a log sheet was prepared that contained sample identification, name(s) of persons performing the analyses, type of samples being analyzed, instrument set-up parameters, and date of samples. The log sheet was stored with the chromatograms generated during an HPLC run. Also recorded on the log sheet were the date the samples were analyzed, the file name that data were stored in, and any comments specific to the samples and/or data.

Several samples in each run were spiked to aid in the identification of specific compounds. By spiking several samples in each run, the range of variability in the matrices of soil/waste contamination was included. Unspiked sample chromatograms were overlain on the spiked sample chromatograms on a light table and peaks were identified and labeled, i.e., specific PAH compounds in samples were identified by matching their respective retention times with retention times of the compounds obtained in the spiked samples. The spiked samples served as "templates" for the identification of peaks.

If the peak area exceeded the linear calibration range of the system for a sample, the extract was diluted or concentrated and re-analyzed. Using an EXCEL 4.0 spreadsheet (Macintosh), the peak area of each PAH compound in a sample was converted to concentration by using the slope and y-intercept of the corresponding calibration standard curve for the specific run of samples. The formula used was:

concentration (mg/L) = (peak area - y intercept)/slope

The concentration was converted to mg/kg (wet weight) by dividing the concentration in mg/L by the weight of the soil extracted and then multiplying by the dilution factor. The concentration was converted to dry weight concentration by dividing the wet weight concentration by the percent dry weight x 100.

Quality control samples analyzed included:

(1) analysis of duplicate extraction samples to check reproducibility of extraction procedure (every twentieth sample was extracted in duplicate);

(2) analysis of procedural blanks to determine if any contamination was associated with the extraction procedure (procedural blanks were run through the extraction procedure every 9-10 samples);

(3) analysis of samples spiked with PAH compounds to determine recovery of PAHs in the spiked samples (duplicate samples were spiked every 9-10 samples); and

(4) analysis of calibration standards randomly during a sample run to check for instrument drift; and

(5) analysis of solvent blanks to determine if any carryover of PAH was occurring during an analytical run.

B-4 Analysis of TPH using Gas Chromatography

To prepare a sample extract (for the sonication procedure see Appendix B-1) for analysis for TPH, 400 mL was removed from the extract storage vial (after thorough shaking) using a syringe and added to a 5 mL volumetric flask. Two hundred (200) mL of the internal standard, oterphenyl diphenyl benzene (from a stock solution prepared with a concentration of 1250 mg/L) was also added to the flask, resulting in a concentration of 50 mg/L. The flask was brought to volume with acetone. One mL of this diluted sample extract was placed in a GC vial for analysis.

For preparation of standard curves for TPH, calibration standards at five concentration levels were prepared using volumetric pipettes and 100 mL volumetric flasks through dilutions of pure diesel fuel with acetone. The source and date of acquisition of the diesel fuel was recorded. Standard concen-

trations used were: 0.01%, 0.05%, 0.1%, 0.5%, and 1%. Dilutions used include 1:10, 1:50, 1:100, 1:250, and 1:500. The calibration standards were stored at 4° C in brown bottles in the dark in a secured area. Standards were replaced every three months or when difficulties were observed with the linearity of the standard curve.

A check standard at 0.4% was prepared using pure diesel fuel from a separate source. The calibration check standard was used to check the standard curve periodically during analyses.

The internal standard o-terphenyl diphenyl benzene was added to both the calibration and check standards to achieve a final concentration of 50 mg/L.

GC analyses were conducted using a Shimadzu gas chromatograph (Shimadzu Instruments, Columbia, MD) equipped with an FID detector and a 10 m long, 0.75 mm i.d. small bore Petrocol 3710 (Supelco, Inc., Bellefonte, PA) fused silica capillary column. Solvent extracts were injected directly into the GC. The system operating conditions were as follows:

Injector temperature: 250° C

Detector temperature: 250° C

Carrier gas: Nitrogen

Carrier Flow: 15 mL/min

Temperature program: 30° C to 280° C at 20° C/min

B-5 Analysis of PAH Compounds and PCP by ManTech Environmental Technology

An LNAPL sample collected from a monitoring well during the Phase II investigation and groundwater samples collected during the Phase III investigation were extracted and analyzed by ManTech Environmental Technology, Ada, Oklahoma, a support laboratory for the U.S. EPA RSKERL.

Five mL of the LNAPL sample was added to 995 mL of GC/MS grade methylene chloride. A 10 mL aliquot of an internal standard mixture containing 1,4-dichlorobenzene-d_4, naphthalened_8, acenaphthalene-d_{10}, phenanthrene-d-$_{10}$, chrysene-d_{12}, and perylene-d_{12}, each at 4000 ppm, was added to the diluted NAPL sample.

Base/neutral and acid extraction of the ground-water samples was performed according to U.S. EPA Methods 3500 and 3510 (U.S. EPA, 1986b). Before the extraction, 1.0 mL of 100 ppm base/neutral surrogates and 1.0 mL of 200 ppm acid surrogates were added to each of the 1 L water samples and to 1.0 L of the method blank water. After the pH of one liter of each water sample was adjusted to slightly above 11.0 with 10 N NaOH, the water sample was extracted three times with 60 mL of methylene chloride. After the methylene chloride fraction was passed through a Na_2SO_4 column, it was concentrated using an evaporative concentrator (Turbo-Vap) to a final volume of 1.0 mL. The water fraction was then acidified to a pH just below 2.0 using 1:1 H_2SO_4. The acidified water sample was then extracted three times with 60 mL methylene chloride. The 180 mL of methylene chloride extract was dried using the Na_2SO_4 and was then concentrated to 1.0 mL using the Turbo-Vap. The acid and base/neutral extracts were combined, the final volume was reduced to 1.0 mL with the Turbo-Vap, and the extract was placed in a vial and crimp capped.

For the semi-quantitative analysis, a 20 mL aliquot of an internal standard mixture containing 1,4-dichlorobenzene-d_2, naphthalene-d_8, acenaphthalene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}, each at 2000 ppm, was added to 1.0 mL of the base/neutral or acid extract.

For both the LNAPL sample and the ground-water samples, the Hewlett Packard 7673 autoinjector delivered 1.0 mL of this sample under splitless conditions to a 30 meter, 0.32 mm DB5-MS capillary column with 1.0 mm film thickness. The column was temperature programmed from 40° to 300° at 8° C/min. The Finnigan 4500 GC/MS was scanned from 45 to 450 m/z in 0.5 seconds. The U.S. EPA tuning criteria for 50 ng of decafluorotriphenylphosphine (DFTPP) was met before starting the analysis.

For the LNAPL sample, standard curves consisting of 1, 5, 12.5, 25, 50, and 100 ppm of PCP and thirteen PAH compounds were established before sample analysis. Ten ppm U.S. EPA quality control standards containing 35 base/neutral and 11 phenolic priority pollutants including 12 PAH compounds were analyzed to provide confirmation of compounds present in the extracts and to provide quality control for the calibration curves.

For the ground-water samples, quality control standards containing 15 PAH compounds and PCP were analyzed to provide quantitation and confirmation of compounds present in the extracts. Calibration standards were run at 1.0, 5.0, 10.0, 25.0, 50.0, and 100 ppm for each of the 15 PAH compounds. Calibration for PCP was obtained at 5.0, 10.0, 25.0, 50.0 and 100 ppm.

Appendix C

Analytical Results from Phase II and Phase III Field Investigations

Table C-1. *Analysis of Aquifer Solids from Borehole No. 2 (31 feet SW of Monitoring Well No. 3026): November 1992.*

Depth Below Surface (ft)	TPAH[1] (mg/Kg)	PCP[2] (mg/Kg)	TPH[3] (mg/Kg)
16.1	89	0.1	561
23.5	416	1.3	2910
26.0	32	0.2	238
29.5	85	0.4	594
31.0	39	0.2	990
32.0	116	0.8	184

1 TPAH = total polycyclic aromatic hydrocarbons; sum of the 16 priority pollutant PAH compounds
2 PCP = pentachlorophenol
3 TPH = total petroleum hydrocarbons

Table C-2. *Analysis of Aquifer Solids from Borehole No. 3 (58 feet NW of Injection Well No. 3007): November 1992.*

Depth Below Surface (ft)	TPAH[1] (mg/Kg)	PCP[2] (mg/Kg)	TPH[3] (mg/Kg)
16.5	122	0.7	360
18.4	22	0.1	258
20.0	5.2	0.2	275
22.3	25	0.1	281
23.3	404	2.8	929
25.8	43	0.1	505
26.7	687	3.2	1924
27.5	443	1.3	1105
30.8	115	1.0	1265

1 TPAH = total polycyclic aromatic hydrocarbons; sum of the 16 priority pollutant PAH compounds
2 PCP = pentachlorophenol
3 TPH = total petroleum hydrocarbons

Table C-3. Analysis of Aquifer Solids from Borehole No. 4 (51 feet N of Injection Well Cluster 9500/9501): November 1992.

Depth Below Surface (ft)	TPAH[1] (mg/Kg)	PCP[2] (mg/Kg)	TPH[3] (mg/Kg)
13.7	24	0.5	702
15.0	171	7.9	2525
17.2	216	2.0	691
18.7	28	0.3	70
20.0	47	0.3	132
30.8	5.8	0.1	109

1 TPAH = total polycyclic aromatic hydrocarbons; sum of the 16 priority pollutant PAH compounds
2 PCP = pentachlorophenol
3 TPH = total petroleum hydrocarbons

Table C-4. Inorganic Compounds in Injection and Monitoring Wells: March, 1993

Sample[1]	Mg/l $NO_2 + NO_3(N)$	Mg/l $NH_3(N)$	Mg/l CL-	Mg/l T-P
Inj. Well 9500	.26	3.32	8.24	1.21
Inj. Well 9500/9501	.26	3.11	8.00	1.40
25-1	.66	.10	9.81	.30
25-1 Dup	.67	.11		
25-2	.69	.06	7.38	.69
25-2 Rep				.40
25-3	1.36	.09	8.19	.35
25-4	.48	.12	9.58	.37
26-1	1.96	< .05	4.17	1.59
26-2	2.08	< .05	5.98	.97
26-2 Dup	2.05	< .05	5.70	
26-3	1.85	< .05	7.85	.93
26-4	1.80	< .05	1.68	1.14
26-5	1.71	< .05	4.64	.61
26-5 Dup				.61
26-6	1.74	< .05	6.35	1.17
26-6 Dup				.91
26-7	1.72	< .05	5.88	.96
26-8	1.71	< .05	6.52	.96
26-9	1.76	< .05	5.58	.73
26-10	1.78	< .05	6.21	.91
26-11	1.84	< .05	5.31	.90
26-12	1.84	< .05	7.25	.92
26-13	1.86	< .05	6.28	1.02
26-13 Dup	1.85	< .05	5.88	
26-14	1.89	.06	5.77	.86
26-15	1.86	.05	8.45	.79
32-1	1.90	.70	7.62	1.03
32-2	2.20	.50	9.20	1.25
32-3	1.97	.53	5.71	1.25
32-4	1.99	.55	10.3	1.20
32-5	2.02	.63	9.16	1.25
32-6	2.04	.63	8.31	1.43
32-7	1.90	.78	9.33	1.26
32-8	1.78	.92	8.67	1.29
32-8 Dup	1.77	.91		
32-9	1.78	.92	9.22	1.53
32-9 Rep				1.39
32-10	1.77	.94	9.92	1.31
32-10 Dup				1.50
AQCWP029	1.24	.27	31.2	.86
				1.03
True Value	1.30	.35	33.3	.94
Spike Recovery	104%	103%	97%	104%
				102%

[1]Sample number nomenclature and depth interval given in Table B-5.

Table C-5. Sample Number Nomenclature and Depth Interval for Sample Results Presented in Table C-4.

Well No.	Field Sample No.(1)	Report Sample No.	Sample Depth (2)
3025	1	SH251	22.5
	2	SH352	19.5
	3	SH253	16.5
	4	SH254	13.5
3026	1	SH261	29.8
	2	broken	28.8
	3	SH263	27.8
	4	SH264	26.8
	5	SH265	25.8
	6	broken	24.8
	7	SH267	23.8
	8	SH268	22.8
	9	broken	21.8
	10	broken	20.8
	11	SH2611	19.8
	12	SH2612	18.8
	13	SH2613	17.8
	14	SH2614	16.8
	15	SH2615	15.8
3032	1	SH321	19.5
	2	SH322	18.5
	3	SH323	17.5
	4	SH324	16.5
	5	SH325	15.5
	6	SH326	14.5
	7	SH327	13.5
	8	SH328	12.5
	9	SH329	11.5
	10	SH3210	10.5

(1)Sample number used in the field when collecting samples.
(2)Depth at which sample was collected, below ground surface.

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